Reductions of thiazenes and some aspects of the chemistry of the RCN(_2)s(_2) ring system

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REDUCTIONS OF THIAZENES AND SOME ASPECTS OF THE CHEMISTRY OF THE RCN_2S_2 RING SYSTEM

A thesis submitted to the University of Durham
for the degree of Doctor of Philosophy

by

Nigel Robert Martin Smith, B.Sc.
(Grey College)

FEBRUARY 1982

To my parents and friends

"There is no end to the writing of books,
and too much study will wear you out."
ECCLESIASTES, Chapt.12 v.12.

ACKNOWLEDGEMENTS

I wish to thank all my colleagues and friends for their helpful assistance and advice during the past four years. In particular I express thanks to Dr. A.J. Banister under whose supervision the work at Durham University was carried out, for his continued encouragement and unfailing optimism. Many thanks also to Dr. Z.V. Hauptman for his invaluable technical advice and friendship.

I am grateful to the academic staff at Durham who have helped me in discussion of ideas and to the technicians without whom there would have been little to discuss.

I am indebted to N.R.D.C. and to the Science Research Council for their grants to the University of Durham.

My special thanks go to Mrs. Connie Dowson for the many exasperating hours spent deciphering and typing this thesis. Finally my most sincere thanks to PJ whose continual support and friendship kept me going when the going was rough.

MEMORANDUM

The work described in this thesis was carried out by me in the Chemistry Department of the University of Durham between October 1977 and May 1981. I declare that the work has not been submitted for any other degree. This thesis is my original work, except where indicated by reference to other work.

Parts of this thesis have been published or submitted for publication to scientific journals, as follows:

1. "Some Reductions of Sulphur-Nitrogen-Chloride Compounds to give Tetrasulphur Tetranitride" by A.J. Banister, A.J. Fielder, R.G. Hey and N.R.M. Smith. J. Chem. Soc., Dalton Trans., 1980, 1457.
2. "Producing Sulphur-Nitrogen Groups" by A.J. Banister, A.J. Fielder, R.G. Hey and N.R.M. Smith. U.K. Patent No.2,038,297A, October 1979.
3. "Preparation of a Conducting Iodinated Poly (sulphur nitride) by A.J. Banister and N.R.M. Smith. J. Chem. Soc., Dalton Trans., 1980, 937.
4. "Some Experiments in Sulfur-Nitrogen Chemistry" by A.J. Banister and N.R.M. Smith. J. Chem. Educt. (in press).
5. "Preparation of Some 4-Aryl-1,2,3,5-dithiadiazolium salts and a Dimeric 4-Phenyl-1,2,3,5-dithiadiazole, $(PhCN_2S_2)_2$" by A.J. Banister, R.G. Hey and N.R.M. Smith (in preparation).

ABSTRACT

Reductions of the chlorothiazenes, $S_3N_2Cl_2$, S_3N_2Cl and S_4N_3Cl were studied using mainly i.r. spectroscopic and thin layer chromatographic techniques. The reactions gave solutions containing S_4N_4, S_4N_2, sulphur and (in the presence of moisture) traces of sulphur imides. A comparison was made between these new routes to, and the traditional preparation of, S_4N_4.

Inorganic applications for these S_4N_4 solutions were investigated, and new routes are reported to S_4N_4-adducts and to $S_4(NH)_4$ which avoid isolating solid (and potentially hazardous) S_4N_4.

Traces of $(SN)_x$ were found in solutions produced by thiazene reductions where moisture was present. Vapour phase reactions of thiazenes with a hot catalytic surface were therefore investigated in attempts to find improved routes to $(SN)_x$, especially with respect to industrial applications. A new iodinated derivative of $(SN)_x$ was discovered, $S_3N_2I_x$, in which the iodine content was strongly dependent upon the reaction conditions. Physical characterisation suggested that it was similar in nature to the recently reported brominated systems.

In Part II of this work, as part of a general study of the 4-substituted -1,2,3,5-dithiadiazolium ring system, the reactions of aliphatic and aromatic nitriles and dinitriles with SCl_2/NH_4Cl were investigated. The new compounds $CH_3CN_2S_2Cl$, $(CH_3CN_2S_2)_2\ SnCl_6$ and $Cl\cdot C_6H_4\cdot CN_2S_2Cl$ are reported and also a new route to the known compound, $Bu^tCN_2S_2Cl$. By attempting the preparation of a series of compounds $R\cdot C_6H_4\cdot CN_2S_2Cl$ (where R was a para-substituted, electron-withdrawing group) some insight was gained into the mechanism of reaction of RCN with SCl_2/NH_4Cl. Whilst investigating the reaction of adiponitrile with SCl_2/NH_4Cl, a carbon-sulphur heterocycle, 3,4-dichloro-2,5-dicyanothiophene, was isolated. This represents the first product of a totally new synthetic route to 2,5-dicyanothiophenes.

Chemistry of the dimeric dithiadiazole system was investigated, in particular, brief attempts were made to synthesise new C-S-N heterocycles by the desulphurisation of $(PhCN_2S_2)_2$.

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CHAPTER 1

BACKGROUND INFORMATION

This chapter contains background information (Tables 1.1 to 1.7) on the S-N compounds which form the basis of Part I of this thesis; namely $S_3N_2Cl_2$, S_3N_2Cl and S_4N_3Cl (Chapter 3), $S_4(NH)_4$ (Chapter 4) and S_4N_4 (Chapters 3 - 5).

It is hoped that the tables which follow will provide future sulphur-nitrogen chemists with a source of quick reference for physical and chemical data for these compounds. More detailed information, if required, can be found in the following recent review articles:

1975	Banister[1]	(S-N compounds)
1976	Mews[2]	(S-N-Hal compounds)
	Roesky[3]	(S-N compounds)
1979	Labes[4]	($(SN)_x$ and derivitives)
	Roesky[5]	(S-N compounds)
1980	Heal[6]	(S, N & P heterocycles)

1.1 Disulphur Dinitride, S_2N_2

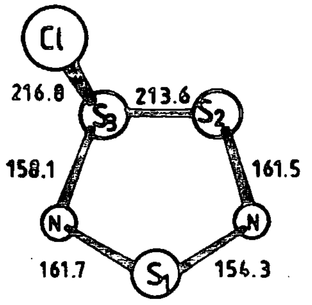
Because it is a relatively small molecule, S_2N_2 has, during the last 10 years, been the subject of many computer studies which have tried to rationalise, in particular, its electronic structure.

Several semi-empirical M.O. calculations have been reported using CNDO/2[7,8] and Extended Hückel methods[9], but the results of "ab initio" studies should be more reliable. The "ab initio" calculations were done using a minimal basis set (of s and p functions)[10,11]. Karpfen[12], Collins and Duke[13,14] and Adkins[8] believe however that inclusion of d-orbital functions is necessary to calculate geometries which closely fit experimental data. Salahub and Messmer[11] performed calculations with and without d partial wave functions and concluded that their effect on the M.O.s was minimal, causing a slight lowering of some orbital energies. The major effect (because of the similarity in energy of the B_{2g} and B_{3g}

In Tables 1.1 – 1.7, bond lengths are in pm and i.r. frequencies in cm^{-1}.

1.1 $S_3N_2Cl_2$

STRUCTURE (15)



$N - S_1 - N = 106.3°$
$S_1 - \hat{N} - S_3 = 118.0°$
$N - \hat{S}_3 - S_2 = 97.8°$
$S_3 - \hat{S}_2 - N = 95.5°$
$S_2 - \hat{N} - S_1 = 120.7°$

INFRARED SPECTRUM

CLARKE (16)	THIS WORK
1015 (s)	1015 (m)
936 (vs)	940 (s)
752 (w)	
719 (sh)	720 (sh)
712 (s)	710 (s)
578 (s)	578 (m)
458 (s)	459 (ms)
400 (s, br)	403 (s)
	380 (ms)

ULTRAVIOLET SPECTRUM (17)

λ(MAX)□	ε(MAX)
416 nm 235 nm	Rapid decomposition occurs.

□Concentrated H_2SO_4 solution

MASS SPECTRAL DATA

CLARKE (18)

m/e	I/I_0 %	ASSIGNMENT
32	156	S° / O_2°
35	21	Cl°
36	23	HCl°
37	9	i-Cl°
38	8	i-HCl°
46	100	SN°
48	40	
62	10	$S_3N_2^{\circ +}$
63	80	
64	47	S_2° / SO_2°
78	27	S_2N°
80	15	
92	87	$S_2N_2^{\circ}$
124	2	$S_3N_2^{\circ}$

N.Q.R. SPECTRUM □

FREQUENCY/MHz	ASSIGNMENT (19)
22.91	35 - Cl
29.02	37 - Cl

□ At 77K

These signals occur in the region expected for chlorine covalently bonded to sulphur.

PROPERTIES

VERY MOISTURE SENSITIVE.
INSOLUBLE IN MOST DRY ORGANIC SOLVENTS.
MELTING POINT = 90 - 92° C (decomposes)

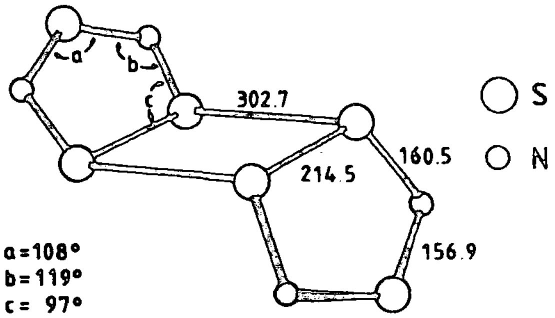
ANALYSIS (CALC)

N	S	Cl
16.36	69.29	36.36

1.2 S_3N_2Cl

STRUCTURE (20)

Structural details are for the $ClS_2O_6^-$ salt.



INFRARED SPECTRUM

THIS WORK	CLARKE (16)
1018 (w)	1015 (w)
964 (m)	962 (s)
941 (s)	943 (s)
	746 (w)
709 (s)	709 (s)
	699 (s)
587 (m)	584 (s)
	570 (w)
	500 (w, br)
438 (m)	431 (m)
409 (m)	
375 (s)	

U.V. SPECTRUM (17)

λ_{max} (nm)	ε_{max}
356	900
248.5	4700
219 ¤	~ 3500

¤ May be due to decomposition since ε_{max} increases with time.

MASS SPECTRAL DATA

m/e	I/Io %	Assignment (18)
32	225	S^{+}/O_2^{+}
35	23	Cl^{+}
36	155	HCl^{+}
37	9	$i\text{-}Cl^{+}$
38	54	$i\text{-}HCl^{+}$
46	100	SN^{+}
62	30	$S_3N_2^{++}$
64	25	S_2^{+}/SO_2^{+}
78	25	S_2N^{+}
92	132	$S_2N_2^{+}$
124	5	$S_3N_2^{+}$

N.Q.R. SPECTRUM (19)

No signals detected in the range 13 - 44 MHz.

Dr. Z.V. Hauptman has recently obtained small crystals of S_3N_2Cl from $SOCl_2/SO_2$ mixtures. We hope for a crystal structure shortly.

PROPERTIES

DARK GREEN SOLID WITH A METALLIC LUSTRE. IS STABLE IN DRY AIR - SLOW HYDROLYSIS IN WATER. INSOLUBLE IN MOST SOLVENTS.

MELTING POINT (in vacuo) = 120 - 140° C

ANALYSIS (CALC)

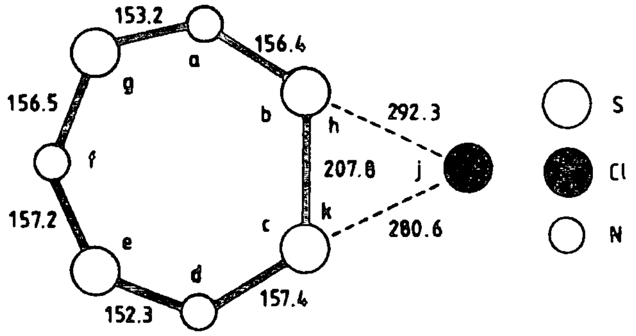
N	S	Cl
17.54	60.23	22.24

S_3N_2Cl HAS NEVER BEEN KNOWN TO EXPLODE BUT AS IT IS THERMODYNAMICALLY UNSTABLE IT SHOULD BE TREATED WITH CARE.

1.3 S_4N_3Cl

STRUCTURE (21)

a = 151.5°
b = 112.0°
c = 111.8°
d = 151.8°
e = 118.4°
f = 135.5°
g = 118.8°
h = 65.7°
j = 42.5°
k = 71.7°



INFRARED SPECTRUM

‡ Solid S_4N_3Cl ¤ Nujol mull / KBr plates

THIS WORK ‡	BAILEY + LIPPINCOTT ¤ (22)	
	I.R.	RAMAN
1164 (s)	1163 (s)	
1132 (w)	1125 (w)	
	1102 (vw)	
1000 (s)	998 (s)	
720 (w)		
682 (m)	678 (s)	
	606 (w)	617 (s)
568 (m)	561 (s)	566 (s)
470 (ms)	466 (s)	
455 (m)	451 (s)	410 (w)
330 (m)	317 (m)	338 (vw)

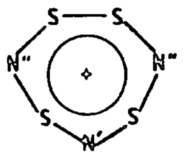
MASS SPECTRAL DATA

CLARKE (18)

M/E	I/Io %	ASSIGNMENT
32		S_2^+ / O_2^+
35		Cl^+
36		HCl^+
37		$i-Cl^+$
38		$i-HCl^+$
46	100	SN^+
64	30	S_2^+ / SO_2^+
76	20	$S_3N_4^{++}$
78	10	S_2N^+
92	20	$S_2N_2^+$
124	10	$S_3N_2^+$
170	3	$S_4N_3^+$

^{15}N NMR SPECTRUM (23)

SHIFT / PPM	ASSIGNMENT	STRUCTURE
343	N′	1:2:1 triplet
355	N″	1:1 doublet



Shift measured with respect to NH_4^+ = 0 ppm

ANALYSIS (CALC)

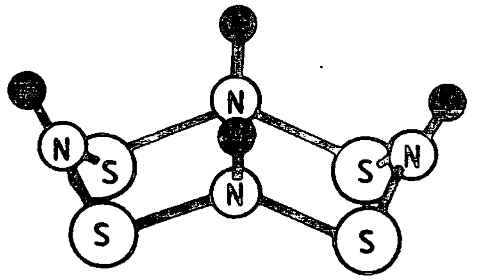
N	S	Cl
20.38	62.34	17.24

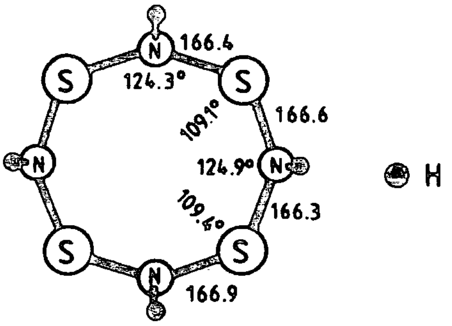
PROPERTIES

BRIGHT YELLOW POWDERY SOLID, STABLE IN DRY AIR BUT HYDROLYSED SLOWLY BY MOISTURE. SOLUBLE IN CH_3NO_2, $SOCl_2$, SO_2 AND H.COOH. MELTING POINT = 180-200 °C

1.4 $S_4(NH)_4$

STRUCTURE[24]





INFRARED SPECTRUM

THIS WORK		DOMINGO + ORZA (25)		LIPPINCOTT + TOBIN (26)	
I.R.(KBr disc)	Raman ‡	Frequency	Assignment	Frequency	Assignment
3320(s)	1325 (vw)	3315 IR/R	ν(NH---S)	3320 (s)	ν(NH)
3290(s)	1302 (w)	3290 "	"	3385 (s)	
3225(s)	856 (w)	3226 "	"	3220 (s)	
	831 (w)	1326 "	δ(NH)	1302 (m)	δ(NH)
1299 (m)	716 (m)	1300 "		1296 (w)	
1260 (w)	541 (w)	1268 "		1262 (w)	
	497 (m)	857 R	ν(SN) B_2		
830(s,br)	461 (m)	828 IR/R	E		
	324 (s)	764 R	B_1	780 (s)	ν(SN)
720 (w)	308 (vw)	717 IR/R	A_1	705 (w)	
700 (w)	263 (ms)	700		693 (w)	
540 (vbr,ms)	218 (s)	540 IR/R	γ(NH) E	541 (m)	
	144 (m)	499 R	B_1	516 (m)	
463 (ms)	117 (m)	461 IR/R	A_1	462 (ms)	
410 (m)	81 (s)	406 "	δ(SNS) E	407 (m)	
	46 (m)	324 R	δ(NSN) B_2		
305 (ms)	39 (m)	293 IR/R	E	302-280 (m)	

‡ Red Laser (He - Ne Spectra Physics Model 125) 14mw Power

X-RAY DIFFRACTION DATA

I/Io %	d-Spacing/Å	I/Io	d-Spacing
25	6.13	30	2.58
70	5.16	85	2.52
40	4.75	15	2.47
20	3.98	25	2.43
100	3.80	25	2.29
30	3.46	30	2.27
90	3.37	27	2.22
90	3.31	40	2.17
60	3.21	40	2.09
75	3.06	20	2.06
50	3.02	25	1.99
55	2.96	20	1.97
70	2.86	10	1.96
50	2.64	15	1.94

MASS SPECTRAL DATA[18]

m/e	I/Io %	Assignment
32	16	S^+ / O_2^+
46	100	SN^+
47	68	SNH^+
62	81	$S(NH)_2^+$
64	14	S_2^+ / SO_2^+
78	33	S_2N^+
92	11	$S_2N_2^+$
93	10	$S_2N_2H^+$
94	7	$S_2N_2H_2^+$
125	40	$S_3N_2H^+$
139	20	$S_3N_3H^+$
186	54	$S_4N_4H_2^+$
188	12	$S_4N_4H_4^+$

PROPERTIES

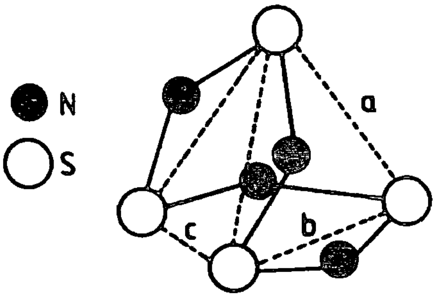
CREAM COLOURED MICRO-CRYSTALLINE SOLID
INSOL. IN ETHERS, $CHCl_3$, CH_2Cl_2, MeOH
SOL. IN CH_3COCH_3, CH_3NO_2, PYRIDINE.
MELTS (DARK RED) 130 - 160° C

ANALYSIS(CALC)

N	S	H
29.75	68.11	2.12

1.5 S_4N_4

STRUCTURE (27)



S---S(a) = 258 pm
S---S(b) = 269 pm
S---S(c) = 258 pm
S—N = 161.6 ± 1.0 pm

$S\hat{N}S$ = 113°
$N\hat{S}N$ = 105°

INFRARED SPECTRUM

($^{\square}$ NOT OBSERVED IN SOLUTION SPECTRUM)

LIPPINCOTT + TOBIN (26)		BRAGIN + EVANS (28)			THIS WORK
IR	RAMAN	IR	RAMAN	ASSIGNMENT	IR (KBr disc)
		1067 w		Combination (552+519)	
		1046 w		" (701+347)	
1040 w					1025 w
1000 w		1007 w		" (2 × 226+552)	
925 s	934	925 s		ν(SN) E	928 s
	888			ν(SN) $B_1^{\square}$	
792 vw		798 w		Combination (226+726−347)	
	785				
		766 w		ν(SN) E	770 w
762 w		760 w		Combination (226+726−109)	
719 s	720	726 s	716	ν(SN) $A_1^{\square}$	728 s
696 s		701 s		ν(SN) B_2	701 s
	615			δ(SSN) $B_1^{\square}$	
557 s	561	555 s	564	δ(SSN) B_2	548 s
552 s					
531 w		529 w		δ(SSN) $A_1^{\square}$	528 w
519 w	519	519 w		δ(SSN) E	520 w
412 w					
397 w					
347 s	347	347 s	341	δ(SSN) E	348 s
	213	226 w	213	ν(SS) A_1	
	177	190 m	177	ν(SS) B_2	
		77 m		?	

UV SPECTRUM (29)

λ (max) / nm	ε (max)
410	250
327	$1\text{–}2 \times 10^3$
257	19,000
204	550
185	6,000

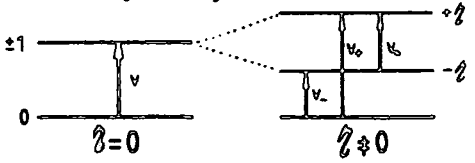
ANALYSIS (CALC)

N	S
30.4	69.6

^{14}N NQR SPECTRUM (30)

	N(1)	N(2)	N(3)	N(4)
ν_+	2.914	2.935	2.868	2.849
ν_-	1.477	1.505	1.440	1.446
ν_0	1.436	1.430	1.428	1.403
η	0.981	0.966	0.995	0.980

η = Asymmetry Parameter



ORIGIN OF TRANSITIONS FOR NUCLEUS I = 1

1.6 S_4N_4

MASS SPECTRAL DATA

m/e	Assignment/I(%)(18)		Assignment/I(%)(31)	
32	S/O_2^+	45	S^+	8.0
46	SN^+	100	SN^+	100.0
62	$S_3N_2^{++}$	10		
64	S_2^+/SO_2^+	8	S_2^+	2.8
76	$S_3N_4^{++}$	32		
78	S_2N^+	30	S_2N^+	38.0
92	$S_2N_2^+$	126	$S_2N_2^+$	72.0
110			S_3N^+	5.3
124	$S_3N_2^+$	26	$S_3N_2^+$	2.1
138	$S_3N_3^+$	120	$S_3N_3^+$	108.0
184	$S_4N_4^+$	40	$S_4N_4^+$	17.5

SOLUBILITY(32)

SOLVENT	ε	WT. (g) S_4N_4 PER 100 ml solvent
Hexane	1.8	0.04
EtOH	24	0.09
MeOH	32	0.10
CCl_4	2	0.33
C_6H_6	2	1.01
$(CH_2Cl)_2$	10	1.28
$CHCl_3$	5	1.30
CH_2Cl_2	9	1.50
Dioxane	24	1.86
$(CHCl_2)_2$	8	1.92

X-RAY DIFFRACTION DATA

HAMADA (33) D-Spacing/Å (hkl)		
6.28 (-101)	6.02 (101)	4.73 (-111)
4.61 (111)	4.38 (200)	4.34 (002)
3.71 (012)	3.58 (020)	3.48 (-211)
3.39 (211)	3.15 (-202)	3.11 (-121)
3.08 (121)	3.02 (202)	2.89 (-212)
2.81 (-301)	2.78 (212, -103, 220)	
2.76 (022)	2.73 (301)	2.71 (103)
2.66 (-221, -122)	2.61 (122, -311)	
2.59 (-113)	2.37 (-222)	2.33 (-312)
2.31 (222)	2.25 (023)	2.23 (-131)

THIS WORK⊞ D-Spacing/Å (I/Io)		
6.35 (60)	6.08 (45)	4.77 (100)
4.65 (85)	4.42 (70)	4.36 (20)
3.73 (40)	3.60 (30)	3.50 (35)
3.41 (30)	3.17 (30)	3.14 (70)
3.09 (35)	3.03 (25)	2.90 (70)
2.82 (75)	2.80 (70)	2.78 (85)
2.75 (25)	2.73 (20)	2.67 (25)
2.62 (40)	2.61 (35)	2.38 (50)
2.34 (20)	2.32 (15)	2.26 (15)
2.25 (45)	2.23 (30)	2.22 (15)

⊞Fe K_α, radiation (Mn filter) 24h 30Kv/10ma

^{14}N NMR SPECTRUM(34)

1 Absorption $\delta = 445$ ppm (measured wrt NO_2^-)

PROPERTIES

M.PT = 178-9°C (35) Explodes above melting point. Sublimes at 90-100°C at 10^{-4} torr. Dipole moment = 0.52 (benzene), 0.72 (CS_2) (36)
S_4N_4 is thermochroic (37), colourless at -190°C, orange-yellow at 25°C and deep red at 100°C. $\Delta H_f^\circ = 462.04$ KJ mol^{-1}

TLC DATA (Chapter 2) SOLVENT	R_f range
Carbon disulphide	0.35 ± 0.06
Carbon tetrachloride	0.26 ± 0.06

1.7 S_4N_4

PURIFICATION (Major impurity usually S_8 -see Chapter 3)

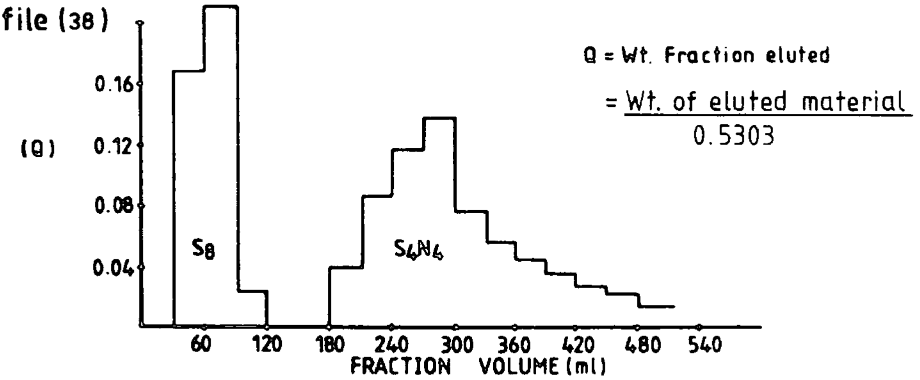
RECRYSTALLISATION

Synthesis	Method of purification	Yield	%N
JOLLY (Chapter 2)	(i) Soxhlet extraction with dioxane	75 %	27.84
	(ii) Dioxane recryst^n	65 %	28.40
	(iii) Double recryt^n from benzene	50 %	29.70
	(iv) Sublimation		29.93

COLUMN CHROMATOGRAPHY (38,39)

COLUMN DETAILS	SOLVENT	RECOVERY PURE S_4N_4
Dried alumina (acidic grade one) (12h/150°C) Column 18 × 2.54 cm Flowrate 1 ml min^{-1}	Benzene (dry)	95 % (see profile)

Profile (38)



M.O. ANALYSIS FOR S_2N_2 (11)

M.O.	%Charge distribution in M.O.				%Hybridisation on S,N in M.O.			
	Q(S)	Q(N)	Q(II)	Q(III)	S(s)	S(p)	N(s)	N(p)
$1B_{2g}$	0	73	24	3	0	0	0	100
$1B_{3g}$	70	0	24	6	0	100	0	0
$2B_{3u}$	23	62	13	2	0	100	6	94
$2B_{2u}$	58	29	8	5	9	91	0	100
$1B_{1u}$	38	33	26	3	0	100	0	100
$3A_g$	26	56	13	5	3	97	19	81
$2A_g$	59	24	11	6	69	31	89	11
$1B_{1g}$	50	47	1	2	0	100	0	100
$1B_{2u}$	75	23	1	2	99	1	0	100
$1B_{3u}$	24	73	2	1	0	100	99	1
$1A_g$	50	50	0	0	72	28	82	18

levels) was that, by invoking a slight interaction of S d-orbitals with the N π-lone pair electrons, the B_{2g} level was stabilised such that the B_{3g} level became the HOMO. Although other workers[8,12–14] may disagree with the orbital energy sequence (Table 1.8) predicted, the symmetry considerations and M.O. description outlined below are still valid.

The percentage electronic charge in the atomic spheres, Q(N) and Q(S), the intersphere region, Q(II) and in the region outside the molecule, Q(III); and also the partial wave analysis ignoring d-functions (after Salahub and Messmer), appear in Table 1.7 for the M.O.s predicted by group theory for S_2N_2. The results showed that charge is distributed in the M.O.s, either equally on N and S (e.g. A_g and B_{1g}) or in pairs where the first M.O. has greatest amplitude on S and the second on N (e.g. $1B_{3u}$/$1B_{2u}$ or $2A_g/3A_g$). The $2B_{2u}$, $2B_{3u}$, $1B_{1u}$, $1B_{2g}$ and $1B_{3g}$ M.O.s are substantially delocalised, as deduced from Q(II). The latter two are antibonding combinations of N and S p_z atomic orbitals and are effectively non-bonding.

1.2 M.O. study of S_2N_2 based on computer calculations[11]

1.2.1 Symmetry considerations

The M.O.s are labelled as follows: A and B are spectroscopic labels for energy levels which designate singlet states (A being of higher symmetry). The subscripts u and g stand for ungerade (uneven) and gerade (even) respectively, and signify that the M.O. either has a centre of symmetry, i (g), or not (u). S_2N_2 has the symmetry elements shown in Figure 1.1 (with the axes defined as shown) and belongs to the point group, D_{2h}.

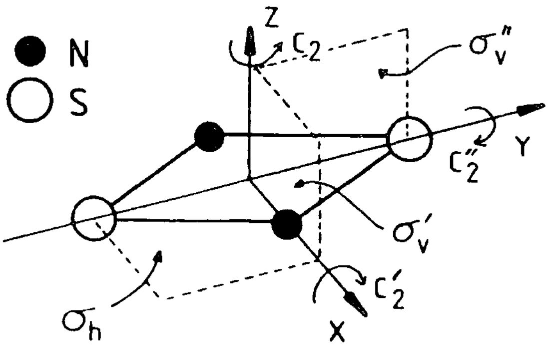


FIGURE 1.1

$D_{2h}: E, C_2, C_2', C_2'', \sigma_h, \sigma_v', \sigma_v'', i$

Application of group theory leads to the symmetry elements listed:

TABLE 1.8

Orbital (sequence after Salahub[11])	**Symmetry elements (+1)**
$2B_{1u}$ (LUMO)	
$1B_{2g}$ (HOMO)*	$1C_2(y) + \sigma xz + i$
$1B_{3g}$	$1C_2(x) + \sigma yz + i$
$2B_{3u}$	$1C_2(x) + \sigma xy, \sigma xz$
$2B_{2u}$	$1C_2(y) + \sigma yz, \sigma xy$
$1B_{1u}$	$1C_2(z) + \sigma xz, \sigma yz$
$3A_g$	$3C_2 + 3\sigma + i$
$2A_g$	$3C_2 + 3\sigma + i$
$1B_{1g}$	$1C_2(z) + \sigma xy + i$
$1B_{2u}$	$1C_2(y) + \sigma yz, \sigma xy$
$1B_{3u}$	$1C_2(x) + \sigma xy, \sigma xz$
$1A_g$	$3C_2 + 3\sigma + i$

* without d-partial waves.

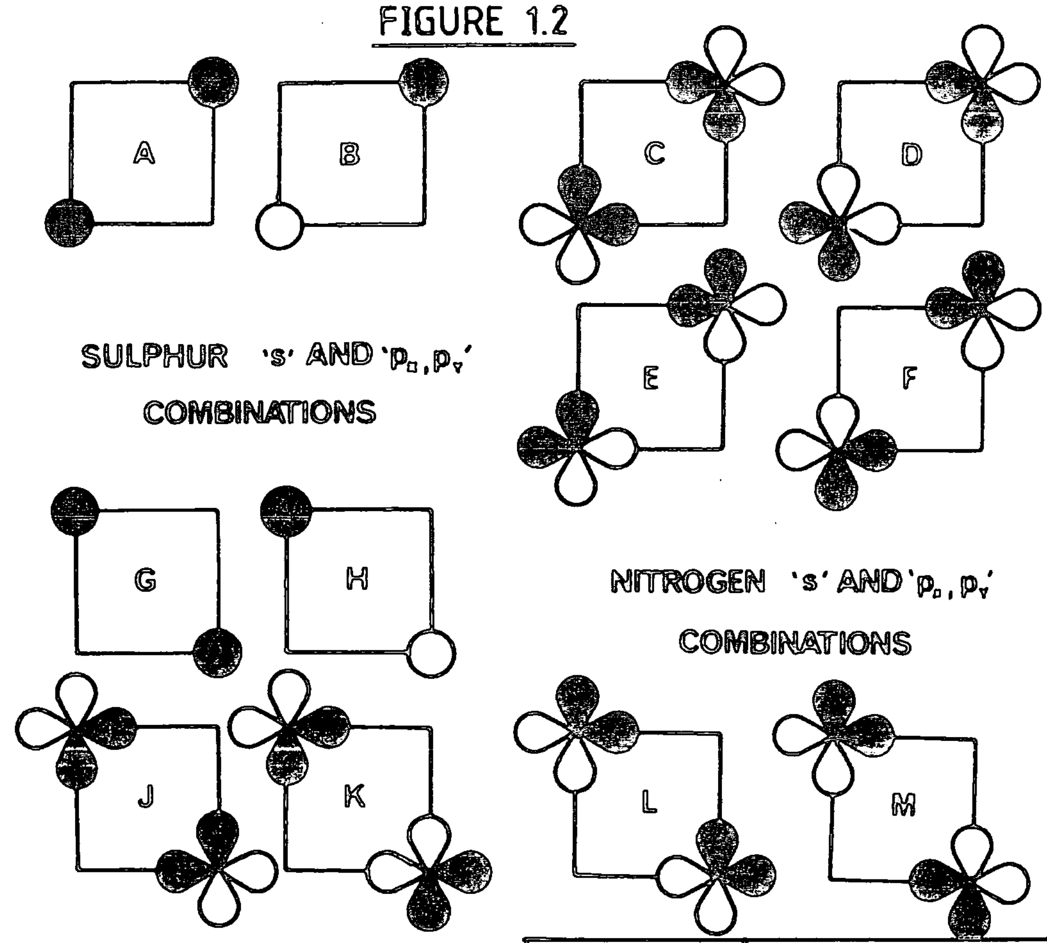
Sulphur and nitrogen atoms have the following electronic structures, and contribute a total of 22 valence electrons (11 pairs) to S_2N_2:

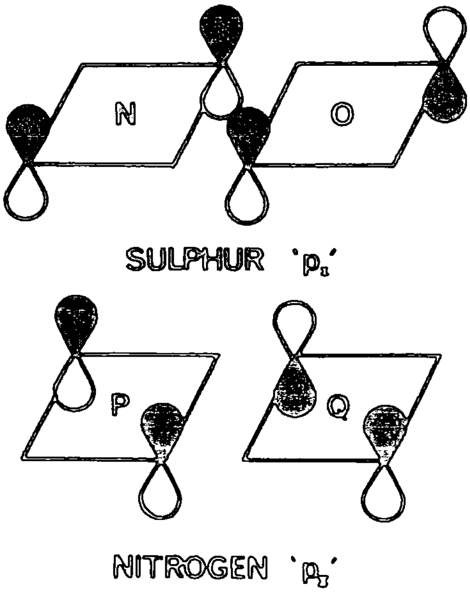
S: $1s^2\ 2s^2\ 2p^6\ \underline{3s^2\ 3p^4}$

N: $1s^2\ \underline{2s^2\ 2p^3}$

Representations of the 11 filled M.O.s (derived by computer calculations)[7-14] are depicted in Figure 1.2. For the in-plane σ-system, each S and N atom provides three atomic orbitals (s, p_x and p_y), and linear combinations of these (A-F for sulphur and G-M for nitrogen) are combined (within the constraints of symmetry) to give 12 σ-M.O.s. Similarly for the π-system, each atom provides the remaining p_z orbital, and in-phase and out-of-phase combinations of these (N-Q) combine to give 4 π-M.O.s. The next section contains a description of the filled M.O.s in S_2N_2 derived from the data presented in Table 1.7 (page 8).

FIGURE 1.2





Molecular Orbitals	Contribution to MOs from LCAOs (above)
$1A_g$	A+G(core) some C+J
$1B_{3u}$	E+H
$1B_{2u}$	B+L
$1B_{1g}$	F+M
$2A_g$	A+G(valence) & C+J
$3A_g$	C+J
$1B_{1u}$	N+P
$2B_{2u}$	D+L
$2B_{3u}$	E+K
$1B_{3g}$	O
$1B_{2g}$	Q

1.2.2 The molecular orbitals

1.2.2.1 $1A_g$, $2A_g$, $3A_g$

$1A_g$ consists largely of S and N s-orbitals with ca. 25% contribution from the $p_{x,y}$-orbitals. The molecular orbital has charge distributed evenly on the S and N atoms with none in the intersphere region. Being of lowest energy, and containing little p-contribution it is likely that $1A_g$ consists of the core N and S s-orbitals (1s,2s). $2A_g$ is largely similar to $1A_g$ except that it is higher in energy and the sulphurs in particular give a much greater contribution from p-orbitals. The s-orbital contribution in $2A_g$ comes from the valence shell, and the greater intersphere charge distribution (11%) shows that unlike $1A_g$ (which is largely σ-nonbonding), $2A_g$ contributes to the bonding in the molecule. $3A_g$ consists mostly of interaction between S and N $p_{x,y}$ combinations, with very little contribution from s-orbitals. It is therefore the highest in energy of the A_g orbitals. All three orbitals have the highest symmetry requirement: 3 C_2, 3σ, i. The calculated contour plot for $3A_g$ is shown in Figure 1.3.

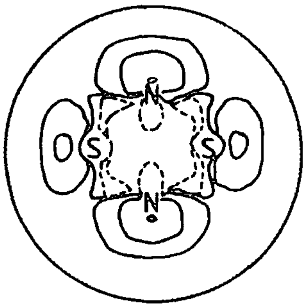


FIGURE 1.3

3Ag Contour plot

1.2.2.2 $1B_{3u}$, $2B_{3u}$

This is a pair of orbitals of similar (B_{3u}) symmetry but which differ in energy and composition. $1B_{3u}$ is composed virtually of S(p)- and N(s)-orbitals and is thus lower in energy than $2B_{3u}$ which consists of S- and N(p)-orbitals. The N sphere contains the greater share of the charge and in both orbitals there is some charge in the intersphere region, although only in $2B_{3u}$ is it significantly high. Both orbitals have the symmetry requirement: $C_2(x)$, $\sigma(xy)$ and $\sigma(xz)$ (Figure 1.4).

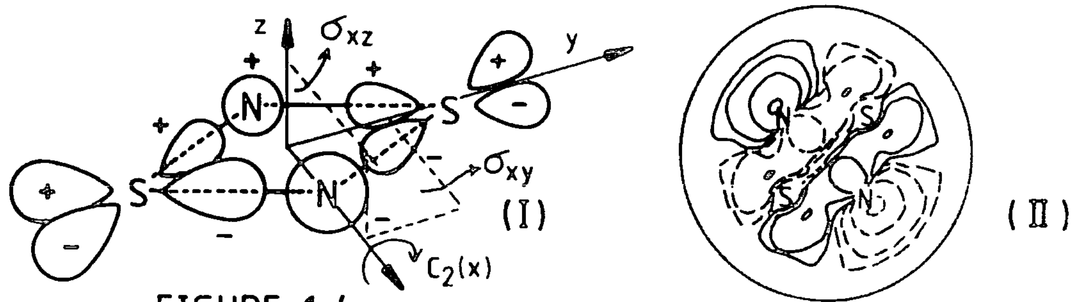


FIGURE 1.4

(I)Combination of at. orbitals ($1B_{3u}$)
(II)Calcd. contour plot ($2B_{3u}$)

1.2.2.3 $1B_{2u}$, $2B_{2u}$

These orbitals are also related by symmetry, $2B_{2u}$ being of higher energy. They are similar to the B_{3u} orbitals, in that the charge distribution and partial wave analysis data (Table 1.7) are almost exactly transposed between N and S. In other words the $1B_{2u}$ orbital consists of an out-of-phase combination of S(s)- and N(p)-orbitals, whilst the $2B_{2u}$ consists of N(p) and virtually 100% S(p)-orbitals. In the same way the N sphere held the greater charge in the B_{3u} orbitals, so the S sphere does in the B_{2u}. The symmetry requirements are as follows: $C_2(y)$, $\sigma(xy)$ and $\sigma(yz)$ (Figure 1.5).

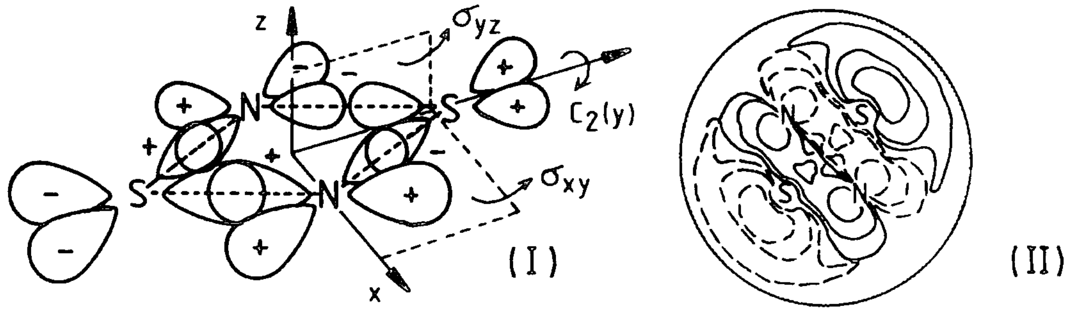


FIGURE 1.5

(I)Combination of at. orbitals } $2B_{2u}$
(II)Calcd. contour plot }

1.2.2.4 $1B_{1g}$

This σ-M.O. is also a combination of S and N p-orbitals, but is of different symmetry from the others. The charge is evenly distributed between both atoms with little in the intersphere region. The symmetry requirements are as follows: $C_2(z)$, $\sigma(xy)$ and i.

1.2.2.5 $1B_{1u}$

This is the π-bonding M.O. and consists of 100% p_z-orbital contribution from S and N. The charge distribution gives a clear indication that it is a delocalised M.O. with 26% of the charge in the intersphere region. The symmetry requirements are $C_2(z)$, $\sigma(xz)$ and $\sigma(yz)$ (Figure 1.6)

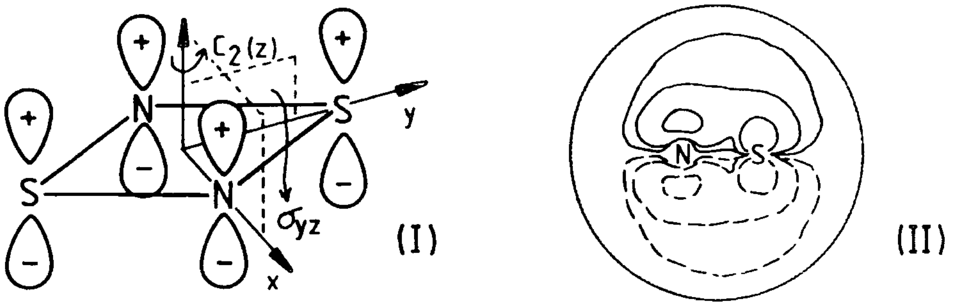


FIGURE 1.6

(I)Combination of at. orbitals }
(II)Calcd. contour plot } $1B_{1u}$

1.2.2.6 $1B_{3g}$ and $1B_{2g}$

These orbitals are regarded as nonbonding M.O.s consisting of out-of-phase (antibonding) combinations of the N (p_z)-orbitals $(1B_{2g})$and S (p_z)-orbitals $(1B_{3g})$with, respectively, no contribution from the S (p_z) and N (p_z) orbitals. The symmetries of these orbitals are as follows (Figure 1.7)

$1B_{2g}$: $C_2(y)$, $\sigma(xz)$, i

$1B_{3g}$: $C_2(x)$, $\sigma(yz)$, i

There is a large charge distribution in the intersphere region of these orbitals, showing that there is some polarisation of charge towards the neighbouring S or N ring atom. The B_{2g} and B_{3g} orbitals are very close in energy, so that a crossover (from B_{2g} to B_{3g} as the HOMO) is observed when d-partial waves are included in the M.O. calculations. This is rationalised as follows. Slight interaction of the N (p_z) orbitals with d-orbitals on S results in stabilisation of the B_{2g} orbital relative to the B_{3g}, to an extent which causes orbital crossover.

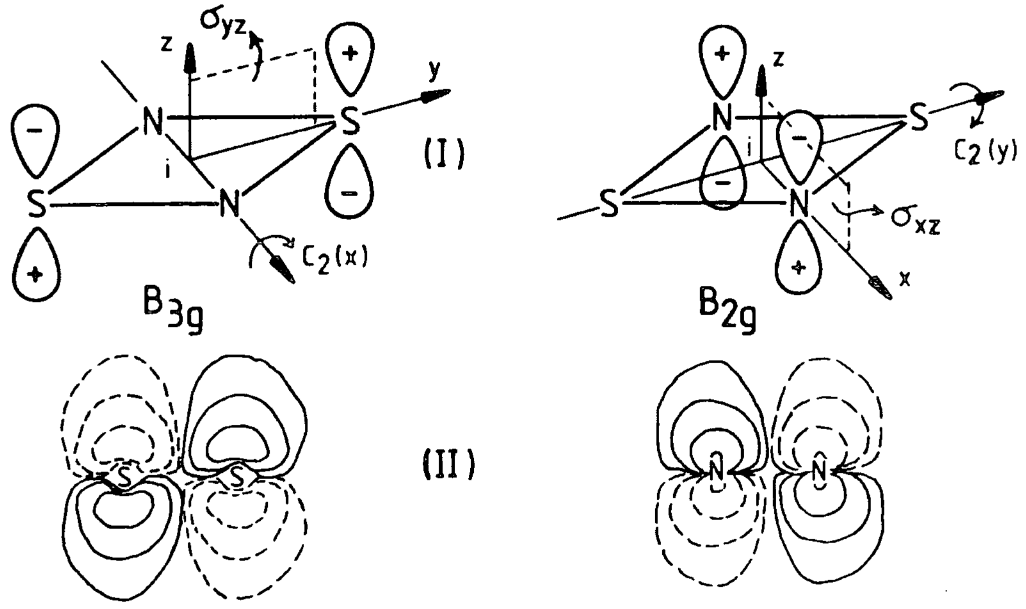


FIGURE 1.7

(I)Combinations of at. orbitals
(II)Calcd. contour plots

1.3 Mass spectroscopy in SN-chemistry

The following information was useful for interpreting mass spectra of sulphur-nitrogen compounds. Table 1.9 lists commonly occurring fragments for compounds containing the elements S, N, O, H, Cl and I.

Since both S and N have isotopes with significant natural abundancies (^{32}S = 95.00%, ^{33}S = 0.76%, ^{34}S = 4.22%, ^{36}S = 0.014%; ^{14}N = 99.63%, ^{15}N = 0.37%), there is usually an isotopic contribution to the m+n peak (n = 1, 2, 3 etc.) in spectra of compounds containing these elements.

Two computer programmes were written by, and jointly developed with, Dr. R.S. Roberts (Durham) in order to aid assignment of mass spectral peaks:

(i) ISOX which calculated isotopic abundancies for any fragment with the major peak normalised, either to 100% (Table 1.10), or a user inputted measurement of peak intensity.

(ii) ANAL1 which determined the mass fragments possible for any value of m/e (containing user specified elements) (Table 1.11)

TABLE 1.9

1	H
14	N
15	NH
16	O,NH_2
17	O_2,NH_3
18	OH_2,NH_4
28	N_2
30	NO
32	S,O_2
34	H_2S
35	Cl
36	HCl
37	i-Cl
38	i-HCl
42	N_3
43	HN_3
44	N_2O,CO_2
46	SN,NO_2
47	SNH
48	SO
60	SN_2
62	$NSO,S(NH)_2$
63	HNSO
64	S_2,SO_2
65	NOCl
67	i-NOCl,SCl
69	i-SCl
71	Cl_2
76	$S_3N_4{}^{2+}$
78	NSO_2,S_2N
79	S_2NH
80	SO_3,S_2O
81	NSCl
83	i-NSCl,SOCl
85	i-SOCl
92	$S_2N_2,S_4N_4{}^{2+}$
93	S_2N_2H
94	$S_2NO,S_2(NH)_2$
96	SO_4,S_3 $SO_2(NH)_2,S_2O_2$
97	NSOCl
103	SCl_2
108	S_3N_3O
110	S_3N,S_2NO_2
113	S_2NCl
115	$i\text{-}S_2NCl$
119	$SOCl_2$
124	$S_2(NO)_2,S_3N_2$
125	S_3N_2H
126	$(HNSO)_2$
127	I
128	HI,S_4,S_2O_4
135	S_2Cl_2
138	S_3N_3
139	S_3N_3H
144	S_2O_5
156	$S_3N_2O_2$ $S_2N_2O_4$ S_4N_2
159	S_3N_2Cl
160	S_5,S_2O_6
162	$S_2N_2Cl_2$
170	S_4N_3
175	$S_2N_3O_4H$
176	S_2O_7
184	S_4N_4
186	$S_3N_3O_3$, $S_4N_4H_2$
188	$S_4(NH)_4$
189	$(HNSO)_3$
192	S_6,S_2O_8
198	S_4N_5
203	$S_3N_3O_4H,S_5N_3H$
204	$S_3N_2O_5$
216	S_5N_4
220	S_6N_2
222	$S_6(NH)_2$
224	S_7,S_4O_6
230	S_5N_5
234	$S_3N_3O_6$
239	S_7NH
240	$(SO_3)_3$
243	$(SNCl)_3$
248	$S_4N_4O_4$
250	$(HNSO)_4$
254	I_2
256	S_8

TABLE 1.10

SN^+	46	100.00
	47	1.17
	48	4.45
$S_2N_2^+$	92	100.00
	93	2.34
	94	8.90
	95	0.14
	96	0.23
$S_3N_3^+$	138	100.00
	139	3.51
	140	13.37
	141	0.36
	142	0.64
$S_4N_4^+$	184	100.00
	185	4.68
	186	17.86
	187	0.69
	188	1.25
S_2N^+	78	100.00
	79	1.97
	80	8.89
	81	0.10
	82	0.23
$S_4N_3^+$	170	100.00
	171	4.32
	172	17.85
	173	0.63
	174	1.25

$S_4N_2^+$	156	100.00
	157	3.94
	158	17.83
	159	0.56
	160	1.25
$SNCl^+$	81	100.00
	82	1.71
	83	36.84
	84	0.39
	85	1.45
$S_3N_2^+$	124	100.00
	125	3.14
	126	13.36
	127	0.31
	128	0.64
$SNBr^+$	125	97.67
	126	1.14
	127	100.00
	128	1.14
	129	4.27
$SNOH^+$	63	100.00
	64	1.22
	65	4.65

TABLE 1.11

Mass	Elements				
	S	N	O	H	I
50	0	0	3	2	0
	0	1	2	4	0
	0	2	1	6	0
	0	3	0	8	0
	1	0	1	2	0
	1	1	0	4	0
51	0	0	3	3	0
	0	1	2	5	0
	0	2	1	7	0
	0	3	0	9	0
	1	0	1	3	0
	1	1	0	5	0
66	0	0	4	2	0
	0	1	3	4	0
	0	2	2	6	0
	0	3	1	8	0
	0	4	0	10	0
	1	0	2	2	0
	1	1	1	4	0
	1	2	0	6	0
	2	0	0	2	0

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CHAPTER 2

EXPERIMENTAL

2.1 Techniques

2.1.1 Manipulation of moisture sensitive compounds

All purifications of solvents by distillation or solution reactions in either room temperature or refluxing solvents, were done under an atmosphere of nitrogen. This was obtained from the supply line and passed through a heated copper tower (to remove oxygen) and several drying reagents (concentrated sulphuric acid, potassium hydroxide and phosphorus pentoxide). The line supplied dry nitrogen directly to the vacuum line so that apparatus could be evacuated and refilled with an inert atmosphere. The vacuum line, fitted with a mercury diffusion pump was able to develop a vacuum of better than 10^{-3} torr.

More complex manipulations (e.g. preparation of moisture sensitive materials for infra-red spectroscopy or analysis) were done in a dry nitrogen glove box. Fresh phosphorus pentoxide was kept in the entry port and inside the box as a precaution against moisture being introduced.

2.1.2 Physical Techniques

Infra-red spectra (4000 - 250 cm^{-1}) of nujol mulls prepared under nitrogen were recorded, using KBr plates, on a Perkin-Elmer 457 prism grating spectrophotometer. If the moisture sensitivity of a compound was low, a better spectrum was often obtained from a KBr or KCl disc of the sample. Discs were prepared in a die with a hydraulic press at 2GPa (maximum) pressure. The following symbols are used in this thesis in the description of spectra.

s	- strong	d	- doublet
m	- medium	sh	- shoulder
w	- weak	fs	- fine structure
v	- very	u	- unresolved
br	- broad	i	- isotope (mass spectra)

Mass spectra were obtained on an A.E.I. MS9 mass spectrometer at 70 eV with an accelerating potential of 8KeV. The samples were mounted on an inert ceramic and introduced on a direct insertion probe. Mass spectral peaks (m/e) are quoted in this thesis complete with probable assignments and relative intensities. The relative intensities were often calculated taking the SN^+ peak (m/e 46) as 100%, since it regularly occurred as the most intense peak in spectra of S-N compounds. Chapter 1 contained useful information to aid assignment of mass spectral peaks.

X-ray spectra were obtained on a Guinier de Wolff fully focussing powder camera (Nönius-Delft, Holland) using Fe $K_{\alpha I}$ radiation (30 kV/10 mA, with exposures ranging from 12 - 48 hours). The diffraction lines were calibrated using a silicon standard (ASTM 5-0565), which was run on each photographic film to exclude errors due to film shrinkage. Results are quoted in this thesis as the calculated crystallographic d-spacing (Å).

Electron Spectroscopy for chemical analysis (ESCA)

Electron spectroscopy for chemical analysis, ESCA (or X-ray photoelectron spectroscopy, XPS) is a technique in which a sample, irradiated with monoenergetic soft X-ray radiation undergoes photoemission. The emitted electrons have energies given by:

$$KE = h\nu - BE - \phi$$

where $h\nu$= energy of the incident photons, BE = binding energy of the atomic orbital from which the detected electron originated and ϕ = a spectrometer work function.

ESCA is essentially a surface technique since only electrons emitted from the surface layers (to a depth of 1-10 μm) of the sample are detected. The output spectrum is a plot of the number of electrons emitted per energy interval versus their kinetic energy. Such a low resolution scan shows peaks of high intensity photoemission corresponding to electronic states of atoms in the sample.

The valence states have small B.E.s thus electrons emitted from them will be detected with high kinetic energies. In the present study, Mg ($K\alpha$) radiation was used ($h\nu$ = 1253.6 eV) and the B.E.s in Chapter 5 for I_{3d}, N_{1s} and S_{2p} were calculated using equation (I).

CALIBRATION....... BE C(1s) = 285.0 eV KE (expt) = 963.5 eV

FOR OTHER STATES...BE = 1248.5 - KE (expt) -(I)

High resolution scans for individual states can reveal splitting due to spin states (e.g. I(3d) has J = $^5/2$, $^3/2$) and the differences in B.E. due to changes in the environment of the atomic states (e.g. the I(3d) is more tightly bound to the nucleus in I^+ than I and has a larger B.E.).

ESCA data were obtained on an AEI 200 Electron spectrometer with a Mg $k_{\alpha 1,2}$ soft X-ray source. The probe chamber was at 10^{-8} torr, and results are quoted as binding energies in electron volts. These were calibrated as described above using the C(1s) spectrum arising from the hydrocarbon contamination layer which builds up on the sample.

Analyses were carried out in this department by Mr. R. Coult (S, Cl and metals) and Mrs. Cocks (C, H and N).

N.Q.R. spectroscopy The ^{35}Cl- n.q.r. studies described in Chapters 6 and 7 were done on an N.Q.R. spectrometer, Decca Radar LTD (super regenerative oscillator). Samples were run at R.T. and 77K (liquid N_2).

^{1}H and ^{13}C n.m.r. spectroscopy Proton n.m.r. data were obtained on a Varian EM360L spectrometer, and 13-carbon results from P.C.M.U. Harwell. In both cases, chemical shifts were measured relative to a $(CH_3)_4Si$ (TMS) internal reference.

^{31}P n.m.r. spectroscopy Spectra were recorded using an F.T. spectrometer built around a Perkin-Elmer R10 thermostated permanent magnet. Chemical shifts were measured with respect to 85% H_3PO_4 ($\delta = 0$ ppm).

Chromatography

Chromatography has been usefully applied to S-N compounds by earlier workers. Heal[1] for example, obtained a good separation of the isomers of the S_6-imides using a silica gel column eluted with CS_2; and Jolly[2] used a similar column with CCl_4 to obtain a separation of S_7NH from a mixture of S_8, S_4N_4 and various sulphur imides. Jolly reports that, using an undried silica (or alumina) column, a good recovery of S_7NH was possible but that S_4N_4 was obtained with low recovery. A good recovery of S_4N_4 was possible using a dried alumina column and benzene elutant (Chapter 1, Table 1.7). Clarke[3] used t.l.c. as a qualitative technique in a study of reactions of S_7NH and $S_4(NH)_4$.

Thin layer chromatography was indispensible as an aid to identifying products from the thiazene reductions studied in Chapter 3. In the technique a solvent contained in a t.l.c. tank (the mobile phase) is allowed to flow up a glass plate, coated on one side with silica gel (the stationary phase). The silica is impregnated with a fluorescent material so that after a chromatographic run the spots on the plate can be located easily by viewing under ultra-violet illumination. Exposure to iodine vapour was also used to aid location of faint spots.

The solvent, moving up the plate, dissolves and carries upwards, at different rates, the components of a mixture spotted about 2 cm from the bottom of the plate. There are three factors which cause the differing rates of travel of the components[4]:

(i) differential adsorption of the components on the static phase

(ii) partitioning of the component spots between the bound aqueous phase and the flowing solvent and

(iii) differential solubility of the components in the eluting solvent.

As a quantitative measurement of spot separation, R_f values are defined - as the ratio of the distance travelled by a component spot, to the distance travelled by the solvent front (both distances measured from the spot origin). R_f values therefore range from 0 to 1 and are affected by the following factors[5]:

(i) Volume of solvent in the t.l.c. tank - the tank should be filled to a depth of *ca*. 0.5 cm.

(ii) Equilibration time - the tank should be shaken after filling, and left for an hour to allow the solvent vapour to saturate the atmosphere inside the tank. The tank top should be greased to avoid solvent evaporation.

(iii) Spot position - this should be further than 2 cm. from the edge of the plate.

The spotting solvent should be allowed to evaporate before the plate is eluted, to avoid streaking from the base line. Streaking also often occurred because of decomposition of the sample on the plate during elution.

Because of the difficulty in obtaining reproducible R_f values, standard compounds were run simultaneously whenever this was possible, so that direct comparisons could be made.

In the reductions of thiazenes studied, the products most frequently encountered were sulphur, S_4N_4, S_4N_2, S_7NH and other lower imides. S_3N_2Cl being insoluble in virtually all organic solvents did not give any useful t.l.c. results, neither did $S_3N_2Cl_2$ which is very moisture sensitive. Fortunately the other compounds could be run successfully using normal t.l.c. techniques.

The ideal low polarity solvent would give an even spread of compounds down the plate as the polarity of the S-N species increased, with the most polar compound, S_4N_3Cl (and other ionic compounds) having very low R_f values. S_4N_4 and $S_4(NH)_4$ were too soluble in methanol and nitromethane, both were taken up to the solvent front. Chloroform did not separate sulphur and S_4N_4 whilst S_4N_3Cl and $S_4(NH)_4$ stayed on the base line. Carbon tetrachloride gave a better separation of sulphur and S_4N_4. Carbon disulphide was similar to CCl_4 but gave a shorter elution time. Butanol was a very slow eluting solvent and caused unsatisfactory streaking of the spots. $S_4(NH)_4$ was slightly soluble in benzene and toluene (R_f = 0.02) but the separation of sulphur and S_4N_4 (R_f = 0.93 and 0.78 respectively) was not as good as in CS_2 or CCl_4. CS_2 and CCl_4 were found to give the best separation of S_8, S_4N_4, S_4N_2, S_7NH and the other imides. Although S_4N_3Cl and $S_4(NH)_4$ had $R_f = 0.00$ in these solvents, the former could be distinguished by its pale yellow colour, and the latter by its dark appearance under U.V. light.

Table 2.1 (of R_f values) was compiled as the result of many t.l.c. experiments.

TABLE 2.1

Compound	R_f range	
	CCl_4	CS_2
S_8	0.85 ± 0.02	0.96 ± 0.02
I_2	0.76 ± 0.02	0.90 ± 0.03
S_4N_2	0.70 ± 0.02 red,faded	0.84 ± 0.04 red,faded
S_7NH	0.54 ± 0.03	0.75 ± 0.04
$S_6(NH)_2$	0.30 (1 result)	-
S_4N_4	0.26 ± 0.06 yellow	0.35 ± 0.06
$S_5(NH)_3$	0.16 (1 result)	-
$S_4(NH)_4$	0.00	0.00
S_4N_3Cl	0.00 yellow	0.00 yellow

The following abbreviations are used in this thesis to indicate the relative intensity of component spots when viewed under U.V. light: s = strong, m = medium and f = faint. Others in Chapter 3 are defined as they are used.

Column chromatography

The column used was a 20 cm x 2 cm glass tube with sinter and socket tap at the bottom to control flow rate. Both silica gel and acidic alumina (activity 1)[6] were tried as column media in attempts to separate a mixture of sulphur and S_4N_4. The tube was packed by adding the medium as a slurry with the eluting solvent, and ensuring no air bubbles were trapped in the column. A 1 cm thick layer of fine, pure sand was added to the top of the column followed by the impure S_4N_4 adsorbed onto a small quantity (ca. 2 g) of medium. This had previously been prepared by taking a mixture of sulphur, S_4N_4 and medium in dioxane and evaporating to dryness, whilst shaking the slurry to ensure an even distribution. The column was eluted with CCl_4 (recovery of S_4N_4 was poor using hexane elutant). Eluted fractions (20 ml) were collected in test tubes and analysed by t.l.c.

In one experiment using an alumina column, eluting with CCl_4, two bands were observed to form; a dark yellow-orange band travelling at ca. 0.75 cm.min^{-1} (1 cm thick) and a more diffuse band (6-7 cm thick) travelling at ca. 1 cm.min^{-1}. As the run progressed the darker band broadened to 3-4 cm. Two fractions, A and B were collected, with A being eluted first.

T.l.c. analysis of these fractions showed that a separation had been achieved (Table 2.2).

TABLE 2.2

Fraction	R_f values	
A	0.18 (f)	0.88 (s)
B	0.18 (s)	0.89 (f)
S_4N_4	0.17	
S_8		0.87

The recovery of S_4N_4 was, however, poor probably due to insufficient drying of the column medium.

Separation of a mixture of S_8, S_7NH and S_4N_4

Column chromatography was used to isolate a pure sample of S_7NH, in order that it could be used as a standard in t.l.c. investigations of the thiazene reductions (Chapter 3). The preparation (page 32)produced a mixture of sulphur, S_4N_4, S_7NH and small quantities of lower imides.

A column of undried silica gel (20 x 2 cm) was prepared with a surface layer of sand (1 cm). The crude S_7NH (0.44 g) was dissolved in CCl_4 (25 ml) and added to the column. Elution was with CCl_4 at a flow rate of 1 ml.min^{-1}. Fractions were collected (10 x 20 ml) and analysed by t.l.c. (Table 2.3). Fraction 5 was evaporated to dryness and the residue analysed.

Found: N, 5.68; S, 91.23 S_7NH required: N, 6.27; S, 93.72.

The infra-red spectrum (cm^{-1}) 3250(m), 1270(w), 815(s), 705(w), 500(m), 460(ms,br), 430(m,br), 360(m), 280(m), 255(m) was in good agreement with that reported by Nelson[7].

TABLE 2.3

Fraction	R_f values			
1				
2	0.91(m)			
3	0.91(s)	0.72(w)		
4	0.91(w)	0.72(s)		
5		0.72(s)		
6		0.71(m)		0.22(w)
7		0.72(w)	0.44(m)	0.22(m)
8			0.43(s)	0.22(m)
9			0.41(s)	0.20(w)
10			0.40(w)	
S_4N_4			0.42(s)	
S_8	0.94(s)			

S_7NH was found to give an R_f value of 0.54 ± 0.03 (in CCl_4) and 0.75 ± 0.04 (in CS_2).

2.2 Preparation and purification of starting materials

2.2.1 Solvents

Methanol. The analar reagent was reacted with magnesium ribbon (1 g. per 100 ml.) until no further effervescence was observed, then distilled under nitrogen onto an activated, 3A molecular sieve. When a scrupulously dry solvent was required, 'Spectrosol' grade methanol was used.

Nitromethane was allowed to stand over P_4O_{10} for 48 hours and distilled three times to obtain a colourless solvent.

Ethanol and dichloromethane were distilled under nitrogen onto activated 3A molecular sieve.

Dioxane, benzene, toluene, pentane and hexane were all dried over sodium. Dioxane was freshly distilled before use.

Isopropyl and diethyl ethers were dried over sodium and distilled once a negative peroxide test had been obtained. The presence of peroxides is indicated by a faint yellow colouration when the ether (10 ml) is shaken with fresh potassium iodide solution (10%, 10 ml) and 2M hydrochloric acid (1 drop). Peroxides are destroyed by shaking the ether with iron (II) sulphate (acidified with dilute sulphuric acid) until the ether phase no longer gives a positive test.

α-picolene was dried over sodium hydroxide for 24 hours and distilled under nitrogen onto molecular sieve, 4A. Only the fraction boiling at 128-9°C was collected.

Carbon tetrachloride and chloroform were dried over P_4O_{10} for 48 hours and distilled under nitrogen.

Disulphur dichloride was used without further purification.

Carbon disulphide was stirred with mercury for 48 hours (10 ml. per 200 ml. solvent) to remove sulphur impurities; then distilled twice.

1,2-Dichloroethane was refluxed over calcium chloride and distilled under nitrogen.

2.2.2 Sulphur-nitrogen starting materials

(i) Thiodithiazyl dichloride, $S_3N_2Cl_2$ was prepared by a method[8] similar to that of Jolly[9,10]. Ammonium chloride (oven dried at 120° for 24 hours, 100 g), powdered sulphur (20 g) and S_2Cl_2 (100 ml) were placed in a 500 ml. flanged top, round bottom flask with a B34 ground glass socket joint fitted with an air condenser (50 x 3 cm. diam.) and an anhydrous calcium chloride drying tube. The flange top joint was lubricated with Kel-F halocarbon grease to prevent it "welding" together. The disulphur dichloride was heated to maintain a reflux level just above the neck of the flask. It was important to keep the fluctuations in air cooling currents to a minimum. Orange-red crystals of $S_3N_2Cl_2$ formed on the condenser walls after 8-10 hours. The apparatus was run until all the S_2Cl_2 was consumed. After cooling, the condenser was removed and attached to a two neck, round bottomed flask with tap (the drying tube was replaced by a stopper). The condenser was evacuated to remove any volatile impurities and the crystals heated gently to loosen them slightly, so that they could be scraped into the flask against a counter current of nitrogen. Yield = 21 g.

Analysis found N, 14.26; S, 49.63; Cl, 35.11; $S_3N_2Cl_2$ required N, 14.36; S, 49.29; Cl, 36.36 (*cf.* Chapter 1, page 2). The $S_3N_2Cl_2$ prepared in this way was converted into S_3N_2Cl and S_4N_3Cl.

(ii) Thiodithiazyl chloride, S_3N_2Cl

This was prepared by heating $S_3N_2Cl_2$ *in vacuo* according to Jolly[10] with the following modifications:

(a) A wide necked, round bottom flask was used instead of a tube, to allow a greater surface area of $S_3N_2Cl_2$ to be in contact with the oil bath.

(b) The flask was shaken regularly to increase the rate of conversion, hence the attachment to the vacuum line was non rigid.

(c) Heating for 2 hours gave a product which had a high chlorine and low sulphur and nitrogen analyses, indicating that the conversion was incomplete. Heating was thus continued for 8 - 10 hours. This period of time gave a fairly pure product.

Found: N, 16.93; S, 54.42; Cl, 25.00.

Required: N, 17.55; S, 60.25; Cl, 22.20

The observed weight loss in this preparation (60%) was greater than that reported by Jolly (45%). Infra-red spectra indicated the presence of some S_4N_3Cl in a solid by-product, which sublimed round the neck of the flask. S_3N_2Cl gave the following infra-red spectrum (cm^{-1})

1018(w), 964(m), 941(s), 709(s), 587(m), 462(w), 438(m), 409(m), 375(s) (*cf.* Chapter 1, page 3).

(iii) Thiotrithiazyl chloride, S_4N_3Cl

This was prepared in one of two ways; from either S_4N_4 or $S_3N_2Cl_2$ depending on which compound was available at the time.

The reaction with S_4N_4 was according to the equation:

$$3S_4N_4 + 2S_2Cl_2 \longrightarrow 4S_4N_3Cl$$

and was carried out in CCl_4 solution[9,10].

S_4N_4 (10 g, 54.0 mmol) in CCl_4 (100 ml) was heated to reflux and a solution of S_2Cl_2 (3 ml) in CCl_4 (10 ml) added. The mixture was refluxed for 2 hours and then stirred at room temperature for 24 hours. The product was isolated by filtration and purified by washing with CCl_4 and drying *in vacuo*. The yield of S_4N_3Cl was 12 g. (80% based on S_4N_4).

Analysis found: N, 20.87; S, 61.67; Cl, 17.23; S_4N_3Cl required N, 20.42; S, 62.34; Cl, 17.25.

Infra-red spectrum: 1163(m), 1129(w), 1000(s), 681(m), 567(m), 470(s), 455(m), 330(m) cm^{-1} (*cf*. Chapter 1, page 4).

The conversion of $S_3N_2Cl_2$ to S_4N_3Cl was done according to Jolly[9,10] using S_2Cl_2. $S_3N_2Cl_2$ (*ca*. 40 g) was refluxed with S_2Cl_2(50 ml) in CCl_4 (50 ml) for 8 hours and finally stirred at room temperature for 24 hours. The bright yellow product was filtered, washed with CCl_4 and pumped dry. Purification (if necessary) was by Soxhlet extraction with pentane.

Analysis found N, 19.70; S, 60.10; Cl, 19.20

S_4N_3Cl required N, 20.42; S, 62.34; Cl, 17.25.

Some problems were encountered with this method. If conversion to S_4N_3Cl was not complete, the presence of a moisture sensitive impurity resulted in the canary yellow sample of S_4N_3Cl rapidly turning a sand-brown colour when let down to "dry" nitrogen prior to the washing stage. The impurity was partially removed by the CCl_4 washing, to give a canary yellow product and a pale yellow solution. (This solution was analysed by t.l.c. which showed the presence of a bright yellow component at $R_f = 0.97$. It was thought not to be due to sulphur since this gives a colourless spot). On refluxing the product with S_2Cl_2 for an extra 2 hours, S_4N_3Cl was isolated without further problems.

(iv) Tetrasulphur tetranitride, S_4N_4

This was prepared according to Jolly[11]. The first stage involved chlorination of S_2Cl_2 (50 ml) in CCl_4 (1400 ml) to give SCl_2. The second, amination stage proceeded according to:

$$6SCl_2 + 16NH_3 \xrightarrow{CCl_4} S_4N_4 + 2S + 12NH_4Cl$$

The ammonia flow rate was adjusted so that the temperature of the reaction was kept below 50°C. The mechanism of the reaction is unknown but the intermediate colours are varied, proceeding from pale yellow, through cream, pale green-yellow, sand green, leaf green, olive green, chocolate brown, brick red, salmon pink to a bronze gold after about two hours. The filtrate was washed with ice cold water to remove the ionic impurities and the crude, Khaki green coloured S_4N_4 air dried for several days between filter paper. About 3.5 g of crude S_4N_4 was recovered from the CCl_4 and the total yield of crude material (45 g) was Soxhlet-extracted with Na-dried dioxane (400 ml) for 6 hours. The final yield of orange crystalline S_4N_4 was ca. 30 g. Analysis found N, 27.84; S_4N_4 required N, 30.40. Infra-red spectrum: 930(s), 770(w), 720(m), 700(s), 548(s), 530(w), 520(w), 350(s) cm^{-1} (cf. Chapter 1, page 6).

(v) Heptasulphur imide, S_7NH

This was prepared according to Heal[12]. S_2Cl_2(20 ml) in CCl_4 (80 ml) was added dropwise over a period of half an hour to concentrated ammonia (ρ = 0.88 g d_m^3, 200 ml) immersed in an ice-salt bath at -15°C. Stirring was continued for a further 15 mins. after the addition was complete. The bottom, red organic layer was separated and washed four times with distilled water. The resulting dark red organic phase was investigated by t.l.c. (below) and separation of the S_7NH from the mixture was by column chromatography as described earlier. The organic phase contained the following components (CCl_4 elutant):

0.16 (faint) - lower imide; 0.26 — S_4N_4(0.25); 0.30 (faint) - S_6-imide; 0.54 - S_7NH; 0.72 (red-faded) - S_4N_2 and 0.89 - sulphur (0.87)

(vi) Tetrasulphur tetraimide, $S_4(NH)_4$

The following procedure, after Brauer[13] was subject to several modifications and is discussed in more detail in Chapter 4. A solution of tin (II) chloride, $SnCl_2.2H_2O$ (4.9 g) in methanol (10 ml) and distilled water (1 ml) was added cautiously to a solution of S_4N_4 (1 g) in benzene (30 ml), which had been refluxed and allowed to cool slightly. After addition was complete, the solution was stirred for half an hour and cooled to room temperature. The white solid was filtered, and washed with 2M hydrochloric acid (10 ml), ethanol (10 ml) and ether (10 ml). Yield was 0.2 g (20% based on S_4N_4).

Analysis found N, 29.25; S, 67.72; H, 1.90;

$S_4(NH)_4$ required N, 29.70; S, 67.90; H, 2.12.

Infra-red spectrum: 3320(s), 3290(s), 3225(s), 1299(m), 830(s,br), 720(w), 700(w), 540(br,sh,s), 463(ms), 410(m), 305(ms,br) cm^{-1}.

Melting point = 156°C (darkens to red at 140°C) (cf. Chapter 1, page 5).

(vii) Tin (IV) chloride adduct of tetrasulphur tetranitride, $(S_4N_4)_2SnCl_4$

S_4N_4 (1.5 g, 8.1 mmol), tin (IV) chloride (0.48 ml, 1.06 g, 4.1 mmol) and dried CCl_4 (50 ml) were stirred for 24 hours at room temperature. The crimson red product, $(S_4N_4)_2$ $SnCl_4$ was filtered and washed with CCl_4(3 x 20 ml).

Analysis found N, 16.17; S, 36.55; Cl, 23.25;

$(S_4N_4)_2SnCl_4$ required N, 17.81; S, 40.77; Cl, 22.57.

Infra-red spectrum showed absorptions at 1043(vs), 1025(w,sh), 965(s), 930(ms), 812(s), 791(m), 728(w), 700(ms), 681(w), 621(mw), 568(s), 522(s), 420(m,br), 370(s), 350(mw), 312(s,br) cm^{-1}.

The yield was 2. g (8 % based on S_4N_4). The adduct was purified by washing with dilute hydrochloric acid (20 ml), ethanol (20 ml) and ether (20 ml). After purification the adduct gave the following analysis: N, 17.30; S, 40.41; Cl, 21.10. Yield was 2.1 g (80% based on S_4N_4).

(viii) Mercury thionitrosyl, $Hg_5(NS)_8$

This was prepared according to Meuwsen[14]:

$$5S_4(NH)_4 + 10Hg(OAc)_2 \xrightarrow{MeOH} 2Hg_5(NS)_8 + S_4N_4 + 20\ AcOH$$

Mercury (II) acetate (1.8 grams, 5.65 mmol) in ice cold methanol (80 ml, -10°C) was added dropwise with vigorous stirring to a solution of

$S_4(NH)_4$ (0.6 gram, 3.18 mmol) in methanol (100 ml). The reaction mixture (in an ice-salt bath at -10°C) was stirred for 45 minutes after the acetate had been added, then continued for a further 30 minutes using a CCl_4 slush bath (at -24°C). The colour changed during this time from pale yellow to deep red and finally to yellow-green. The solution was filtered cold (with a number four sinter) and the solid washed with methanol,acetone and ether (ice-cold in each case) $Hg_5(NS)_8$ is a pale green yellow compound. It was stored over potassium hydroxide in a vacuum desiccator. Analysis found Hg, 74.70; N, 7.68; S, 15.70; $Hg_5(NS)_8$ required Hg, 73.17; N, 8.17; S, 18.68. Yield was 1.3 grams and infra-red absorptions were at 1055(s,br), 685(m), 605(m), 440(m) cm^{-1}.

(ix) Tetrasulphur dinitride, S_4N_2

A solution of mercury thionitrosyl (0.1 gram, 0.07 mmol) in CS_2 (5 ml) was shaken with S_2Cl_2 (5 ml) in a test tube for 10 minutes. T.l.c. (CS_2) on the solution showed two components; at R_f = 0.00, and 0.79 (red,faded). The latter spot was due to S_4N_2. Heal[15] reported an R_f value of 0.8. The infra-red CS_2 solution spectrum (CsI cell) showed peaks due to S_4N_2 at 1037, 940, 629 and 620 cm^{-1}.

(x) Pentathiazyl tetrachloroferrate, $S_5N_5FeCl_4$

This was prepared according to Banister[16] as follows. $(NSCl)_3$ (6.1 g, 25 mmol) was stirred for about 2 hours with iron (III) chloride (12.2 g, 75 mmol) in thionyl chloride (130 ml). S_4N_4 (13.8 g, 75 mmol) was then added with vigorous stirring for 2 hours, during which time the pentathiazyl salt precipitated from solution. The solution was reduced to low volume, cooled to -10°C, filtered and dried in vacuo. Recrystallisation, if required was from thionyl chloride as described in reference 16. Yield of pure material was ca. 20 g (60% based on S_4N_4). Infra-red absorptions were at 1138(s,br), 1040(w,sh), 728(mw), 690(mw,br), 608(w,br), 528(s), 372(vs,br), 330(m,br) cm^{-1} (CsCl disc). Analysis found S, 36.51; N, 15.79; Fe, 14.59; Cl, 33.10 Calculated for $S_5N_5FeCl_4$ S, 37.44; N, 16.35; Fe, 13.04; Cl, 33.16.

2.3 Preparation of other materials

(i) Finely divided, active copper metal, Cu

This was prepared according to Dr. Z.V. Hauptman by hydrogen reduction of finely powdered copper (II) oxide, CuO.

$$CuO_{(s)} + H_{2(g)} = Cu_{(s)} + H_2O$$

Hydrogen gas was passed through an electrically heated glass tube containing a pre-weighed crucible of copper oxide. The system was purged with hydrogen before and after heating to avoid the possibility of heating a mixture of hydrogen and oxygen. The reduction was complete after 1½ hours (97% conversion by weight). The copper was pumped (2 hrs., R.T., 10^{-2} torr) to remove surface hydrogen and was used immediately.

(ii) Tin (IV) chloride, $SnCl_4$

This was purified by vacuum distillation, stored in a "Rotaflo" tube and manipulated under dry nitrogen.

(iii) Tetraethyl thiuram disulphide, $Et_2NCSS\text{-}SSCNEt_2$

Sodium diethyldithiocarbamate (2 g, 8.8 mmol) in methanol (15 ml) was added to iodine (1.13 g, 4.3 mmol) in methanol (10 ml). After 10 mins. stirring there was a colour change from deep red-brown to a faint brown-green, with the formation of a pale green solid. The dimer was recrystallised from methanol. Infra-red absorptions (cm^{-1}): 2970(s), 2928(s), 2910(s), 2865(s), 1488(vs), 1452(ms), 1440(m), 1417(vs), 1377(ms), 1350(s), 1293(ms), 1272(vs), 1196(vs), 1150(s,sh), 1092(m), 1073(m), 1061(m), 999(m), 968(ms), 913(ms), 819(ms), 780(mw), 770(mw), 554(m), 485(mw,br), 432(mw), 377(mw,br), 295(mw). Analysis found N, 9.17; S, 43.48; H, 7.50; C, 39.89. $Et_2NCSS\text{-}SSCNEt_2$ required N, 9.45; S, 43.29; H, 6.75; C, 40.50.

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PART I

REDUCTIONS OF THIAZENES

CHAPTER 3

SOME REDUCTIONS OF THIAZENES

3.1 Introduction

Durrant[1] found that S_4N_4 was the major product of the reaction between $(NSCl)_3$ and cyclohexene. A dechlorination of the trimer had occurred and a mechanism involving NS° radicals was proposed. Dechlorination reactions were further studied by Hey[2a], who found that S_4N_4 was also formed by reactions of $(NSCl)_3$, $S_3N_2Cl_2$, S_3N_2Cl and S_4N_3Cl with metals.

The main aim of the present work was to study these reductions more systematically (to fully characterise the products and determine the yield of S_4N_4). It was hoped to obtain a high yield synthesis of S_4N_4 which could be used in the preparation of other compounds (Chapter 4). The advantage of such an <u>in situ</u> source of S_4N_4 was that the explosion hazards of pure, solid S_4N_4 could be avoided. Background information on the thiazenes studied ($S_3N_2Cl_2$, S_3N_2Cl and S_4N_3Cl) appeared in Chapter 1.

3.2 Experimental

3.2.1 Reaction between $S_3N_2Cl_2$ and sodium thiosulphate

$S_3N_2Cl_2$ (3.0 g, 15 mmol) was stirred with a suspension of anhydrous sodium thiosulphate (4.0 g, 25 mmol) in dry nitromethane (30 ml). The solution turned from green-black to deep red-orange. After 1 hour a sample was chromatographed in CS_2 (Table 3.1, TLC1). This was repeated after refluxing the solvent for ½ hour (TLC2). Refluxing produced a bright yellow precipitate and an orange solution. The yellow solid (1.4 g) was filtered and tested as follows:

i) Reaction with water caused rapid hydrolysis and formation of a green-black solid.

ii) An aqueous solution of iodine was rapidly decolourised. The black solid product was shown to contain ammonium sulphate.

iii) Extraction with hot nitromethane produced an orange solution which contained four species (TLC3).

TABLE 3.1

TLC1	TLC2	TLC3	Assignment (Standard)
0.00$^{\neq}$ y	0.00$^{\neq}$ y		$S_4N_3Cl/Na_2S_2O_3$
0.00 b	0.00 b		
0.07	0.06		
	0.18 f		
0.43 y	0.45 y	0.45 y	S_4N_4(0.45)
0.65			
0.78	0.79	0.80 f	S_7NH (0.80)
0.89 r,h	0.90 r,f	0.90 r,h	S_4N_2
0.96	0.97	0.96	S_8 (0.97)

y = yellow b = black r = red f = faint h = hydrolysed

≠ part of spot unaffected by iodine.

The reaction was repeated using a 1:1 ratio of $S_3N_2Cl_2$ (2.8 g) and $Na_2S_2O_3$ (2.2 g) and heating at 60°C in nitromethane (30 ml) for 3 hours. A green-yellow solid (1.3 g) was isolated which gave i.r. absorptions at 1164 (s), 1134 (mw), 1000(s), 963 (mw), 943 (mw), 720 (m), 709 (m), 682 (ms), 587 (mw), 568 (ms), 470 (s), 455 (m), 462, 438 and 429 (all unresolved) and 375 (m) cm^{-1}. The absorptions underlined were characteristic of S_4N_3Cl whilst the rest were assigned to S_3N_2Cl.

3.2.2 Reaction between S_3N_2Cl and sodium thiosulphate

S_3N_2Cl (1.7 g, 10.6 mmol) was stirred at room temperature with a suspension of anhydrous $Na_2S_2O_3$(2.0 g, 12.6 mmol) in dry nitromethane (10 ml). After 2 hours a red-orange solution had formed. T.l.c. (in CS_2) showed components with R_f = 0.00 (yellow, faint), 0.31 (yellow) and 0.86 (red, faded) - S_4N_3Cl, S_4N_4 and S_4N_2 respectively. A dark green solid (0.6 g) remained which showed i.r. absorptions due to unreacted starting material.

In a repeat experiment, S_3N_2Cl (1.5 g, 9.3 mmol) and $Na_2S_2O_3$(2.9 g, 18.0 mmol) in dry CH_3NO_2 (40 ml) were heated at 90°C for 3 hours. The solution was filtered to give a yellow-brown solid and a deep red solution. The solid analysed as N, 21.15, S, 62.10, and gave i.r. absorptions as shown in Table 3.2 .

TABLE 3.2

Absorptions	Compound (Ref)
1200 (mw,br), 1060 (w)	$Na_2S_4O_6$ (3)
1164 (m,br), 1035 (mw), 997 (s), 680 (mw) 564 (mw), 468 (s), 452 (m)	S_4N_3Cl (Chapter 1)
1112 (w), 995 (w,sh), 665 (w), 525 (w,br)	$Na_2S_2O_3$ (4)
935 (w), 628 (mw), 620 (w), 475 (sh) 380 (ms)	S_4N_2 (5)
925 (ms), 720 (s), 700 (w), 548 (m)	S_4N_4 (Chapter 1)

3.2.3 Reaction between S_4N_3Cl and sodium thiosulphate

S_4N_3Cl (1.0 g, 4.8 mmol) was stirred with anhydrous $Na_2S_2O_3$ (1.2 g, 7.6 mmol) in dry nitromethane (20 ml) for 3 hours at 90 - 100°C. T.l.c. (in CS_2) showed five components:

0.00 (colourless in iodine)	$Na_2S_2O_3$
0.06 (faint)	
0.40	S_4N_4(0.42)
0.86 (red, faded)	S_4N_2
0.96	S_8 (0.96)

Crystallisation of orange S_4N_4(0.15 g) occurred on cooling. Analysis found N, 25.8; S_4N_4 required N, 30.4 (i.e. a 15% by weight sulphur impurity).

The same products were identified when the ratio of S_4N_3Cl (0.5 g) to $Na_2S_2O_3$ (0.8 g) was changed to 2:1. In this experiment tin (IV) chloride (2 ml, 17 mmol) was stirred with the nitromethane solution for 24 hours at room temperature. The crimson solid thus formed was filtered, washed with CCl_4, and pumped dry. Yield (of $(S_4N_4)_2$ $SnCl_4$) was 0.3 gram. This was equivalent to a 66% yield (0.22 g) of crude S_4N_4(based on S_4N_3Cl). Analysis of the crimson product gave N, 16.00; S, 43.43; Cl, 20.14; $(S_4N_4)_2SnCl_4$ required N, 17.81; S, 40.77; Cl, 22.54. I.r. absorptions were at 1049 (s,sh), 968 (m), 930 (mw), 813 (m,br), 795 (w), 728 (w,br), 702 (mw,br), 680 (w,br), 620 (mw,br), 575 (w), 558 (w), 523 (ms), 420 (mw,br), 371 (m), 350 (w and 318 (m,br) cm^{-1}. (cf. Chapter 2, page 33).

A higher yield (0.68 g) of this adduct was obtained by reacting a 1:1 ratio of S_4N_3Cl (1.0 g) and $Na_2S_2O_3$ (0.8 g) and adding $SnCl_4$ (2 ml) under the same experimental conditions. This would represent a 75% yield of crude S_4N_4. The adduct was, however, less pure that that obtained in the reaction of 2:1 stoichiometry. (Analysis found N, 15.14; S, 44.54; Cl, 18.30). (See Table 3.8, page 52).

3.2.4 Reaction between S_4N_3Cl and sodium oxalate

S_4N_3Cl (0.7 g, 3.4 mmol) and $Na_2C_2O_4$ (0.68 g, 5.1 mmol) were refluxed in nitromethane (20 ml) for 1 hour. The deep-red solution contained three components (t.l.c. in CS_2).

0.33 (yellow)	S_4N_4 (0.36)
0.82 (red, faded)	S_4N_2
0.94 (faint)	S_8 (0.96)

Carbon dioxide was detected as a product of the reaction. The same products resulted when a 1:1 ratio of reagents (1.0 g of S_4N_3Cl) was used. In this case, $SnCl_4$ (2 ml) was added to the filtered nitromethane solution and the mixture stirred for 24 hours at room temperature. Yield of $(S_4N_4)_2SnCl_4$ was 0.63 g (69% yield of crude S_4N_4 based on S_4N_3Cl). Analysis found: N, 16.42; S, 41.52; Cl, 20.46; Required N, 17.81; S, 40.77; Cl, 22.57. I.r. absorptions were at 1046 (s,sh), 966 (m), 930 (m), 810 (s), 790 (w), 728 (w,br), 700 (m), 681 (w,br), 625 (w,br), 570 (mw), 555 (w), 520 (m), 420 (w,br), 371 (m), 350 (w) and 318 (m,sh,br) cm^{-1}. (cf. Chapter 2, page 33).

S_4N_3Cl (0.5 g, 2.4 mmol) in nitromethane (40 ml) was stirred at room temperature with a solution of anhydrous sodium oxalate in dry methanol (10 ml). After 20 minutes, a yellow-white solid was filtered from a deep-red solution. The solid had the infra-red absorptions shown in Table 3.3.

TABLE 3.3

Absorption	Compound (Ref)
3600 - 3400 (br)	ν_{OH}
3200 - 3300 (br), 1405 (s,br)	ν_{NH} and δ_{NH}
2940 (m), 2765 (mw), 1700-1550 (s,br), 1330 (s,br), 775 (s,br,sh), 520 (s,br)	$Na_2C_2O_4$ (6)
930 (w,br), 700 (sh), 550 (w,sh), 365 (mw)	S_4N_4 (Chapter 1)

The reaction of S_4N_3Cl with $Na_2C_2O_4$ was also investigated in dioxane and toluene, but isolation of S_4N_4 was not achieved from reactions involving these solvents. For example, in a typical experiment, a 1:1 ratio of reactants was refluxed in dioxane for 2 hours. T.l.c. (in CS_2) on the deep red solution revealed three components: S_4N_4 (0.36), S_4N_2 (0.86 red, faded) and S_8(0.94). Evaporating this solution to dryness produced a dark red sticky resin.

3.2.5 Reaction between S_4N_3Cl and hypophosphorous acid

S_4N_3Cl (0.5 g, 2.4 mmol) was stirred at room temperature with hypophosphorous acid (3.0 ml, 2.4 mmol, as a 50% W/W solution in HCl). A vigorous exothermic reaction occurred, and a cloudy white suspension formed. Strong evolution of hydrogen sulphide was observed.

The reaction was repeated using S_4N_3Cl (0.5 g) and H_3PO_2 (3 ml) diluted in ice-cold methanol (25 ml). A less violent reaction occurred, again producing a pale yellow-white suspension and H_2S.

3.2.6 Reaction between S_4N_3Cl and sodium hypophosphite

NaH_2PO_2 (0.43 g, 4.8 mmol) in dry methanol (15 ml) was added to S_4N_3Cl (1.0 g, 4.8 mmol) in nitromethane (40 ml), and the mixture stirred for 2 hours at 80°C. The deep red solution contained five components: 0.00 (dark under u.v. irradiation) - NaH_2PO_2; 0.13; 0.40 (yellow) - S_4N_4 (0.42) 0.93 (red, faded) - S_4N_2; 0.98 - S_8 (0.97). The solution was cooled and filtered to give a yellow-white solid. The i.r. spectra of this solid (IR1) and of the white solid formed by evaporating the solution to low bulk (IR2) appear below (Table 3.4). Evaporation to dryness produced a yellow-orange tarry residue. Analysis of the white solid gave P, 21.10; N, 2.98; S, 1.72; Na, 17.80; NaH_2PO_2 required P, 36.40; Na, 26.10.

The reaction was repeated using a 1:1 ratio of S_4N_3Cl (0.5 g) and NaH_2PO_2(0.2 g) in ice cold, demineralised water (10 ml). Stirring at -10°C for 10 minutes, followed by filtration, produced a fine black solid which had i.r. absorptions at 3200 (w,br), 1410 (mw,br), 1270 - 1170 (w,br), 1110 (ms,br), 1022 (ms,br), 935 (w) and 700 (s,br,sh) cm^{-1}. The black solid was Soxhlet-extracted with dioxane (30 ml) to give a deep red

TABLE 3.4

IR1	IR2	IR1	IR2
3460 (ms,br)*	3600-3400 (s,vbr)*	1082 (s)*	1082 (s,br,sh)*
	3200 (s,vbr)	1065 (s,br)*	1065 (s,br,u)*
2320 (s,br)*	2310 (s,vbr)*		1000 (sh)≠
2200-2100 (w)*	2200-2100 (w)*	812 (vs)*	810 (vs,br)*
1960 (w)*	1965 (w,br)*		770 (mw,br)
	1700 (w,br)		688 (w,u)≠
1658 (s)	1630 (m,sh)	610 (mw)	620 (s,br)
	1555 (mw,br)		600 (m)
	1455 (m,br)		565 (sh)
1400 (mw)	1400 (ms,br)		550-530 (mw)*
1185 (vs)*	1260-1150 (s,u)*	485 (ms)	488 (s,br)
1160 (vs)*	1160 (mw,u)*≠		475 (s,sh)*
	1135 (mw,u)*		460 (mw,sh)≠

* Sodium hypophosphite (7) ≠ S_4N_3Cl (Chapter 1)

solution containing S_4N_4, S_4N_2 and S_8 (R_f values 0.65, 0.90 and 0.97 respectively, CS_2 elutant).

An infra-red spectrum was also recorded for the black product from a test tube reaction between S_4N_3Cl and NaH_2PO_2 in aqueous solution, shaken for 10 minutes at room temperature: 3200 (w,vbr), 1400 (mw,br) ν_{NH} and δ_{NH}; 1225 (w,br), 1085 (w,br), 1025 (mw,br), 620 (mw,br)[8]; and 930 (vs), 730 (mw), 700 (s,br), 552 (s), 352 (ms) cm^{-1} (S_4N_4).

The reaction between S_4N_3Cl (0.5 g, 2.4 mmol) in nitromethane (40 ml) and NaH_2PO_2(0.2 g, 2.4 mmol) in methanol (4 ml) and water (4 ml) at 90°C gave S_4N_4 and S_4N_2 as major products.

S_4N_3Cl (1.0 g, 4.8 mmol) was refluxed with NaH_2PO_2 (0.4 g, 4.8 mmol) in nitromethane (40 ml) for 2 hours. After hot filtration, the solution was cooled and $SnCl_4$ (2 ml) added. The mixture was stirred for 24 hours at room temperature and the purple adduct, $(S_4N_4)_2$ $SnCl_4$ isolated. The yield was 0.4 g (which represented a 44% yield of crude S_4N_4). Analysis found N, 15.08; S, 46.10; Cl, 19.75; $(S_4N_4)_2$ $SnCl_4$ required N, 17.81; S, 40.77; Cl, 22.57.

3.2.7 Reaction between S_3N_2Cl and sodium iodide

(a) S_3N_2Cl (1.5 g, 9.4 mmol) and NaI (2.5 g, 16.6 mmol) were ground together and stirred in methanol (20 ml) for ½ hour at room temperature.

A dark green solid (0.6 g) was filtered from a red-brown solution. After shaking with hexane until the washings were pale yellow, it gave the following i.r. absorptions (cm^{-1}): 3150 (vw), 1400 (mw) (γ_{NH} and δ_{NH}); 1230 (w,vbr,u), 1020 (w,vbr,u), 800 (w,u), 615 (mw,vbr)^{8}; and 925 (s), 725 (mw), 698 (s), 545 (s), 345 (ms) (S_4N_4).

(b) In a repeat experiment, the dark green solid was treated with ice cold water (500 ml) and aliquots (2 x 50 ml) of potassium iodide solution (1.2 M). The i.r. spectrum showed predominantly S_4N_4 absorptions but also weaker peaks at 3400, 1060, 800 and 615 cm^{-1}. Extraction with dioxane (100 ml) gave an orange solution. After evaporation of the dioxane, the brown residue was recrystallised twice, from dichloromethane and dioxane, to give a yellow product (0.5 g). Analysis found N, 15.55; S_4N_4 required N, 30.4. T.l.c. (in CS_2) showed that sulphur was an impurity (45% by weight according to analysis). A white solid, insoluble in dioxane, remained on the sinter after extraction. Its i.r. spectrum suggested that it contained ammonium sulphate : 3400 (s,br), 1400 (ms), 1250 (m), 1100 (s,br,sh), 875 (m), 720 (mw) and 614 (s) cm^{-1} (underlined peaks *cf*. 9).

(c) Sodium iodide (5.4 g, 36.0 mmol) in methanol (30 ml) was added dropwise to S_3N_2Cl (5 g, 31.3 mmol) at 0°C, and stirred for ½ hour. Aqueous sodium thiosulphate (0.4 M, 60 ml) was added with vigorous stirring. A black solid (4.0 g) was isolated which had the following i.r. absorptions (cm^{-1}): 3400 (m,br), 1630 (mw,br) (γ_{OH} and δ_{OH}); 3200 (mw,br), 1400 (w) (γ_{NH} and δ_{NH}); 1224 (mw,br), 1015 (mw), 610 (mw,br)^{8} and 925 (mw), 725 (mw), 699 (m), 345 (m) (S_4N_4). The black solid decomposed (with evolution of ammonia) over 1 - 2 hours to give a dark green material. This was extracted with dioxane (50 ml) and crystallisation of S_4N_4 occurred after reducing the volume of solvent. I.r. absorptions (cm^{-1}) were at 925 (s), 722 (s), 695 (s), 550 (s). Analysis found N, 18.1; S_4N_4 required N, 30.4. T.l.c. (in CS_2) showed sulphur to be the major contaminant (40% based on analysis). Yield of impure S_4N_4 was 1.1 g (38% based on S_3N_2Cl).

This procedure was repeated using a suspension of anhydrous sodium thiosulphate (9.2 g, 58.3 mmol) in dry methanol (80 ml) and the mixture stirred for 24 hours. Initially, a black precipitate formed. After a day however, filtration produced a yellow-green solid and a red-brown solution. The solid had absorptions at 1125 (s,br), 998 (ms,br), 915 (ms,br), 720 (sh,u), 700 (sh,u), 670 (s,vbr) and 530 (ms,br) cm^{-1}. Underlined absorptions were due to sodium thiosulphate[4]. Dioxane extraction (100 ml) of the solid produced crude S_4N_4 (1.8 g, 62% based on S_3N_2Cl). Analysis found N, 19.3; S_4N_4 required N, 30.4.

Table 3.5 reports t.l.c. analysis (in CCl_4) of the methanol solution; ½ hour after mixing the S_3N_2Cl and NaI (I), after 48 hours (II) and after adding a quantitative amount of thiosulphate (III).

TABLE 3.5

I	II	III	Assignment (standard)
0.00 f	0.00 f	0.00	
0.17≠			
		0.19	
0.30 y	0.26 y	0.25 y	S_4N_4 (0.27)
	0.54	0.51	S_7NH (0.54)
0.76 b	0.75 b		I_2 (0.75)
0.87 f	0.87	0.87	S_8 (0.88)
f = faint	y = yellow	b = brown	≠ streaked from baseline

The yellow-white precipitate formed on addition of sodium thiosulphate showed i.r. absorptions due to S_7NH (underlined): 3260 (s), 1220 (vw,br), 1145 (w,br), 1020 (w,br), 1000 (w,br), 815 (s), 680 (w,br), 500 (w,br), 460 (m,br), 430 (m,br), 400 (w), 350 (w) and 280 (m) cm^{-1} (cf. S_7NH Chapter 2, page 32).

(d) S_3N_2Cl (6 g, 37 mmol) and NaI (8.45 g, 56 mmol) in dry methanol (50 ml) were stirred at 0°C for 45 minutes. Diethyl ammonium diethyldithiocarbamate $(Et_2NH_2)(SSCNEt_2)$ (12.54 g, 56 mmol) in methanol (20 ml) was added with stirring. Filtration gave a green-white solid and a brown-green solution, which contained six components (Table 3.6, TLC1). The green-white solid was extracted with dioxane (100 ml), and the solution (TLC2) reduced to low bulk to give S_4N_4(1.0 g, 29% based on S_3N_2Cl) which contained 45% sulphur by weight. The white, dioxane-insoluble residue had i.r. absorptions at 2970 (m), 2935 (m), 2910 (m), 2868 (m), 1488 (ms), 1450 (m,u), 1440 (m,u), 1412 (s), 1375 (m), 1346 (ms), 1291 (m), 1271 (s), 1194 (s), 1150 (s,sh), 1090 (mw), 1060 (m), 997 (mw), 965 (ms), 910 (ms), 817 (ms), 788 (w), 770 (mw), 554 (mw,br), 482 (mw,br), 430 (mw,br) and 370 (mw,br) cm^{-1}. (<u>cf</u>. Tetraethyl thiuramdisulphide, Chapter 2, page 35).

TABLE 3.6

TLC1	TLC2	Assignment (Standard)
0.00 w		Et_2NH_2I
0.19≠	0.14 ≠	
0.40 y	0.36 y	S_4N_4 (0.44)
0.51 f		
0.79	0.78 f	S_7NH
0.96 f	0.96	S_8

w = white   y = yellow   f = faint   ≠ streaked from baseline

(e) S_3N_2Cl (2.2 g, 13.8 mmol) and NaI (2.48 g, 16.5 mmol) in nitromethane (30 ml) were stirred at 0°C for 45 minutes and the mixture filtered to give a green-black solid with i.r. absorptions at 3200 (mw), 1405 (ms,br), 1140 (m,br), 620 (mw,br) - $(NH_4)_2 SO_4$ <u>cf</u> Ref.9; 3200 (mw), 1230 (sh,u), 840 (vw,br), 430 (vw) (S_7NH - Chapter 2, page 32); 1160 (sh,u), 1005 (w,br), 470 (mw), 325 (w,u) (S_4N_3Cl) and 927 (s), 725 (m), 699 (s), 550 (ms), 345 (m) cm^{-1} (S_4N_4). The nitromethane solution contained nine components (t.l.c. in CS_2) with R_f values at 0.00 (became dark-brown when exposed to iodine vapour); 0.06; 0.17 (faint, purple); 0.29 (yellow) - S_4N_4(0.39); 0.45 (faint); 0.75 (faint) - S_7NH (0.77); 0.87 (red,faded) - S_4N_2; 0.92 (purple) - I_2(0.92) and 0.97 - S_8(0.96). The yield of S_4N_4 from the reaction in nitromethane was determined by isolating the adduct, $(S_4N_4)_2$ $SnCl_4$. Yield of adduct was 0.5 g (from 2.2 g S_3N_2Cl). This represented a 29% yield of crude S_4N_4. Analysis found N, 15.44; S, 44.87; Cl, 19.57; required N, 17.81; S, 40.77; Cl, 22.57.

(f) Experiment (c) above was repeated and the black solid formed after addition of aqueous sodium thiosulphate was filtered rapidly, washed with ethanol (20 ml) and ether (20 ml), and dried in vacuo to minimise hydrolysis. I.r. absorptions confirmed those reported in Experiment (c). When heated to 100°C the black solid became brick-red, and a sample in a sealed tube, heated inadvertently, exploded leaving a red-brown residue. The brick-red solid had an i.r. spectrum similar to the black solid. Room temperature extractions of the black solid with acetone, carbon tetrachloride, dioxane and nitromethane gave orange-yellow solutions which contained S_4N_4 (t.l.c.). The black solid was largely insoluble, but S_4N_4 and S_8 were extracted from it by carbon disulphide. Analysis of the black solid (a) and the brick-red residue (b) found:

(a) N, 13.20; S, 51.85; Cl, 12.73; H, 1.69

(b) N, 12.84; S, 50.43; Cl, 12.76; H, 1.47

Mass spectral data are recorded in Table 3.7.

TABLE 3.7

$^m/_e$	Relative Intensity		Assignment	$^m/_e$	Relative Intensity		Assignment
	(a)	(b)			(a)	(b)	
15	14	8	NH	76	11	14	S_3N_4
16	15	51	O, NH_2	78	36	24	NSO_2, S_2N
17	85	120	OH, NH_3	92	93	127	S_2N_2
18	175	285	H_2O	96	13	8	S_3, SO_4
28	53	178	N_2	110	6	4	S_3N
32	19	15	S, O_2	124	3	2	S_3N_2
35	3	6	Cl	128	31	20	S_4, S_8^{2+}
36	18	35	HCl	138	109	106	S_3N_3
46	100	100	SN	156	3	2	S_4N_2
47	6	6	iSN, SNH	160	28	18	S_5
48	9	8	iSN, SO	162	6	4	$S_2N_2Cl_2$?
58	118	11	?	184	21	25	S_4N_4
62	6	6	$S_3N_2^{2+}$, NSO	192	11	8	S_6
63	6	4	HNSO	254	9	2	I_2
64	111	74	SO_2, S_2	256	39	29	S_8

i = isotope

The finely divided black powder also exploded after being washed with ice cold water, ethanol and ether and dried <u>in vacuo</u>. Both black and brick-red solids showed some room temperature d.c. conductivity (ca 10^{-2} and 10^{-1} ohm^{-1} cm^{-1} respectively).

3.2.8 Reaction between S_4N_3Cl and sodium iodide

S_4N_3Cl (1.0 g, 4.8 mmol) and NaI (0.8 g, 5.7 mmol) were stirred in nitromethane (30 ml) for 15 minutes. The solution changed from green to red-brown, and t.l.c. (in CS_2) revealed four components, with R_f values at 0.06 (yellow-brown); 0.42 - S_4N_4 (0.43); 0.91 (S_4N_2) and 0.96 - S_8(0.96). The spot at 0.06 showed streaking from the baseline. The mixture was heated at 80°C for 1½ hours, and repeat t.l.c. detected only four components (S_4N_4, S_4N_2, I_2 and S_8). Iodine vapour was observed above the solvent. The reaction mixture was filtered at room temperature and a yellow-white solid isolated (0.23 g) which had i.r. absorptions characteristic of a mixture of S_4N_3Cl and S_4N_4 with additional weak absorptions (at 3450, 1630; and 3150, 1400 cm^{-1}) due to hydrolysis products. Other weak absorptions were at 1265, 1030, 770, 620, 600 and 530 cm^{-1}.

In a repeat experiment $(S_4N_4)_2SnCl_4$ was precipitated from the nitromethane solution as previously described. Yield was 0.2 g (representing a 22% yield of crude S_4N_4). Analysis after washing with dilute hydrochloric acid (20 ml), ethanol (20 ml) and ether (20 ml) found N, 15.29; S, 43.28; Cl, 19.34; required for $(S_4N_4)_2SnCl_4$, N, 17.81; S, 40.77; Cl, 22.57.

3.2.9 Reaction between S_4N_3Cl and metallic iron

S_4N_3Cl (3.5 g, 17 mmol) and iron turnings (1.0 g, 18 mmol) were refluxed in dry nitromethane (40 ml) for 2 hours. T.l.c. (in CCl_4) revealed the presence of S_4N_3Cl (R_f = 0.00), S_4N_4(R_f = 0.34) and S_8 (R_f = 0.86). The mixture was filtered at 0°C and the crude solid extracted with dry dioxane (90 ml). Evaporation of the dioxane to low bulk produced orange needle-like crystals of S_4N_4. Yield was 0.5 g (21% based on S_4N_3Cl). Analysis found N, 29.6; S_4N_4 required N, 30.4.

In a repeat preparation, the reaction mixture was filtered hot, then cooled and the tin (IV) chloride adduct precipitated by addition of $SnCl_4$ (2 ml). Yield after washing with dilute hydrochloric acid (20 ml), ethanol (20 ml) and ether (20 ml) was 2.6 g (81% yield of crude S_4N_4). Analysis found N, 15.66; S, 42.70; Cl, 19.35; required for $(S_4N_4)_2SnCl_4$, N, 17.81; S, 40.77; Cl, 22.57.

The reduction of S_4N_3Cl by metallic iron in toluene gave similar products, but t.l.c. (in CS_2) revealed an extra dark-brown component at R_f = 0.04 (see discussion, pages 57-8).

3.2.10 Effect of refluxing nitromethane on S_4N_3Cl.

S_4N_3Cl (1.0 g, 4.8 mmol) was refluxed in nitromethane (30 ml) for 2 hours. T.l.c. (in CS_2) revealed three components: S_4N_3Cl (R_f = 0.00), S_4N_4(R_f = 0.42) and sulphur (R_f = 0.95). Addition of $SnCl_4$ (2 ml) to the mixture at room temperature and stirring for 24 hours produced the crimson adduct. Yield was 0.3 g (33% yield of crude S_4N_4). Analysis found N, 15.82; S, 40.33; Cl, 21.03; required for $(S_4N_4)_2SnCl_4$; N, 17.81; S, 40.77; Cl, 22.57.

3.2.11 Effect of refluxing chloroform on S_4N_3Cl

S_4N_3Cl (1.0 g, 4.8 mmol) was refluxed in dry chloroform (30 ml) for 2 hours. The red solution contained six components: S_4N_3Cl (R_f = 0.00), S_4N_4 (R_f = 0.46), S_7NH (R_f = 0.86 faint), S_4N_2 (R_f = 0.93 red, faded), S_8 (R_f = 0.96) and an unknown one at R_f = 0.68 (faint). A cream-brown solid was isolated which had i.r. absorptions at 3100 (vs,br,u), 3050 (vs,br,u), 2000(mw,br), 1400 (vs,br), 1100 (w,br) and 620 (w,br) cm^{-1} - (cf. $(NH_4)_2SO_4$[9]).

Other peaks, at 928 (mw), 728 (mw), 699 (m), and 550 (m) cm^{-1} were due to S_4N_4. Isolation of S_4N_4 in solution as the tin (IV) chloride adduct (0.47 g) indicated that the yield of crude S_4N_4 was 51%. The adduct analysed as N, 16.22; S, 39.17; Cl, 17.26 after washing with dilute HCl, ethanol and ether. $(S_4N_4)_2SnCl_4$ required N, 17.81; S, 40.77; Cl, 22.57.

3.3 Discussion

Padma and Vasudeva-Murthy[10] have reported that reducing reagents such as HI and KI (in conc. HCl) cause ring degradation of S_4N_3Cl with reduction to sulphur or hydrogen sulphide, ammonia and hydrogen chloride.

The reductions of $S_3N_2Cl_2$, S_3N_2Cl and S_4N_3Cl were therefore studied under milder conditions using:-

(i) Metals (e.g. Iron) which are good reducing agents due to their electropositivity: $M = M^{n+} + ne^-$ (E^o = +ve)

(ii) Reducing anions (e.g. $S_2O_3^=$)

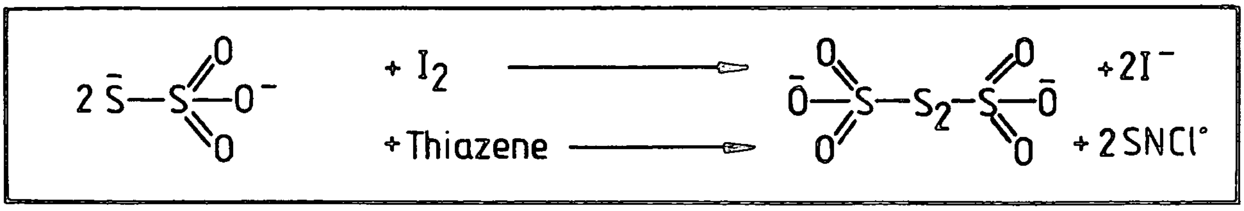
On the basis of electrode potentials (which are strictly only valid when considering reactions in aqueous media), the reagents chosen were mild reducing agents. Those containing hydrogen were tried in attempts to produce $S_4(NH)_4$, or other imides.

3.3.1 Reaction between $S_3N_2Cl_2$ and sodium thiosulphate

$S_3N_2Cl_2$ is very reactive and extremely susceptible to hydrolysis. It reacted strongly with sodium thiosulphate and results indicated that S_4N_4 and S_4N_2 were the major sulphur-nitrogen products at room temperature, with some S_4N_3Cl (less soluble in nitromethane). The reaction mixture was very complex (as shown by chromatography) with traces of S_7NH (due to the presence of some moisture) and sulphur. Other, fainter spots were probably due to the S_6- and S_5- imides. The spot at R_f = 0.07 was not identified and is discussed later (pages 57-8).At temperatures above 60°C in nitromethane the major solid product was S_4N_3Cl, confirmed by chemical tests and i.r. evidence (page 39). The data (TLC3) showed that S_4N_3Cl will undergo thermal rearrangement in nitromethane to give S_4N_4 (see section 3.3.10). Attempts to record t.l.c. plates photographically were unimpressive because of problems with lighting and spot resolution.

3.3.2 Reaction between S_3N_2Cl and sodium thiosulphate

S_3N_2Cl is less reactive than $S_3N_2Cl_2$ and was less readily reduced by sodium thiosulphate. Reaction was slow at room temperature but virtually complete in 2 hours at 90^{o}C. T.l.c. showed fewer components in the reaction mixture, mainly S_4N_4 and S_4N_2. Absorptions at 1200 and 1060 cm^{-1} were assigned to the sulphur anion, $S_4O_6^{=}$ which was believed to be the oxidation product of the reaction. An analogy can be drawn with the iodine-thiosulphate reaction:



The nature and subsequent fate of the "SNCl$^{\bullet}$" radical is discussed later.

3.3.3 Reduction between S_4N_3Cl and sodium thiosulphate

S_4N_3Cl is the most stable of the three thiazenes studied, but it is readily reduced by sodium thiosulphate in nitromethane at 90^{o}C (3 hours) to give S_4N_4, S_4N_2 and sulphur. It was possible to isolate S_4N_4 from this reaction (albeit contaminated with sulphur) in contrast to previous systems where its crystallisation was inhibited by the complexity of species in solution.

The approximate yield of S_4N_4 from thiazene reductions was determined by precipitation as the adduct, $(S_4N_4)_2SnCl_4$. The percentage yields quoted in section 3.2 were calculated assuming a pure adduct and that the conversion rate (K), as determined in Chapter 2 (page 33), was only 80%.

$$2S_4N_4 + SnCl_4 \longrightarrow (S_4N_4)_2SnCl_4 \qquad (K)$$

Although the i.r. absorptions compared well with authentic data, chemical analysis showed that the adducts isolated were invariably contaminated with sulphur (Table 3.8).

Table 3.8 contains consistent evidence for a sulphur impurity. It also shows clearly that $(S_4N_2)_2SnCl_4$ is an unlikely contaminant.

3.3.4 Reaction between S_4N_3Cl and $Na_2C_2O_4$

Sodium oxalate also reduced S_4N_3Cl to S_4N_4, S_4N_2 and S_8. The reaction was rapid in refluxing nitromethane, but it did proceed at room temperature. T.l.c. data demonstrated that sodium oxalate was a "cleaner"

TABLE 3.8

Section	Reaction	Sulphur Ratio (to nitrogen)	Elemental Composition (%)		
			S	N	Cl
3.2.3	$S_4N_3Cl/Na_2S_2O_3$				
	2:1	1.18	43.43	16.00	20.14
	1:1	1.28	44.54	15.14	18.30
3.2.4	$S_4N_3Cl/Na_2C_2O_4$				
	1:1	1.10	41.52	16.42	20.46
3.2.5	S_4N_3Cl/NaH_2PO_2				
	1:1	1.33	46.10	15.08	19.75
3.2.7	S_3N_2Cl/NaI				
	1:1.2	1.27	44.87	15.44	19.57
3.2.8	S_4N_3Cl/NaI				
	1:1.2	1.24	43.28	15.29	19.34
3.2.9	S_4N_3Cl/Fe				
	1:1	1.19	42.70	15.66	19.35
3.2.10	S_4N_3Cl/CH_3NO_2	1.11	40.33	15.82	21.03
3.2.11	$S_4N_3Cl/CHCl_3$	1.05	39.17	16.22	17.26
	$(S_4N_4)_2SnCl_4$	1.00	40.77	17.81	22.57
	$(S_4N_2)_2SnCl_4$	2.00	44.76	9.77	24.77

reducing agent than sodium thiosulphate and on the basis of spot intensity, S_4N_2 was formed in the higher yield. Since S_4N_2 can be produced from S_4N_4 and S_8[11]:

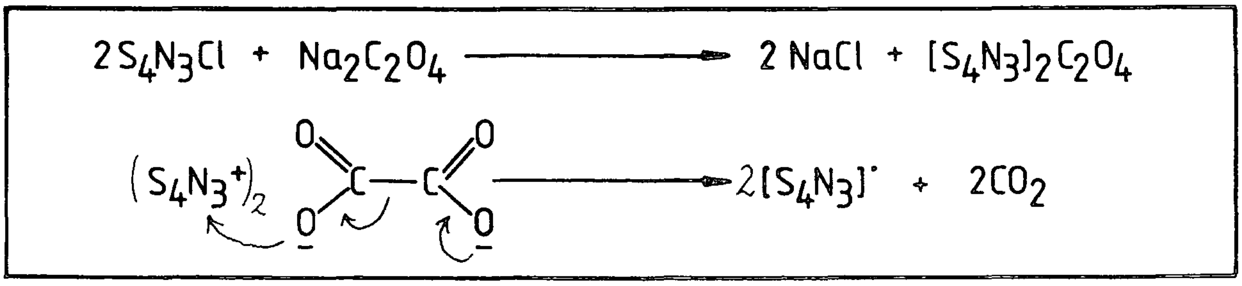
$$S_4N_4 + \tfrac{1}{2}S_8 \rightleftharpoons 2S_4N_2$$

a high yield of S_4N_2 would explain the low intensity of sulphur on the chromatogram. As a consequence of the lower yield of sulphur, the $SnCl_4$ adduct isolated was purer than the product obtained from the thiosulphate systems.

The rate of room temperature reaction was increased by using the reducing agent in methanol, since electron transfer from reducing anion to SN- cation was favoured by the more polar medium. (In aqueous solution reducing anions can be very strong reductants). The use of a protic solvent however, caused some hydrolysis as shown by ν_{NH} and δ_{NH} absorptions in the i.r. spectrum of the solid residue.

The reaction was more complex in dioxane and toluene. Although reduction occurred, S_4N_4 would not crystallise from solution, presumably because of strong interactions with these solvents. Solutions pumped to low volume invariably produced sticky resins.

The sodium oxalate reaction probably proceeded by metathesis followed by electron transfer to the sulphur-nitrogen cation:



The free radical species $S_4N_3^{\bullet}$ is discussed in section 3.3.12. That the oxidation product was gaseous contributed to the cleanliness of the reaction.

3.3.5 Reaction between S_4N_3Cl and hypophosphorus acid

Hypophosphorus acid was found to be too vigorous a reducing agent when used in both hydrogen chloride solution and diluted in ice-cold methanol. The thiotrithiazyl cation was rapidly destroyed, with sulphur being reduced down to S(0) in colloidal sulphur and S(-2) in hydrogen sulphide.

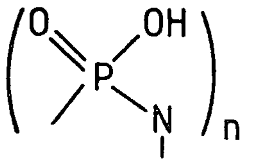
3.3.6 Reaction between S_4N_3Cl and sodium hypophosphite

Sodium oxalate and thiosulphate were chosen as representative oxyacid reducing agents of groups IV and VI respectively, and sodium hypophosphite (group V) completed the comparison. As with the sulphur and carbon oxyanions, reduction gave mainly S_4N_4 and S_4N_2. There was no t.l.c. evidence for the presence of imides, and , as with the group IV and VI oxyanions, reduction appeared to be by electron transfer (after initial metathesis) to form the free radical species, $S_4N_3^{\bullet}$ (see section 3.3.12).

Of the solids isolated, the first filtration produced mainly unreacted ionics, i.e. S_4N_3Cl and NaH_2PO_2. However the white solid produced by second filtration, after reducing the volume of solvent, was more interesting. As well as absorptions due to NaH_2PO_2 and S_4N_3Cl, medium to strong i.r. bands at 1630, 1455, 810, 620, 600 and 488 cm^{-1} were observed, which could not be assigned to standard S-N compounds.

Elemental ratios, calculated from chemical analysis were Na:P:N:S = 14:13:4:1. The nitrogen analysis was higher than would be expected for a mixture containing only sodium hypophosphite and S_4N_3Cl.

The phosphorus analysis however does not give very strong evidence for the presence of, for example, a cyclophosphazane (I) or other phosphorus (V)-nitrogen compound.



(I)

The yellow-orange tarry residue probably contained polyphosphoric acid or polyphosphates, these being likely oxidation products of hypophosphite.

When the reduction was repeated in ice-cold, aqueous solution, i.r. analysis showed not only the presence of S_4N_4 and some hydrolysis product, as expected; but also weak, broad absorptions at 1225, 1085, 1025 and 620 cm^{-1} which were believed to be due to $(SN)_x$[8]. These absorptions were similar to those recorded for the finely divided black precipitate produced in the

S_3N_2Cl/NaI reaction (section 3.2.7). It is not clear what role the water plays in its formation but there was certainly no sign of $(SN)_x$ in anhydrous conditions. The formation of $(SN)_x$ in T.H.F. solution has recently been reported[12] and thin films of $(SN)_x$ have been sublimed from finely divided black powder[13] obtained in the solution reaction of $(NSCl)_3$ with azides (e.g. $(CH_3)_3SiN_3$)[14].

3.3.7 Reaction between S_3N_2Cl and sodium iodide

I.r. spectra of S_3N_2Cl (made up as potassium iodide discs) contained strong absorptions due to S_4N_4, showing that solid state reduction had readily occurred. The solution reaction of S_3N_2Cl with NaI was therefore investigated.

The presence of impurities, in particular the oxidation product, iodine, made it difficult to purify the S_4N_4 from this reaction. Various methods of room temperature iodine extraction were tried:-

(i) with hexane

(ii) with potassium iodide solution

(iii) with aqueous thiosulphate and with anhydrous thiosulphate in methanol

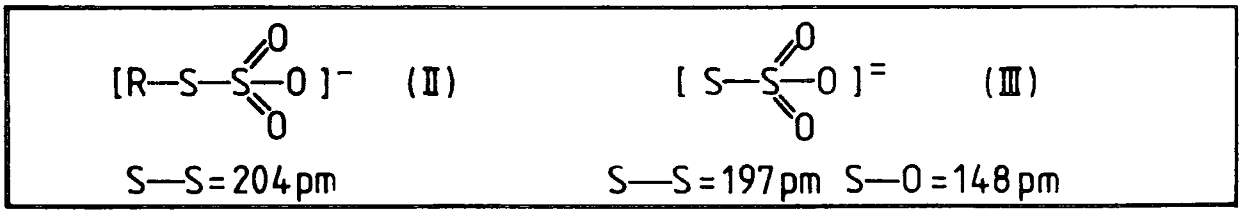
(iv) with organic thiosulphates and thiocarbamates.

The first two methods, followed by Soxhlet extraction in dioxane (to remove the ionic impurities ammonium sulphate and sodium chloride) and recrystallisation, gave mixtures of S_4N_4 and sulphur in yields of approximately 50%.

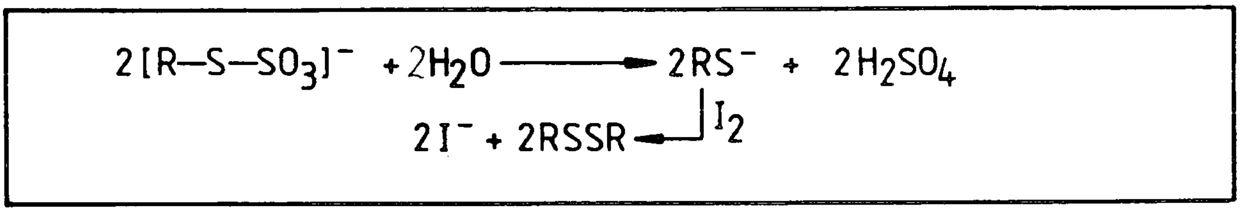
The presence of water in method (ii) and to a greater extent in method (iii) caused a complication in the formation of a finely divided black powder similar in nature to that already described in section 3.3.6. With anhydrous thiosulphate (in methanol) the iodine removal was slower, however dioxane extraction of the resulting solid produced a reasonable yield of S_4N_4 (albeit with a 35-40% sulphur impurity).

Method (iv) was an attempt to replace sodium thiosulphate with a thiosulphate salt containing a large cation which would be soluble in organic solvents (thus avoiding aqueous solutions). However, attempted syntheses (by double decomposition) of $R_2S_2O_3$ where R = $Me_4\overset{+}{N}$, $Bu_4\overset{+}{N}$ and $Ph_4\overset{+}{N}$ were unsuccessful because the salt could not be precipitated from solution (the solubility product at room temperature was too large).

Bunte salts (alkyl thiosulphates) (II) are known to reduce iodine in aqueous alcoholic solutions[15].



Bonding to the alkyl group in Bunte salts weakens the sulphur-sulphur bond (cf. S-S bonds lengths in II and III)[16]. It is likely that reduction occurs in aqueous solution because of the generation of S^- in an alkyl sulphide:



These salts were therefore considered unlikely to reduce iodine in organic solvents such as nitromethane.

Instead, the dithiocarbamate salt, Et_2NCSS^- was used, after an initial experiment had confirmed that it would reduce iodine in methanol solution (see Chapter 2, page 35). The organic group aided its non-aqueous solubility and this method of iodine removal worked quite well - it was possible to characterise tetraethyl thiuram disulphide (reaction (d) section 3.2.7). In this method, the yield and purity of the S_4N_4 isolated compared favourably with that obtained from other systems (see section 3.3.11).

In general, imides were not formed as major products from the reductions studied, although small quantities of S_7NH were detected (by t.l.c.) in solutions from S_3N_2Cl/I^- and $S_3N_2Cl_2/S_2O_3^=$ (section 3.2.1). Its formation was thought to be due to S-N free radicals reacting (by proton abstraction) with the water present in low concentration in solution.

It was significant therefore that S_7NH was only detected in reactions of the more moisture sensitive thiazenes ($S_3N_2Cl_2$ and S_3N_2Cl). It is possible that small concentrations of lower imides (e.g. $S_6(NH)_2$) were also present (see t.l.c. data, sections 3.2.1 and 3.2.7) but these were not positively identified.

In experiments (a), (b), (d) and (e), filtrations of the non-aqueous reaction mixture produced a dark green solid from which S_4N_4 was directly extracted with no complications arising from the presence of black polymeric material. The presence of water, introduced in experiments (c) and (f), caused rapid precipitation from organic solution of finely divided S_4N_4 and amorphous $(SN)_x$ (with varying chain lengths) as well as products such as ammonium sulphate (from complete hydrolysis) and possibly compounds containing the thionyl imide fragment, HNSO (from partial hydrolysis). Finely divided materials, particularly metals, are known to be highly active and pyrophoric, and both of these properties were possessed by the black solid. For instance, when the black material was not rapidly dried (experiment (c)), hydrolysis of a moisture sensitive component occurred, releasing ammonia and (probably) sulphur dioxide. Even with anhydrous thiosulphate in methanol there was sufficient moisture present to cause (in the course of 24 hours) initial formation and then decomposition of the finely divided black solid.

There are three possible explanations for the black solid containing chlorine. It was present as

(i) ammonium or sodium chloride,

(ii) as unreacted S_3N_2Cl, intermediate S_4N_3Cl

or (iii) as some other sulphur-nitrogen-chlorine compound.

The first two are unlikely since the ionics would be expected to remain in aqueous solution, and sodium iodide was used in excess over S_3N_2Cl. The traces of S_4N_3Cl isolated in experiment (e) showed that it was an intermediate in the reaction which would be further reduced to S_4N_4 and S_4N_2 via the free radical $S_4N_3^{\bullet}$(discussed in section 3.3.12):

This is in agreement with Hey who postulated the intermediacy of S_4N_3Cl in the reduction of S_3N_2Cl by metals in refluxing nitromethane.[2b]

The third possibility above therefore seems most likely though the nature of the S-N-Cl compound was not determined.

T.l.c. data on the solutions of thiazene reductions consistently showed a component with a low R_f value (typically 0.06 - 0.17) which streaked upwards from the baseline, a behaviour characteristic of slow hydrolysis on the silica gel. This component also decomposed in solution over the period 12-24 hours (experient (c)) and may represent an unstable sulphur-nitrogen-chlorine product.

Mass spectral and i.r. evidence suggested that the black solid contained the groups S=O and N-H. These were probably present in hydrolysis products.

The colour change, from black to brick-red at 100°C was accompanied by a slight increase in conductivity, however i.r. and mass spectral data were similar for both solids. The change may therefore be due to a greater degree of alignment of polymer chains (crystallinity) in the annealed solid.

No further work was done on this reaction because of the complexity of the system. It was not felt worthwhile to attempt to isolate and characterise the unknown sulphur-nitrogen products because of their low yield, instability and because their study was outside the specific aims of the work (as described at the beginning of this chapter). Sufficient work was done to enable an assessment of commercial viability to be undertaken (section 3.3.11).

3.3.8 Reaction between S_4N_3Cl and sodium iodide

This reaction was less complex than the corresponding sodium iodide reduction of S_3N_2Cl. The major products were S_4N_4, S_4N_2, S_8 and I_2. In general, the yields of S_4N_4 isolated from thiazene reductions as $(S_4N_4)_2SnCl_4$ were quite high (44-81%). This was not so for the iodide systems (S_4N_3Cl/I^- and S_3N_2Cl/I^-) where corresponding values were only ca 20% (see section 3.3.11). The maximum yield of solid S_4N_4 obtained from the

S_3N_2Cl/I^- reaction was 40% (section 3.2.7c). Clearly some side reaction of the tin (IV) chloride must have occurred in these reactions such that the yield values determined were unrealistically low.

3.3.9 Reaction between S_4N_3Cl and metallic iron

Hey studied in detail the reductions of thiazenes by a whole series of transition and main group metals[2c]. The reduction of S_4N_3Cl by iron was however included in this thesis in order to form a link between the two studies. No yield was reported by Hey for S_4N_3Cl/Fe, so this was determined both for pure crystals of S_4N_4 and for it isolated as the $SnCl_4$-adduct. A comparison was therefore possible between the two types of reducing agents.

The S_4N_4 crystals isolated, although low in yield (22%), were purer than those obtained from any of the other systems studied (a 3% impurity of sulphur based on chemical analysis). The yield of S_4N_4 precipitated as the adduct, $(S_4N_4)_2SnCl_4$ was very high (81%) suggesting that the reduction of S_4N_3Cl by iron might be useful for reactions involving in situ S_4N_4. Indeed, the system was subsequently used extensively for this purpose (see Chapter 4).

Although in general yields of S_4N_4 were quite high from reduction of thiazenes by metals (section 3.3.11), there were potential problems resulting in some yield reduction, due to the Lewis acidity of the metal chloride (formed as the oxidation product). This was the case with the iron system where formation of the tetrachloroferrate anion, $FeCl_4^-$ served to stabilise the $S_4N_3^+$ cation against reduction. ($S_4N_3FeCl_4$ has been isolated from this reaction[17,18]).

3.3.10 Effect of refluxing solvents on S_4N_3Cl

It was observed (section 3.2.1) that S_4N_3Cl will undergo thermal rearrangement in nitromethane, one product of which is S_4N_4. It was realised that, in the case of reductions of this thiazene in refluxing solvents, the formation of S_4N_4 would be due to a combination of thermal decomposition and reduction pathways. The effect of refluxing solvents on S_4N_3Cl with regard to yield of S_4N_4 was therefore investigated (sections 3.2.10 and 3.2.11).

In chloroform, the presence in low yield, of S_7NH (and possibly an S_6-imide at $R_f = 0.68$) was attributed to moisture present in, rather than interaction with, the solvent. Justification for this was gained from the isolation of $(NH_4)_2SO_4$ (a regular hydrolysis product of S-N compounds) and from the fact that products such as Cl_3C-CCl_3 were not detected.

The results showed that thermal decomposition was a significant factor in the formation of S_4N_4 in reactions involving refluxing solvents. There was, however, clear evidence that S_4N_3Cl was also reduced by the added solid, since

(i) reductions at room temperature (or below) in nitromethane produced S_4N_4 (sections 3.2.1; 3.2.2; 3.2.4; 3.2.7(e) and 3.2.8) and

(ii) the yields of S_4N_4 were always higher when a reducing agent was added.

<u>e.g.</u> $S_4N_3Cl \xrightarrow[\text{reflux}]{CH_3NO_2} S_4N_4$ (31%)

$S_4N_3Cl + Fe \xrightarrow[\text{reflux}]{CH_3NO_2} S_4N_4$ (75%)

3.3.11 Conclusion: Yields

Table 3.9 summarises the yields of S_4N_4 produced by some reductions of thiazenes.

The following conclusions can be drawn from this summary:

(1) In general, reductions by metals produced the highest yields of the purest S_4N_4. The recommended systems are (i) S_4N_3Cl/Fe in nitromethane and (ii) $(NSCl)_3/Fe$ in monoglyme. These are particularly useful for small scale preparations of reasonably pure S_4N_4.

(2) Sodium iodide was not a good reducing agent; the complexity of the reactions with S_3N_2Cl and S_4N_3Cl resulted in consistently low yields of S_4N_4 which was highly contaminated with sulphur.

(3) The best systems involving a reducing anion were probably (i) $S_4N_3Cl/S_2O_3^=$ in nitromethane and (ii) $S_4N_3Cl/C_2O_4^=$ in nitromethane. Yields were 60-70% when using the S_4N_4 *in situ* (precipitating it as the $SnCl_4$-adduct).

TABLE 3.9 SUMMARY OF YIELDS

Reduction system	Ref.	S_4N_4 Yield (%)		Comments
		I	II	
$S_3N_2Cl/S_2O_5^{=}$	2d	53	-	Difficulty in removing water of crystallization led to hydrolysis problems and low yields.
$S_3N_2Cl_2/S_2O_5^{=}$	2d	37	-	
$S_4N_3Cl/S_2O_5^{=}$	2d	40	-	
S_3N_2Cl/Fe	2e	28-35	-	In general quite high yields of good purity S_4N_4 from reductions by metals.
S_4N_3Cl/Zn	2e	60	-	
S_4N_3Cl/Fe (THF)	2e	60	-	
$(NSCl)_3/Fe$	2e	67	-	
$S_4N_3Cl/S_2O_3^{=}$	3.2.3	23	19	Solid S_4N_4 (15% sulphur by weight)
$S_4N_3Cl/S_2O_3^{=}(SnCl_4)$	3.2.3	66-75	61-66	As adduct (7 - 10% sulphur by weight)
$S_4N_3Cl/C_2O_4^{=}(SnCl_4)$	3.2.4	69	65	As adduct (4% sulphur by weight)
$S_4N_3Cl/H_2PO_2^{-}(SnCl_4)$	3.2.6	44	38	As adduct (12% sulphur by weight)
S_3N_2Cl/I^{-}	3.2.7(b)	58	32	Sulphur 45% by weight
S_3N_2Cl/I^{-} (aq S_2O_3)	3.2.7(c)	38	23	Sulphur 40% by weight
S_3N_2Cl/I^{-} (anhyd. S_2O_3)	3.2.7(c)	62	40	Sulphur 36% by weight
S_3N_2Cl/I^{-} (Et_2NCSS^{-})	3.2.7(d)	29	16	Sulphur 45% by weight
S_3N_2Cl/I^{-} ($SnCl_4$)	3.2.7(e)	29	26	As adduct (10% sulphur by weight)
S_4N_3Cl/I^{-} ($SnCl_4$)	3.2.8	22	20	As adduct (9% sulphur by weight)
S_4N_3Cl/Fe (CH_3NO_2)	3.2.9	21	20	Sulphur 3% by weight
S_4N_3Cl/Fe ($SnCl_4$)	3.2.9	81	75	As adduct (7% sulphur by weight)
S_4N_3Cl/CH_3NO_2 ($SnCl_4$)	3.2.10	33	31	As adduct (4% sulphur by weight)
$S_4N_3Cl/CHCl_3$ ($SnCl_4$)	3.2.11	51	50	As adduct (2% sulphur by weight)

S_4N_4 yields in column II have been corrected for the presence of sulphur and are based on the starting thiazene in each case.

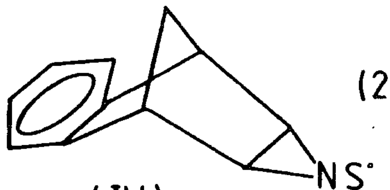
The systems mentioned in (1) and (3) above could be industrially useful since they allow a considerable number of synthetic reactions involving S_4N_4 to be done without isolation of the hazardous solid. For large-scale preparation of S_4N_4, none of the systems described in this chapter would rival the conventional method of Jolly[19], because the synthetic route to the thiazene starting materials ($NH_4Cl/SCl_2 \rightarrow S_3N_2Cl_2 \rightarrow S_4N_3Cl$) is less convenient and more expensive by comparison. A few however (e.g. S_4N_3Cl/Fe) are more convenient than the Jolly preparation for laboratory synthesis on the 5-10 g scale.

Although the present study was mainly concerned with preparations of S_4N_4; S_4N_2 was consistently detected as a major by-product, and some of the reactions would be suitable for low temperature isolation of S_4N_2. On the basis of t.l.c. observations the best routes to S_4N_2 would be (i) $S_4N_3Cl/C_2O_4^=$ and (ii) $S_4N_3Cl/S_2O_3^=$.

The reductions of thiazenes described in this chapter form the basis for an international patent[20] and are reported in the literature (1980)[18]. Since early 1979, Berthet et al have independently reported the preparation of S_4N_4 from the reduction of $(NSCl)_3$ by metals (Hg, Cu and Sn)[21] and Apter et al have prepared S_4N_4 and S_4N_2 in milligram quantities (suitable for isotopic labelling) from S_2Br_2 and ammonia in carbon tetrachloride[22]. Also, S_4N_4 has been found to be a product of pyrolysis of tetrathiotetraimide together with S_4N_2, sulphur and S_7NH[23].

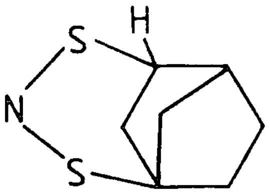
3.3.12 Mechanistic discussion

The reductions of $S_3N_2Cl_2$, S_3N_2Cl and S_4N_3Cl were highly complex but the products were invariably a mixture of S_4N_4, S_4N_2, S_8 and (in the presence of moisture) trace amounts of imides, usually S_7NH. This fact suggested that the mechanism probably involved S-N free radicals. This is not surprising since a number of extremely stable S-N free radicals are known, among them $S_2N_2^{+\circ}$[24], $PhCN_2S_2^{\bullet}$(see Chapter 8), thiyl radicals (IV) and dithiazolidine derivatives(V):



(25)

(IV)



(26)

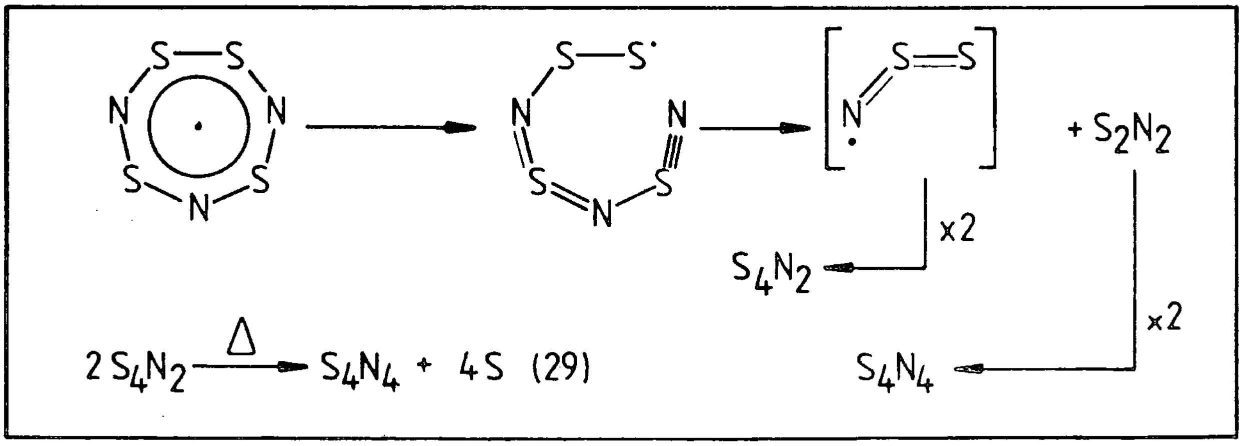
(V)

In reactions of S_4N_3Cl with reducing anions, metathesis is probably the first reaction step (to maximise lattice energies). This occurs readily even at room temperatures[2f]. The solubility of S_4N_3Cl, hence the rate of exchange, is favoured by the use of a high polarity solvent such as nitromethane.

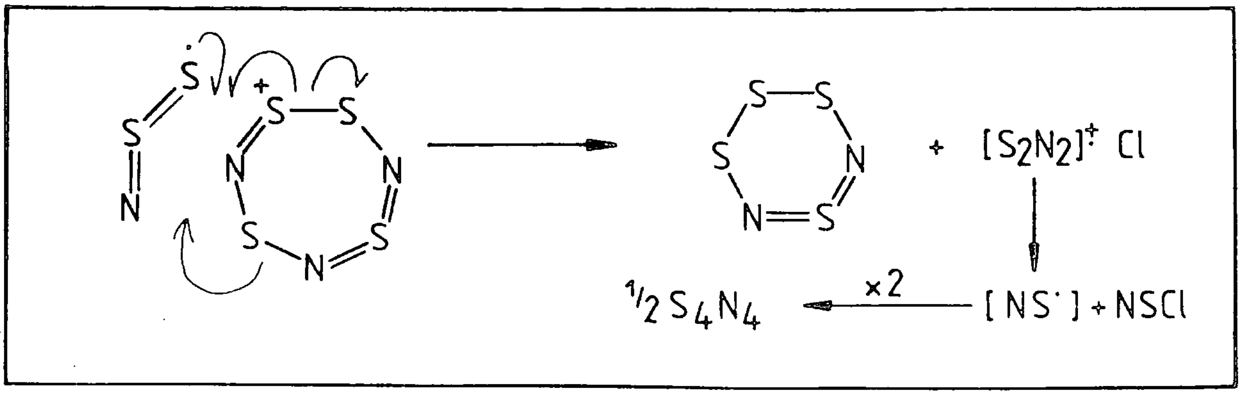
$$[S_4N_3]Cl + Na^+red^- \longrightarrow NaCl + [S_4N_3][red]$$

Electron transfer in the intermediate is then likely to occur giving the sulphur-nitrogen free radical species, $S_4N_3^{\bullet}$ and an oxidation product, dependent on the reducing agent used (e.g. I_2 from I^-; CO_2 from $C_2O_4^=$). Svenningsen and Hazell have shown[27] that the lowest unoccupied molecular orbital (LUMO) in $S_4N_3^+$ is anti-bonding with respect to the bonds from disulphide sulphur to nitrogen and bonding with respect to S-S. Confirmation of this was obtained from an MNDO calculation for $S_4N_3^+$[28].

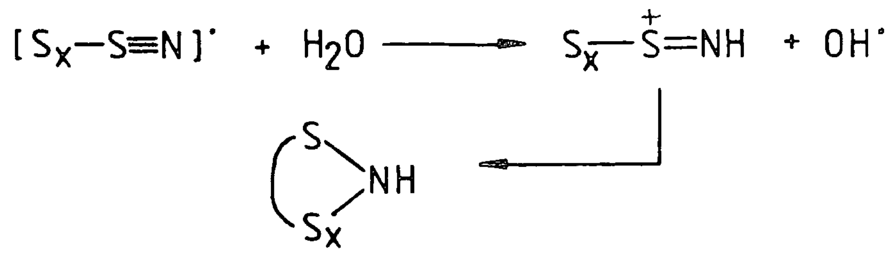
Likely bond scission can therefore be represented as follows:



There are other free radical processes which could occur including:



The breakdown into smaller sulphur and sulphur-nitrogen radicals, and their subsequent recombination, would rationalise formation of the observed products. Protonation of the terminal nitrogen of the radical species (in the presence of trace water) would explain the formation of imides:



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CHAPTER 4

REACTIONS INVOLVING "IN SITU" PREPARED S_4N_4

4.1 Introduction

In the last chapter, several new preparations of S_4N_4 were described and discussed. Crystalline S_4N_4 was isolated from a few of the reactions (although its purity was variable), however all of them produced solutions of S_4N_4. Because of the explosion hazards associated with solid S_4N_4, these new routes[1,2] would be of greater interest to industry if the S_4N_4 product could be used in situ , i.e. without isolation as a solid. The aim of this chapter, therefore, was to find and investigate uses for this in situ source of S_4N_4.

Although there are hundreds of known S_4N_4 reactions[3] which could have been studied, the experimental work was restricted to a few useful intermediates to other species, viz:

(i) Synthesis of the imide, $S_4(NH)_4$.

(ii) Preparation of adducts of S_4N_4.

(iii) One example of an S_4N_4/organic alkene reaction (i.e. with norbornene) and

(iv) Synthesis of the $S_5N_5^+$ cation.

It was felt that if these examples of inorganic and organic reactions of S_4N_4 were successful using the in situ source of S_4N_4, then it might reasonably be expected that other S_4N_4 reactions could be reproduced similarly.

4.2 Experimental

4.2.1 Standard synthesis of $S_4(NH)_4$

The standard synthesis of $S_4(NH)_4$, originally described by Brauer (Chapter 2, page 32) was found to give a product which, although pure, was rather low in yield. The modifications described by Younger[4] were repeated but did not significantly improve this yield. Table 4.1 gives details of three repeats of the standard synthesis using S_4N_4 from different sources.

A sample of pure imide (preparation 1) had i.r. absorptions at 3320(vs), 3290(vs), 3225(vs), 1299(s), 1261(w), 830(vs,br), 700(w), 540(vs, vbr,sh), 463(s), 410(s), 309(m), 305(s,sh) cm^{-1}. (*cf*. 3315, 3290, 3226, 1326, 1300, 1268, 828, 717, 540, 461, 406 and 293 cm^{-1})[5]. See also Chapter 1, page 5 .

Raman bands were at 716(m), 541(w), 497(m), 461(m), 324(s), 263(ms), 218(s), 144(m), 117(m), 81(s), 44(m) and 39(m) cm^{-1}. (*cf*. 744, 717, 540, 499, 461, 324 and 293 cm^{-1})[5]. X-ray diffraction data (for a recrystallised sample, see section 4.2.2) were as follows: d-spacing/Å (relative intensity): 6.13(25); 5.16(70); 4.75(40); 3.98(20); 3.80(100); 3.44(30); 3.37(90); 3.31(90); 3.21(60); 3.06(75); 3.02(50); 2.96(55); 2.86(70); 2.64(50); 2.58(30); 2.52(85); 2.47(15); 2.43(25); 2.29(25); 2.27(30); 2.22(25); 2.17(40); 2.09(40); 2.06(20); 1.99(25); 1.97(20); 1.96(10); 1.94(15). Mass spectral peaks were at $^{m}/e$ (%): 46(100)-SN^+; 47(57)-SNH^+; 62(73)-$S_2N_2H_2{}^+$; 78(28)-S_2N^+; 92(8)-$S_2N_2{}^+$; 93(8)-$S_2N_2H^+$; 94(4)-$S_2N_2H_2{}^+$; 125(40)-$S_3N_2H^+$; 139(18)-$S_3N_3H^+$; 186(49)-$S_4N_4H_2{}^+$; 188(18)-$S_4N_4H_4{}^+$ (*cf*. Reference 6, see also Chapter 1, page 5).

Melting point = 154°C (darkens to red at 140°C) (Younger[4] reported M.Pt = 156°C).

Modifications of the standard synthesis

Attempts were made to replace benzene in the standard synthesis by a less toxic solvent. Table 4.2 summarises the experimental work done. The best alternative was found to use dichloroethane. A typical preparation was as follows:

Tetrasulphur tetranitride (1.1 g, 0.0059 mol) in dichloroethane (30 ml) was brought to reflux temperature, cooled slightly, and tin (II) chloride, $SnCl_2 \cdot 2H_2O$ (5.0 g, 0.022 mol) in methanol/water (20 ml : 2 ml) was added rapidly with vigorous stirring. Continued heating (80°C/10 min) and stirring produced a pale yellow solution and a white precipitate. After

TABLE 4.1

Prepn.	Origin of S_4N_4	Quantities (mmol)		Volume of benzene (ml)	Volume of		Yield of $S_4(NH)_4$ (g)	Analysis (calc)		
		S_4N_4	$SnCl_2 \cdot 2H_2O$		MeOH	H_2O		S	N	H
1	Jolly (7)	5.4	21.6	30	12	1.0	0.2 (20%)	67.7 (68.1)	29.3 (29.8)	1.9 (2.1)
2	S_4N_3Cl/Fe (8)	8.1	49.8	30	15	1.5	0.8 (53%)	68.5 (68.1)	28.4 (29.8)	1.7 (2.1)
3	S_3N_2Cl/I^-(9)	8.1	49.8	30	15	1.5	Few mg. of dirty white solid	-	-	-

TABLE 4.3 T.L.C. DATA (see Table 4.2)

Sample	R_f values (CS_2)				
S_4N_4 (in toluene)		0.47 (s)			
Toluene solution after reduction	0.00 (m)		0.78 (m)	0.92 (m)	0.98 (s)
S_4N_4 standard		0.46 (s)			
S_8 standard					0.97 (s)

TABLE 4.2 MODIFICATIONS TO STANDARD $S_4(NH)_4$ SYNTHESIS

Solvent (ml)	Temp/°C	Quantity (mmol)		Volume (ml)		Comments
		S_4N_4	$SnCl_2 \cdot 2H_2O$	MeOH	H_2O	
Dioxane (60)	100	6.5	a) 11.7 b) 22.0	60 60	3 3	Solution went orange → pale yellow after 4 hours at 100°C and both additions of $SnCl_2$. No solid ppt^d. No imide isolated by evaporation/filtration.
$CHCl_3$ (60)	62 reflux	5.4	21.6	95	5	Rapid decolourisation. Cooled overnight. Solid isolated S, 97.7%. No i.r. absorptions.
Toluene (30)	110 reflux	5.4	27.0	15	1	Exothermic reaction. Solution decolourised then turned red-orange after 1 h. Brown solid isolated S, 79.0; N, 26.6; H, 1.75. I.r. absorptions due to $S_4(NH)_4$.
Toluene (30)	110 reflux	5.4	27.0	10	3	Reaction stirred for 15 mins after addition of $SnCl_2$. Isolated white solid 0.1 g (10%) S, 66.3; N, 28.8; H, 1.8. I.r. showed $S_4(NH)_4$. TLC (see Table 4.3).
$ClCH_2CH_2Cl$ (30)	83 reflux	3.8	23.1	16	1	Pale yellow solution rapidly formed. White solid filtered. S, 68.5; N, 27.15; H, 1.82 MPt 161°C. I.r. showed $S_4(NH)_4$. Filtrate reduced to low volume gave sticky oil.
$ClCH_2CH_2Cl$ (35)	83 reflux	8.1	48.0	20	2	Imide isolated 0.3 g (25%) I.r. showed impurity peaks at 1450, 1140, 1010, 2920 and 2855 cm^{-1}.
$ClCH_2CH_2Cl$ (35)	83 reflux	17.9 (35% S_8)	66.5	60	6	No precipitate. Solid isolated by evaporation/filtration shown to be sulphur.

cooling to 0°C, the solid was filtered and washed with dilute hydrochloric acid (10 ml), ethanol (10 ml) and ether (10 ml). Yield 0.60 g (53% based on S_4N_4). I.r. spectrum: 3305(s), 3280(s), 3220(s), 1295(m), 1261(w), 820(s, vbr), 533(s,br,sh), 460(ms), 409(m), 305(ms) cm^{-1}. (KBr disc). Melting point 150° (darkened to red at 130°C). Analysis found S, 68.90; N, 28.57; H, 1.88. Calculated for $S_4(NH)_4$: S, 68.11; N, 29.76; H, 2.12. An increase in purity was achieved by recrystallisation from nitromethane (see section 4.2.2). Found: S, 68.20; N, 29.20; H, 1.98.

4.2.2 Purification of tetrasulphur tetraimide

A series of solubility tests was carried out on the imide in order to find a suitable recrystallisation solvent. $S_4(NH)_4$ was insoluble in chloroform, methylene chloride, methanol and ethanol, dimethyl and isopropyl ethers; slightly soluble in nitromethane and cyclic ethers (such as dioxane and T.H.F.) and very soluble in solvents such as pyridine, α-methyl pyridine and acetone. On heating in acetic acid a deep red solution formed (t.l.c. in CS_2 showed components at R_f = 0.23(f); 0.46(s)- S_4N_4 ; 0.52(f); 0.70(f) — S_7NH ; 0.83(s) — S_4N_2 ; and 0.93 - S_8). An orange precipitate was isolated after cooling the solution, which was identified as S_4N_4. Recrystallisation was attempted from nitromethane and from mixtures of ether/acetone of varying composition. Table 4.4 gives details of the best recrystallisation procedures developed with these solvents.

An attempt was made to purify a sample of $S_4(NH)_4$ (1.0 g) by Soxhlet extraction with dichloroethane (80 ml). Extraction was stopped after 2 hours and the following solids investigated by chemical analysis and i.r. spectroscopy:

(i) Solid (X) remaining on the sinter (0.7 g)

(ii) Solid (Y) precipitated from the cooled dichloroethane solution (0.1 g) and

(iii) Solid (Z) remaining after evaporation of the dichloroethane.

TABLE 4.4

<table>
<tr><th>Solvent mixture</th><th>Procedure</th><th>Results</th></tr>
<tr><td>Acetone/ether (3:5)
(40 ml g^{-1})</td><td>Added acetone/ether to the imide with heat/stirring until dissolved. Filtered hot and cooled. Added hexane (25 ml g^{-1})</td><td>50% yield of white powder. I.r. (KBr disc) showed $S_4(NH)_4$ absorptions with low background.
<table>
<tr><th></th><th>Crude</th><th>Recrysd.</th><th>(Calc)</th></tr>
<tr><td>S</td><td>67.96</td><td>68.05</td><td>(68.11)</td></tr>
<tr><td>N</td><td>29.44</td><td>29.50</td><td>(29.76)</td></tr>
<tr><td>H</td><td>2.29</td><td>2.28</td><td>(2.12)</td></tr>
</table></td></tr>
<tr><td>Nitromethane
(80 ml g^{-1})</td><td>Heated to 90°C (max) and filtered hot. Allowed to cool slowly.</td><td>60% yield white micro-crystalline solid. I.r. showed slight impurity peaks at 2570 (w,br) and 1400 (vbr). % S = 68.20 (68.11) % N = 29.20 (29.76).</td></tr>
</table>

TABLE 4.5

	Crude $S_4(NH)_4$	X	Y	(Calc)
S	68.50	68.48	68.08	(68.11)
N	27.15	27.42	29.56	(29.76)
H	1.82	1.87	1.92	(2.12)
	97.47	97.77	99.56	(99.99)

TABLE 4.6

Experiment	Reaction conditions		Results
	Stage 1	Stage 2	
1	S_4N_3Cl (7.28 mmol) Fe (12.5 mmol) CH_3NO_2 (12 ml) 3h/110°C Produced a dark-red solution. Stage 2 followed on directly.	Benzene (70 ml) $SnCl_2$ $2H_2O$ (39.6 mmol) in MeOH (26 ml) and H_2O (2 ml) 80°C/15 min produced a pale yellow solution.	Small amount of brown-white solid filtered at R.T. This was soluble in dilute hydrochloric acid and thus not $S_4(NH)_4$.
2	S_4N_3Cl (6.31 mmol) Fe (12.5 mmol) CH_3NO_2 (7 ml) 10h/110°C Filtered hot before Stage 2.	Toluene (70 ml) $SnCl_2$ $2H_2O$ (39.6 mmol) in MeOH (29 ml) and H_2O (1 ml) 80°C/15 min. Colour change from dark-red to pale yellow.	Two immiscible layers formed, a pale yellow, methanolic layer (A) and a yellow-orange toluene layer (B). These were separated, evaporated to dryness and the solids (dissolved in acetone) investigated by TLC (in CS_2). (Data in Table 4.7).
3	S_4N_3Cl (7.28 mmol) Fe (12.5 mmol) CH_3NO_2 (12 ml) 3h/110°C Produced a dark-red solution. Stage 2 followed on directly.	Toluene (60 ml) $SnCl_2$ $2H_2O$ (39.6 mmol) in MeOH (22 ml) and H_2O (1.5 ml) 80°C/15 min. Produced a pale yellow-green solution. Cooled and filtered at R.T.	Small amount of white solid isolated. I.r. showed broad absorptions at 3240 and 1410 cm^{-1} (due to the presence of -NH); and a strong peak at 320 (νSn-Cl). Apart from a peak at 820 cm^{-1}, there was no evidence for $S_4(NH)_4$ being present.
4	S_4N_3Cl (4.86 mmol) Fe (8.96 mmol) Toluene (40 ml) 80-95°C/2h. Filtered hot to give clear red solution - analysed by TLC (Sample C, Table 4.7)	$SnCl_2 \cdot 2H_2O$ (26.4 mmol) in MeOH (10 ml) and H_2O (1 ml) 80°C/15 min Colour changed from dark red to pale yellow.	Two immiscible layers were separated - the bottom (toluene) layer cooled to -20°C and filtered. White solid was very moisture sensitive (turned yellow). I.r. (decomp^{n} product) had peaks at 3200 (vbr), 1600 (mw), 1400 (s) and 320 (m) cm^{-1}. White needle crystals formed in toluene overnight but decomposed due to moisture on sinter.
5	S_4N_3Cl (4.86 mmol) Fe (44.8 mmol) $ClCH_2CH_2Cl$ (50 ml) 85°C/5h. Filtered hot.	$SnCl_2 \cdot 2H_2O$ (39.6 mmol) in MeOH (20 ml) and H_2O (1 ml). Solution turned pale yellow from dark red.	Two immiscible layers - the bottom (dichloroethane) layer was evaporated to dryness to give a yellow-white solid, soluble in dilute HCl. Smell of H_2S was observed.

All three solids had i.r. spectra characteristic of $S_4(NH)_4$ but analysis indicated that sample (Y) was the purest (Table 4.5). Sample Z was heavily contaminated with Apiezon grease.

4.2.3 Attempts to produce $S_4(NH)_4$ from S_4N_3Cl/Fe and $SnCl_2$

The general experimental procedure was as follows. Stage 1 (Table 4.6), reduction of S_4N_3Cl by iron, was done as described in Chapter 3 (section 3.2.9) either in nitromethane (experiments 1-3) or toluene or dichloroethane (experiments 4 and 5 respectively). In experiments 1-3, a low volume of nitromethane was used in the first stage which was subsequently diluted (with benzene or toluene) in stage 2. In experiments 4 and 5, the same solvent was used for both stages. The experimental procedure for stage 2 was similar to that described in Chapter 2 (section 2.2.2(vi)). In experiments 1 and 3, the S_4N_4 solutions were used directly for the second stage, whereas in experiments 2, 4 and 5 they were filtered first. This procedure removed the excess iron and small amounts of fine yellow-white solid ($S_4N_3^+FeCl_4^-$), leaving clear, dark red solutions containing S_4N_4. Some of the solutions (samples A, B and C) were investigated by t.l.c. (Table 4.7).

TABLE 4.7

Experiment	Sample	R_f values					
2	A	0.00(f)*			0.74(m)		0.96(m)
	B	0.00(m)*					0.96(m)
	S_7NH				0.73(s)		
	S_8						0.95(s)
	$S_4(NH)_4$	0.00(m)*					
4	C	0.00(f)	0.04(f)	0.28(m)		0.85(m)	0.95(m)
	S_4N_2					0.80(s)	
	S_4N_4			0.33(s)			
* dark under UV		--- streaked from baseline					

4.2.4 Attempts to produce $S_4(NH)_4$ from $S_4N_3Cl/SnCl_2$ systems

The following attempts were made to produce $S_4(NH)_4$ by direct reduction of S_4N_3Cl with $SnCl_2$ in various solvents.

(i) $S_4N_3Cl/SnCl_2$ in benzene

S_4N_3Cl (1.0 g, 4.86 mmol) was heated to reflux in benzene (30 ml) and a solution of tin (II) chloride, $SnCl_2 \cdot 2H_2O$ (2.5 g, 11 mmol) in methanol (7 ml) and water (0.5 ml) was added with rapid stirring. A dark red solution formed after 15 minutes which turned pale yellow after addition of further reducing agent (2.5 g in 7 ml methanol: 0.5 ml water). The upper, pale yellow (methanolic) and lower dark green-brown layers were investigated by t.l.c. (in CS_2):

Sample	R_f values		
Upper layer	0.00(f)	0.77(m)	0.95(m)
Lower layer	0.00(m) (dark under UV)	0.76(f)	0.95(m)
S_7NH		0.75(s)	
S_8			0.94(s)

A yellow-white solid isolated by evaporating the solution to low volume, was characterised as sulphur (i.r. and analytical evidence).

(ii) $S_4N_3Cl/SnCl_2$ in dichloroethane

S_4N_3Cl (1.5 g, 7.29 mmol) was refluxed in dichloroethane (50 ml) and a solution of $SnCl_2 \cdot 2H_2O$ (7 g, 30.8 mmol) in methanol (30 ml) and water (1.5 ml) added with stirring. Addition of further $SnCl_2$ (7 g in 30 ml methanol and 1.5 ml water) caused the red-brown solution to turn pale yellow. T.l.c. (in CCl_4) showed the presence of four components in solution.

Sample	R_f values			
Reaction mixture	0.00(f)	0.20(f)	0.56(m)	0.83(m)
S_4N_4		0.20(s)		
S_7NH			0.57(s)	
S_8				0.85(s)

A small amount of white solid was filtered from the cooled solution. It was soluble in dilute hydrochloric acid. The pale yellow solution had i.r. absorptions at 2950(s), 2840(s), 1448(m), 1428(m), 1313(w), 1284(ms), 1232(ms), 942(m), 880(m) and 710(s) (due to dichloroethane) and some extra ones (due to hydrolysis) at 3350(s,vbr), 1640(w,br), 1110(w,br) and 1025(vs,br) cm^{-1} There was no indication that $S_4(NH)_4$ was present in solution.

(iii) $S_4N_3Cl/SnCl_2$ in toluene

S_4N_3Cl (0.5 g, 2.43 mmol) was heated (80-90°C/12 h) in toluene (40 ml) to form a dark red-brown solution. The addition of $SnCl_2 \cdot 2H_2O$ (6 g, 26.4 mmol) in methanol (10 ml) and water (1 ml) caused the formation of two immiscible layers. The upper, pale yellow (toluene) layer was reduced to low volume to give a brown-white powder (characterised as sulphur). The lower, methanolic layer was dark red and oily in nature after evaporation, and was not investigated further.

(iv) $S_4N_3Cl/SnCl_2$ in nitromethane

S_4N_3Cl (1.0 g, 4.86 mmol) was heated (100°C/2 h) in nitromethane (20 ml) to give a dark red solution. Solid $SnCl_2 \cdot 2H_2O$ (5 g, 22 mmol) in water (1 ml) was added with stirring. After ½ h a pale yellow solution, consisting of two immiscible layers had formed, and there was a solid suspension (of unreacted S_4N_3Cl and $SnCl_2$). The upper (nitromethane) layer was reduced to low volume and a white solid isolated which had strong i.r. absorptions at 3220(s,br), 1405(vs), 1280(m), 1020(m), 840(m,br) and 320 cm^{-1} (see discussion, page 89).

(v) $S_4N_3Cl/SnCl_2$ in dioxane

S_4N_3Cl (1.0 g, 4.86 mmol) was heated (80°C/½ h) in dioxane(40 ml) to give a deep red-orange solution. $SnCl_2 \cdot 2H_2O$ (5 g, 22.0 mmol) was added in water (2 ml) which resulted in the formation of a pale yellow solid and a yellow-orange solution. The solid was filtered, washed with dilute hydrochloric acid (10 ml), ethanol (10 ml) and ether (10 ml) and characterised as sulphur (i.r./analysis). T.l.c. (CS_2) on the yellow-orange solution indicated that four components were present:

Sample	R_f values			
Reaction mixture	0.00(f)	0.39(m)	0.78(f)	0.96(s)
S_4N_4		0.40(s)		
S_7NH			0.80(s)	
S_8				0.97(s)

Similar results were obtained for a repeat of this experiment in acetone solution.

(vi) $S_4N_3Cl/SnCl_2$ in methanol

S_4N_3Cl (1.5 g, 7.29 mmol) was stirred at room temperature with $SnCl_2 \cdot 2H_2O$ (7 g, 30.8 mmol) in methanol (30 ml). Initially an orange-red solution formed, but this turned brown-black after 10-15 minutes. T.l.c. (CCl_4 elutant) showed the presence of six components. No $S_4(NH)_4$ could be isolated using the usual technique of evaporation to low volume and cooling to -20°C.

Sample	R_f values					
Reaction mixture	0.00(f) (yellow)	0.00(m) (black)	0.26(m)	0.51(m)	0.69(s) (red,faded)	0.83(m)
S_4N_4			0.24(s)			
S_7NH				0.51(s)		
S_4N_2					0.71(s)	
S_8						0.84(s)

4.2.5 Synthesis of $S_4(NH)_4$ from thiotrithiazyl chloride, S_4N_3Cl

S_4N_3Cl (3.5 g, 17 mmol) and iron turnings (1.0 g, 18 mmol) were stirred in refluxing nitromethane (40 ml) for 2 hours, and the mixture filtered at 0°C. The crude solid was Soxhlet extracted using dioxane (90 ml).

Evaporation of the solution to half volume and cooling to -20°C gave crystalline S_4N_4 (0.5 g). Analysis found N, 21.69; S_4N_4 required N, 30.40. T.l.c. (CS_2) confirmed that sulphur was the major impurity (R_f = 0.96, 29% by weight based on analysis).

Tin (II) chloride, $SnCl_2 \cdot 2H_2O$ (3.0 g, 13.5 mmol) in methanol/water (5 ml : 2 ml) was added rapidly to the crude S_4N_4 (0.5 g, 2.7 mmol) in toluene (20 ml) at 90°C. Cooling and filtration at 0°C produced a white crystalline solid. This was washed with dilute hydrochloric acid (10 ml), ethanol (10 ml) and ether (10 ml). Yield was 0.2 g (6% based on S_4N_3Cl, 40% based on crude S_4N_4). I.r. spectrum: 3305(s), 3275(s), 3215(s), 1293(ms), 825(s,br), 535(s,br,sh), 460(ms), 405(ms), 305(s) cm^{-1}. Analysis found N, 26.96; S, 65.43; $S_4(NH)_4$ required N, 29.76; S, 68.11.

4.2.6 Attempts to produce tetrasulphur tetraimide from other reducing systems

(i) S_3N_2Cl/Fe with $SnCl_2$ in dichloroethane

S_3N_2Cl (4.0 g, 25 mmol) and iron (1.4 g, 25 mmol) were placed in a side arm sinter. This was connected between a reflux condenser and a 2-necked round-bottomed flask containing dichloroethane (50 ml). The solvent was refluxed and after 2 hours, extraction had occurred to give an orange-red solution. Some yellow solid (characterised as S_4N_3Cl) precipitated on cooling.

Aqueous $SnCl_2 \cdot 2H_2O$ (30 ml, 0.6 M) was then added with rapid stirring. There was an immediate colour change to pale yellow and formation of a small amount of white solid. This solid (dissolved in methanol) and samples of both the upper (pale yellow) aqueous, and the lower (yellow) organic layers, were investigated by t.l.c. (CCl_4) to give the following results.

Sample	R_f values		
Aqueous layer	0.00(f) (dark under UV)		0.86(s)
Organic layer	0.00(f) (dark under UV)	0.57(m)	0.86(s)
White solid	0.00(m) (dark under UV)	0.57(m)	0.87(s)
$S_4(NH)_4$	0.00(m) (dark under UV)		
S_7NH		0.55(s)	
S_8			0.85(s)

(ii) $S_4N_3Cl/Na_2S_2O_3$ with $SnCl_2$ in nitromethane

S_4N_3Cl (1.0 g, 4.86 mmol) and sodium thiosulphate (1.2 g, 7.29 mmol) were refluxed (3 hours) in nitromethane (20 ml) to form a dark red solution containing a fine powdery suspension. The solution was filtered hot and a sample investigated by t.l.c. (in CS_2):

Sample	R_f values				
Reaction mixture	0.00(f)	0.06(f)	0.40(m)	0.86(m) (red,faded)	0.96(s)
S_4N_4			0.42(s)		
S_4N_2				0.85(s) (red,faded)	
S_8					0.96(s)

$SnCl_2 \cdot 2H_2O$ (3.0 g, 13.2 mmol) in methanol (15 ml) was added with stirring, to the solution at 90°C. This caused an exothermic reaction and formation of a pale yellow cloudy suspension. The solid filtered from this mixture was characterised as sulphur.

(iii) $S_4N_3Cl/Na_2C_2O_4$ with $SnCl_2$ in various solvents

Table 4.8 summarises the experimental work done on this system:

TABLE 4.8

Quantities (mmol)			Solvent (ml)	Conditions	Results
S_4N_3Cl	$Na_2C_2O_4$	$SnCl_2$			
3.40	5.10	13.20	CH_3NO_2 (40)	Reflux/1 h	Formation of light-brown solution. White-brown solid filtered and characterised as sulphur.
2.44	2.44		CH_3NO_2 (40) and MeOH (10)	RT/1 h	Dark red solution.
		8.86	MeOH (20) and H_2O (2)	60°C/½ h	No exothermic reaction. Cooling gave white solid (0.1 g). Washed with dil HCl/Ethanol and ether. Characterised as sulphur.
2.43	3.64		Toluene (25) and MeOH (2.5)	RT/2 h	Some unreacted solid filtered to leave dark red solution.
		13.2	MeOH (10) and H_2O (2)	Reflux/½ h	Two immiscible layers. Pale yellow solution. Yellow-brown solid filtered soluble in dil HCl.

TABLE 4.9

Reaction	Yield of crude adduct	Chapter 3, section
$S_4N_3Cl/Na_2S_2O_3$	53 - 60	3.2.3
$S_4N_3Cl/Na_2C_2O_4$	56	3.2.4
S_4N_3Cl/NaH_2PO_2	35	3.2.6
S_4N_3Cl/NaI	18	3.2.8
S_3N_2Cl/NaI	23	3.2.7
S_4N_3Cl/Fe	65	3.2.9

4.2.7 Preparations of the adduct, $(S_4N_4)_2SnCl_4$ from "in situ" S_4N_4

The preparation of $(S_4N_4)_2SnCl_4$ was described in Chapter 2 (page 33) and its precipitation as a method of S_4N_4 yield determination was discussed in Chapter 3 (page 51). Methods of preparation of this adduct from various sources of in situ S_4N_4 are summarised in Table 4.9 along with calculated yields (based on the thiazene starting material).

4.2.8 Attempts to prepare other adducts from "in situ" S_4N_4

(i) Preparation of $(S_4N_4)_2SnBr_4$

S_4N_3Cl(0.5 g, 2.44 mmol) was stirred for 1 hour at room temperature with sodium oxalate (0.3 g, 2.44 mmol) in a mixture of nitromethane (40 ml) and methanol (10 ml), during which time the solution became orange-red in colour. Tin(IV) bromide (0.4 g, 0.9 mmol) in acetone (3 ml) was added and stirring continued for 48 hours. Precipitation of a brown solid resulted from addition of hexane (30 ml). The solid (0.3 g) was filtered, washed with hexane (2 x 10 ml) and dried *in vacuo*. Strong i.r. absorptions were at 1042(s), 962(s), 798(s), 673(m), 515(vs), 420(s) and 359(vs) cm^{-1} (KBr disc). Chemical analysis found S, 33.48; N, 11.92; Br, 38.64. $SnBr_4 \cdot 2S_4N_4$ required S, 31.79; N, 13.89; Br, 39.61. Based on this analysis, the sample had a 4% sulphur impurity (by weight).

(ii) Attempted preparation of $S_4N_4(AlCl_3)_2$

S_4N_3Cl (1.0 g, 4.88 mmol) was refluxed with Fe (0.27 g, 4.88 mmol) for 2 hours in nitromethane (40 ml), filtered hot to give a clear, deep red solution, and allowed to cool to room temperature.

Aluminium trichloride, $AlCl_3$ (1.0 g, 7.64 mmol) was then added with vigorous stirring for 24 hours. Addition of hexane (20 ml) caused precipitation of a fine red-orange solid (1.4 g), which was filtered, washed with hexane (2 x 10 ml) and dried *in vacuo*. I.r. absorptions were at 1150(m,br), 1044(s), 990(m,br), 963(ms), 861(s,sh), 783(m), 670(mw), 570(br), 507(s,br) and 478(vs) cm^{-1}. (Nujol mull). Analysis found

S, 17.65; N, 7.83; Cl, 58.65; $S_4N_4(AlCl_3)_2$ required S, 28.42; N, 12.42; Cl, 47.20. $S_4N_4(AlCl_3)_4$ required S, 17.85; N, 7.80; Cl, 59.31. The adduct was very moisture sensitive and readily turned dark-brown.

4.2.9 Attempts to prepare $S_4(NH)_4$ from $(S_4N_4)_2SnCl_4$

(i) $(S_4N_4)_2SnCl_4$/toluene

$(S_4N_4)_2SnCl_4$ (0.2 g, 0.32 mmol) was refluxed in toluene (20 ml) and the resulting orange solution was shown by t.l.c. (CS_2) to contain two components: R_f = 0.32 and 0.85 (broad). R_f(S_4N_4 standard) = 0.40. On cooling, a purple-red solid was isolated which was found to be unchanged adduct (i.r. evidence).

(ii) $(S_4N_4)_2SnCl_4/SnCl_2$ $2H_2O$ in toluene

A solution of $SnCl_2$ $2H_2O$ (1.5 g, 6.65 mmol) in methanol (5 ml) and water (1 ml) was added to $(S_4N_4)_2SnCl_4$ (0.5 g, 0.79 mmol) in toluene (35 ml) at 90°C. An exothermic reaction occurred with a colour change from orange to pale yellow. The reaction was stirred for ½ hour and cooled to room temperature. Hexane (30 ml) was added to cause precipitation of a white solid. This was filtered and found, on washing, to be soluble in dilute hydrochloric acid.

(iii) $(S_4N_4)_2SnCl_4/SnCl_2\cdot 2H_2O$ in benzene

Experimental results for this reaction are summarised in Table 4.10.

A typical preparation

Tin (II) chloride, $SnCl_2\cdot 2H_2O$ (6 g, 26.5 mmol) in methanol/water (8 ml : 1 ml) was added rapidly with vigorous stirring to $(S_4N_4)_2SnCl_4$ (2.6 g, 4.1 mmol) in refluxing benzene (40 ml). After 30 minutes the mixture was filtered at 0°C to give a pinkish-white sample of crude $S_4(NH)_4$. Yield 0.5 g (32% based on S_4N_4). I.r. spectrum: 3320(s), 3295(s), 3230(s), 1301(s), 1264(w), 830(s,br), 540(br,sh), 469(s), 415(s), 300(s,br) cm^{-1}. Chemical analysis found S, 65.34; N, 26.78; H, 1.86. $S_4(NH)_4$ required S, 68.11; N, 29.76; H, 2.12. Analysis found after recrystallisa-

TABLE 4.10

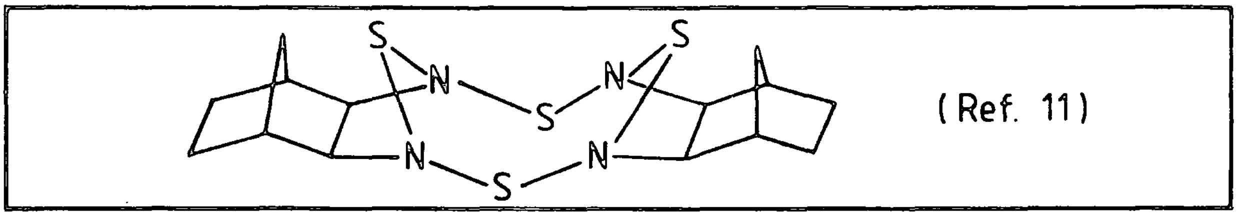
Quantities				Conditions	Results
Adduct (mmol)	Benzene (ml)	$SnCl_2$ (mmol)	MeOH (ml) : H_2O (ml)		
2.70	30	21.60	5 : 0.5	Reflux/15 min	Pink-white solid obtained. I.r. showed it to be a mixture of $S_4(NH)_4$ and unreacted adduct. TLC (CS_2) on orange solution showed 4 components: R_f = 0.00, 0.34 (S_4N_4), 0.81 (S_7NH), 0.96 (S_8)
0.63	15	2.22	2 : 0.1	Reflux/20 min	Pink-white solid. I.r. showed mainly $S_4(NH)_4$ with some unreacted adduct.
2.06	20	26.60	8 : 1	Reflux/½ h	Pink-white solid (0.2 g, 26% based on S_4N_4). I.r. showed mainly imide peaks at 3320(s), 3295(s), 3230(s), 1301(ms), 830(s,br), 540(s,br), 525(s), 469(s), 415(s), 300(s,br). Very weak absorptions due to unreacted imide. %S = 65.80; N = 25.02 (Calc %S = 68.11 N = 29.76).

tion from nitromethane (80 ml g^{-1}): S, 67.92; N, 29.43; H, 1.95 (99.3%).

4.2.10 Preparation of other useful products from "in situ" S_4N_4

Two other uses for in situ S_4N_4 were developed (mainly by Fielder[10]) and are mentioned here for the sake of completion:

(i) The reaction of in situ S_4N_4 with norbornene (C_7H_{10}) to form the derivitive:



(ii) The formation of $S_5N_5^+FeCl_4^-$ from in situ S_4N_4 produced by the reaction of $(NSCl)_3$/Fe in monoglyme[1,2].

Attempted preparation of the norbornene-S_4N_4 derivative from $(S_4N_4)_2SnCl_4$

Norbornene (0.5 g, 6.36 mmol) and $(S_4N_4)_2SnCl_4$ (0.2 g, 0.32 mmol) were refluxed in monoglyme (20 ml). There was no apparent reaction until reflux, when a rapid colour change, from red-purple to pale yellow, occurred with formation of a white solid. This was filtered, washed with hexane and dried in vacuo. I.r. absorptions were at 3500(w,br), 3200(w,br), 2960(s), 2875(m), 1690(w,br), 1620(w,br), 1469(m), 1455(s), 1400(m,br), 1313(s), 1300(s), 1262(m), 1255(m), 1234(m), 1222(m), 1202(m), 1188(m), 1110(m,br), 1040(sh), 1020(vs,br), 940(w), 922(m), 894(s), 878(s), 840(s), 820(s), 770(m), 760(s), 730(s,br), 689(w), 600(w,br), 540(m), 402(m), 340(sh), 320(vs,br) cm^{-1}. (cf. S_4N_4-norbornene derivative, prepared as described in ref. 2: 2961(s), 2955(sh), 2920(w), 2875(m), 1462(w), 1450(m), 1309(m), 1300(s), 1250(m), 995(w), 951(vs), 920(ms), 900(s), 878(s), 760(w), 723(w), 692(s), 623(w), 590(mw), 565(w), 530(w) and 332 cm^{-1}). This reaction was not investigated further because of the lack of evidence for the presence of $S_4N_4(C_7H_{10})_2$.

4.3 Discussion

4.3.1 Introduction

As mentioned in section 4.1, the original aim of the work described in this chapter, was to demonstrate that the S_4N_4 produced by reductions of thiazenes (Chapter 3) could be used *in situ* (*i.e.* without isolation as a solid) for the synthesis of useful derivatives.

The experiments (sections 4.2.3 - 4.2.6) were mainly concerned with finding an inorganic application, *i.e.* the preparation of $S_4(NH)_4$. (One organic application, *viz.* the reaction with norbornene, was investigated by Fielder.)[10] Tetrasulphur tetraimide was chosen for study because of its ready conversion to other compounds. For example,

(i) Organic addition

e.g. $(SNH)_4 \xrightarrow{HCHO} (SN\cdot CH_2OH)_4$ (12,13)

(ii) Adduct formation with Lewis acids

e.g. $(SNH)_4\cdot TeBr_4$ (14)

$(SNH)_4\cdot AlCl_3$ (4)

(iii) Hydrogen substitution

e.g. $(SNH)_4 + Hg(OAc)_2 \longrightarrow Hg_5(NS)_8$ (Chapter 2, page 33)

$(SNH)_4 + Bu^tLi \longrightarrow S_4N_4Li_4$ (4)

(iv) Hydrogen abstraction

e.g. $3S_4(NH)_4 + 4(NSCl)_3 \longrightarrow 6S_4N_4 + 12HCl$ (15,16)

(v) Oxidation

e.g. $S_4(NH)_4 \xrightarrow[120^\circ C]{[O]} (SONH)_4$ (17)

(vi) Ring degradation

e.g. $S_4(NH)_4 + Pt(PPh_3)_4 \longrightarrow (PPh_3)_2Pt(OSNH)_2$ (18)

(vii) Ring contraction

e.g. $S_4(NH)_4 \longrightarrow S_4N_3Cl,\ (NSCl)_3$ (4)

S_7NH, another sulphur imide has been patented as a powerful fungicide[19], and it is possible that $S_4(NH)_4$ and/or its derivatives may have similar biocidal properties. However, only a cheap, high yield synthesis (avoiding S_4N_4) would be of industrial interest.

In sections 4.2.7 and 4.2.8, S_4N_4 was precipitated as an adduct from solutions produced by reduction of thiazenes. This process fulfilled several functions, it allowed determination of the yield of S_4N_4 from each reduction system (Chapter 3) and it served as (i) an inorganic application for in situ S_4N_4 and (ii) a safe way of isolating and handling it. The possibility of decomposing the adduct in solution in order to release the S_4N_4 for further reaction was investigated in section 4.2.9.

4.3.2 Standard preparation of $S_4(NH)_4$

The standard preparation of $S_4(NH)_4$ was quite sensitive to S_4N_4 purity. In preparations 1 and 2 (Table 4.1), imide of a reasonable purity was obtained (in yields of 20 - 53%) when the S_4N_4 had had at least one stage of purification. However, in preparation 3, where the S_4N_4 had a 49% sulphur impurity, no imide was isolated at all under similar experimental conditions. From the present work and considering the past work of Younger[4], it would appear that the best yields are obtained using an $SnCl_2:S_4N_4$ ratio of about 6:1 with approximate volumes of benzene and methanol of 20 ml and 10 ml (per gram of S_4N_4) respectively, and a 5-10% addition of water.

$S_4(NH)_4$ had a very characteristic i.r. spectrum with very strong, broad peaks, particularly when the sample was run as a KBr disc. I.r. and chemical analysis were generally sufficient therefore to detect $S_4(NH)_4$ as a reaction product. Thin layer chromatography, although useful as a guide, did not alone provide satisfactory evidence for its presence, for reasons suggested in Chapter 2 (page 26).

The strong, sharp i.r. absorptions at 3320, 3290 and 3225 were assigned[5] to N-H stretch. These are red-shifted by 5-10 cm^{-1}, compared with to ν(N-H) in secondary amines, because of hydrogen bonding to other nitrogen atoms within the crystal lattice. Domingo and Orza[5] assigned the bands at 1299/1266 and 540/463 to N-H bending vibrations and N-H deformations respectively; those at 830 and 717 to S-N stretching and at 410, 309 and

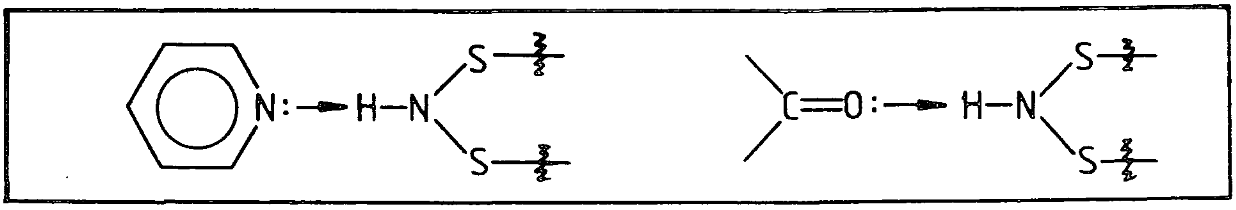
305 cm^{-1} to complex S-N ring bending vibrations (Chapter 1, page 5).

Chemical industry would show little interest in the standard preparation of $S_4(NH)_4$ since it uses benzene, which is carcinogenic and has a threshold limit value of 10 p.p.m.[20] Consequently attempts were made to find a more acceptable alternative. Ideally such a solvent should reflux at about 80°C (to minimise decomposition of $S_4(NH)_4$); be a good solvent for S_4N_4 and a poor one for the imide. Solubility of $S_4(NH)_4$ in organic solvents is discussed in section 4.3.3. Dioxane, chloroform, toluene and dichloroethane were investigated, however $S_4(NH)_4$ was too soluble in dioxane and decomposed in chloroform to give sulphur. Toluene gave satisfactory results, although the temperature had to be kept well below reflux and the imide was generally less pure than that produced in benzene.

Dichloroethane was found to be the best alternative, giving a good yield (50%) of a reasonably pure compound. Once again the purity of S_4N_4 was critical for formation of $S_4(NH)_4$ - no product was isolated when S_4N_4 containing 35% sulphur was used (Table 4.2).

4.3.3 Purification of tetrasulphur tetraimide

$S_4(NH)_4$ is very soluble in solvents to which it can strongly hydrogen bond, such as pyridine and acetone:



Pyridine, α-methyl pyridine and acetone were therefore unsuitable recrystallisation solvents.

In alcohols (e.g. methanol) there is a large degree of intermolecular H-bonding. In order to dissolve in such a solvent, $S_4(NH)_4$ would have to break this structure and form a new hydrogen bonding interaction with the solvent molecules. This is apparently energetically unfavourable since $S_4(NH)_4$ was only slightly soluble in alcohols even at high temperatures.

It was also insoluble in chlorinated solvents such as chloroform and dichloromethane and in low polarity ethers, benzene and toluene, where there is little or no solvating interaction. Nitromethane, in which there was probably a slight hydrogen bonding interaction with the nitro group, was found to be the best recrystallisation solvent.

Heating the imide in acetic acid caused thermal decomposition of the ring and rearrangement to form S_4N_4 and S_4N_2, sulphur and S_7NH all of which were detected by t.l.c. S_4N_4 was also isolated as a solid product.

In the attempt to purify $S_4(NH)_4$ by Soxhlet extraction (with dichloroethane) a pure, crystalline sample (Y) was obtained by slowly cooling the extraction solvent. The yield was quite low (10%) since most of the starting material (X) remained on the sinter. A higher yield could probably be obtained by increasing the extraction time.

4.3.4 Attempts to produce $S_4(NH)_4$ from "in situ" S_4N_4

Of the new routes to S_4N_4 developed in Chapter 3, the reduction of S_4N_3Cl by iron was considered to be the best in terms of S_4N_4 yield and purity. This reaction was chosen therefore as the source of *in situ* S_4N_4 for the experiments described in section 4.2.3.

The initial strategy was to combine the standard reductions (I) and (II) directly by finding a solvent compatible with both stages (*i.e.* solvent X = solvent Y):

$$S_4N_3Cl + Fe \xrightarrow{\text{Solvent X}} (S_4N_4) + \cdots\cdots\cdots \qquad (I)$$

$$(S_4N_4) + SnCl_2{\cdot}2H_2O \xrightarrow[\text{MeOH / H}_2\text{O}]{\text{Solvent Y}} S_4(NH)_4 \qquad (II)$$

A variety of experimental procedures were investigated but in all cases $S_4(NH)_4$ was not isolated as a solid product, even though its presence in solution was inferred by the colour change accompanying the second stage, $SnCl_2$ reduction. T.l.c. evidence for the presence of $S_4(NH)_4$ was not particularly strong in view of the absence of i.r. characterisation. T.l.c. did, however, clearly indicate (i) the absence of S_4N_4 in solution after stage 2 and (ii) the formation of S_7NH (this was not detected as a product of the stage 1 reduction - see Chapter 3).

The solid products isolated were either identified as sulphur, or were soluble in dilute hydrochloric acid (which $S_4(NH)_4$ is not). The latter products were probably partially hydrolysed tin chlorides (e.g. $(NH_4)_2Sn(OH)_2Cl_4$) which are basic in nature[21].

I.r. spectra of these products contained an absorption at 320 cm^{-1} which was assigned to an Sn-Cl stretching vibration (cf. a strong, broad absorption at 345 cm^{-1} which occurred in the spectrum (KBr disc) of $SnCl_2 \cdot 2H_2O$). No attempt was made to confirm the nature of these products because of their low yield and high moisture sensitivity.

In section 4.2.4 the direct reduction of S_4N_3Cl with $SnCl_2$ was investigated in various solvents. Results were very similar to those obtained in the two-stage reductions (section 4.2.3). Once again, although the solutions showed colour changes indicative of the formation, firstly of S_4N_4 and then $S_4(NH)_4$ (and t.l.c. suggested its presence in solution),no solid imide was isolated using the usual experimental techniques. S_7NH was regularly detected in solution and the solid products were either characterised as sulphur, or presumed to be hydroxy-tin chlorides.

It was concluded that the in situ S_4N_4 obtained from reductions of thiazenes was unsuitable for direct conversion to $S_4(NH)_4$ because of the complexity of species in solution. Although t.l.c. suggested that $S_4(NH)_4$ was being formed,the impurities in the S_4N_4 solutions confounded attempts to isolate it (section 4.3.2.)

4.3.5 Synthesis of $S_4(NH)_4$ from thiotrithiazyl chloride, S_4N_3Cl

Because of the difficulties encountered in converting in situ S_4N_4 directly to $S_4(NH)_4$, a two stage preparation (section 4.2.5) was investigated which involved intermediate isolation of crude S_4N_4 (III).

$$S_4N_3Cl + Fe \xrightarrow{CH_3NO_2} S_4N_4\ (s) \qquad (III)$$

$$(S_4N_4)^{toluene} \xrightarrow[MeOH/H_2O]{SnCl_2 \cdot 2H_2O} S_4(NH)_4\ (s) \qquad (IV)$$

The S_4N_4 isolated from stage III was subjected to a minimum of purification (dioxane extraction) before being used in stage IV.

From results quoted (in sections 4.2.1, 4.2.3 and 4.2.4) it would seem that the maximum sulphur impurity which can be tolerated with S_4N_4 is ca. 30-35%.

Another important factor for the isolation of $S_4(NH)_4$ was the ratio of solvent volume: weight of S_4N_4. For instance, in the successful preparations of the imide in toluene (sections 4.2.1 and 4.2.5) the volume was fairly low (30-40 ml g^{-1}). In the in situ preparations involving toluene, however (sections 4.2.3 and 4.2.4), the volume was much greater (60-80 ml g^{-1}). It may be important for the imide to precipitate from solution as it is formed in which case solvent volume must be carefully chosen with regard to solubility of $S_4(NH)_4$.

4.3.6 "In situ" S_4N_4 from other reducing systems

Other thiazene reduction systems from Chapter 3 ($S_4N_3Cl/Na_2S_2O_3$ and $S_4N_3Cl/Na_2C_2O_4$) were investigated (section 4.2.6) as sources of in situ S_4N_4 for preparation of $S_4(NH)_4$ in two-stage reactions such as described in section 4.2.3. It is likely that $S_4(NH)_4$ was formed in these reactions, however, isolation problems were encountered similar to those already described.

Conclusions

In the two stage reactions involving $SnCl_2$ as the second reductant, reduction of the sulphur-nitrogen rings occurred as noted by the colour change from orange-red to pale yellow, and the major products were S_7NH and sulphur. The formation of S_7NH can be rationalised by protonation (in aqueous methanolic solution) and recombination of the short chain

SN radicals formed by reduction and ring-opening of, for example, S_4N_4. It is likely that the second stage reduction involved a free radical mechanism similar to that discussed in Chapter 3, page 62, because (i) in the $SnCl_2$ reductions (section 4.2.4) solutions exhibited similar intermediate colours, and (ii) because S_7NH was a major product of these reductions as it was in the reductions of thiazenes when moisture was present in solution (e.g. section 3.2.7c).

4.3.7 Formation of adducts from "in situ" S_4N_4

Alange[23] has shown that S_4N_4 reacts with many Lewis acids to form adducts of stoichiometry 2:1, 1:1, 1:2 and 1:4 (S_4N_4 : Lewis acid) in which the nitrogen of S_4N_4 is co-ordinated to the metal of the Lewis acid.

Solutions containing S_4N_4 produced by reductions of thiazenes reacted readily (sections 4.2.7 and 4.2.8) with $SnCl_4$ and $SnBr_4$ to form the adducts $(S_4N_4)_2SnCl_4$ and $(S_4N_4)_2SnBr_4$ respectively, which were fully characterised by i.r. and chemical analysis.

$(S_4N_4)_2SnCl_4$ was formed in yields which varied from 18-65% (Table 4.9) compared with 80% in the preparation of the adduct from pure S_4N_4 (Chapter 2, page 33). The highest yield of $(S_4N_4)_2SnCl_4$ came from the S_4N_3Cl and iron reaction. When prepared from in situ S_4N_4 the adduct was invariably contaminated with sulphur (5-25% by weight, Chapter 3, page 51). The purest samples of $(S_4N_4)_2SnCl_4$ were obtained from the reaction of S_4N_3Cl and $Na_2C_2O_4$ (56% yield) and when S_4N_3Cl was refluxed in chloroform (42% yield).

Good yields were also obtained of the $SnBr_4$ and $AlCl_3$ adducts (41% and 85% respectively). As with the $SnCl_4$ adduct, $(S_4N_4)_2SnBr_4$ was slightly contaminated with sulphur (4% based on elemental analysis).

Analysis of the $AlCl_3$ adduct indicated an empirical formula, $SNAlCl_3$. This would be consistent with either (i) a mixture containing 1 mole of $S_4N_4(AlCl_3)_2$ and 2 moles of unreacted $AlCl_3$ (i.e. a 54% impurity by weight) or (ii) an adduct of stoichiometry 1:4 (S_4N_4:$AlCl_3$). Both the 1:1 and 1:2

$AlCl_3$ adducts have been reported, $S_4N_4.AlCl_3$[22] and $S_4N_4.2AlCl_3$[23], however the only 1:4 adducts known involve strong Lewis acids such as SO_3, SbF_5 and TiF_4[24]. In view of the fact that the product was formed by precipitation, it seemed unlikely that it should contain $S_4N_4(AlCl_3)_2$ and $AlCl_3$ in the exact ratio 1:2, thus possibility (ii) above was favoured.

The structures of only three S_4N_4 adducts have been determined, $S_4N_4.SbCl_5$ and $S_4N_4.BCl_3$[25] and $S_4N_4.SO_3$[26]. In these adducts charge is donated from the nitrogen atoms of S_4N_4 to a metal of the Lewis acid and although the ring remains intact, the S_4N_4 molecule becomes flattened, with less S...S bonding and various different SN-bond lengths. In the limit (of removing two electrons from S_4N_4 to form $S_4N_4^{2+}$) a planar structure might be expected with a 10 π-electron delocalised system. The $S_4N_4^{2+}$ cation has been prepared in the salts $S_4N_4(SbCl_6)_2$ and $S_4N_4(SbF_6)(Sb_3F_{14})$[27] however, in the former it is nonplanar, whilst two, slightly different planar structures exist in the unit cell of the latter.

As expected, significant differences are observed in the i.r. spectra of S_4N_4 adducts compared with S_4N_4, and the similarities between spectra of different adducts have been taken as evidence of their structural similarity to, for example, $S_4N_4.SbCl_5$. The i.r. spectra (4000-250 cm^{-1}, KBr discs) of the SnX_4 adducts were very similar. Sn-N absorptions occur[28] in the far infra-red, below 265 cm^{-1} and octahedral Sn(VI) complexes show no absorptions above 400 cm^{-1}, thus most of the absorptions (Table 4.11) were assigned to S-N vibrations and ring deformations, by analogy with S_4N_4. The extra bands (at ca. 1045, 800, 680 and 420 cm^{-1}) are probably caused by the lowering of symmetry upon co-ordination)[24]. The band at 318 cm^{-1} was assigned to ν(Sn-Cl) because it was absent from the spectrum of the $SnBr_4$ adduct and because a standard spectrum of $SnCl_2.2H_2O$ had an Sn-Cl absorption at 345 cm^{-1}. The medium-strong ν(Sn-Br) absorption occurs[28,29]

TABLE 4.11

$(S_4N_4)\ SnCl_4$ (section 3.2.4.)	$(S_4N_4)_2SnBr_4$ (section 4.2.8.)	Assignment (S_4N_4 cm^{-1})
1046 s,sh	1042 s	
966 m	962 s	ν(S-N) (928)
810 s	798 s	
700 m		ν(S-N) (701)
681 w,br	673 m	
520 m	515 vs	δ(SSN) (548)
420 w,br	420 s	
371 m	359 vs	δ(SSN) (348)
318 m,sh,br		ν(Sn-Cl)

in the region of 220-240 cm^{-1} and was therefore not observed in the KBr disc spectrum. Because of the size of the S_4N_4 ligand a trans arrangement at Sn(VI) is more likely than cis, a fact which was also deduced from the number of observed metal-halide absorptions[30].

There was some similarity between the i.r. spectrum of $S_4N_4\cdot 2AlCl_3$[23] and the product isolated in section 4.2.8(ii) (Table 4.12), however, the intensities of some of the absorptions (e.g. those at 990, 670 and 507 cm^{-1}) were completely different.

TABLE 4.12

"$S_4N_4\cdot 4AlCl_3$"	$S_4N_4\cdot 2AlCl_3$	"$S_4N_4\cdot 4AlCl_3$"	$S_4N_4\cdot 2AlCl_3$
1150 m,br	1162 vw	783 m	755 ms
1044 s	1046 vs	670 mw	680 ms
990 m,br	998 w	570 br	573 w
963 ms	967 vs	507 s,br	507 w,br
861 s,sh	866 vs	478 vs	476 w

Fundamental vibrations in solid Al_2Cl_6 give rise to absorptions at 625, 608, 501, 484, 438, 420, 336, 217, 168 and 115 cm^{-1}[31]. It is likely therefore that the absorptions at 507 and 478 cm^{-1} (Table 4.12) were caused by Al-Cl vibrations. Absorptions at 1044, 963 and 670 cm^{-1} had counterparts in the spectra of the SnX_4 adducts and were probably due to S-N vibrations. The absence of absorptions at 625 and 608 cm^{-1} suggested that $AlCl_3$ was not an impurity in the isolated product.

Conclusions

It would seem likely that most of the known S_4N_4-adducts could be isolated from solutions of in situ prepared S_4N_4. There was some evidence for the isolation of a new adduct, viz. $S_4N_4(AlCl_3)_4$, further confirmatory work is however necessary.

4.3.8 Attempts to prepare $S_4(NH)_4$ from $(S_4N_4)_2SnCl_4$

Because S_4N_4 can be safely handled in the form of adducts (section 4.3.7) and, in view of the lack of success in reducing in situ S_4N_4 directly to $S_4(NH)_4$ (sections 4.3.4 and 4.3.6), it was decided to attempt reductions of $(S_4N_4)_2SnCl_4$ (section 4.2.9).

Initial experiments showed that S_4N_4 was released from $(S_4N_4)_2SnCl_4$ by refluxing in toluene, however $SnCl_2$ reduction of the adduct produced a white solid which was acid soluble and was probably similar to the tin hydroxychloride products described in section 4.3.4.

$S_4(NH)_4$ resulted from the reaction of $(S_4N_4)_2SnCl_4$ with $SnCl_2 \cdot 2H_2O$ in carefully chosen volumes of benzene, methanol and water. The best preparation used 82% benzene, 16% methanol and 2% water in a total volume of 16 ml per gram of $(S_4N_4)_2SnCl_4$. The $S_4(NH)_4$ produced was characterised by i.r. and chemical analysis and a good microcrystalline sample was obtained by careful recrystallisation from nitromethane.

4.3.9 Other uses for "in situ" S_4N_4

Fielder has shown that in situ S_4N_4 can also be used for the preparation of $S_5N_5FeCl_4$ and organic derivatives such as the norbornene complex $(C_7H_{10})_2S_4N_4$. Since $(S_4N_4)_2SnCl_4$ was useful as a labile source of S_4N_4 in the preparation of $S_4(NH)_4$ (section 4.2.9) a similar reaction was attempted involving norbornene.

The white solid isolated (section 4.2.10) had i.r. absorptions due to N-H and O-H vibrations (3500, 1400 and 3200, 1620 cm^{-1} respectively) and a strong absorption (at 320 cm^{-1}) similar to the Sn-Cl absorption in $(S_4N_4)_2SnCl_4$. The spectrum did not correlate well with the S_4N_4∘norbornene complex[2] so it was decided not to pursue the reaction further.

Conclusions

In situ S_4N_4 produced by reductions of thiazenes (Chapter 3) was shown to have a number of inorganic and organic applications. The S_4N_4 can be used directly (in solution) or as the solid, Lewis acid adduct. In either form the S_4N_4 is safer to handle than the pure, crystalline solid.

4.4 References

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8. See Chapter 3, page 48 (section 3.2.9) for the origin of this S_4N_4 (%N = 29.6).

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CHAPTER 5

VAPOUR PHASE STUDIES

5.1 Introduction

5.1.1 Polythiazyl, $(SN)_x$

Although $(SN)_x$ was known as early as 1910[1] it was not studied systematically until 1956, when Becke-Goehring found it to be conducting[2,3]. Recent discoveries (of its metallic properties) have caused intense study of the material and its halogenated derivatives.

The classical and usual preparation of $(SN)_x$ is the solid state polymerisation of the S_2N_2 crystals produced by catalytically cracking S_4N_4 vapour:

$$S_4N_4\ (v) + 8Ag \longrightarrow 4Ag_2S + 2N_2$$

$$S_4N_4\ (v) \xrightarrow{Ag_2S} 2S_2N_2$$

Good quality S_2N_2 crystals (grown at 0°C) and a controlled polymerisation (RT/3-4 weeks) are essential for formation of $(SN)_x$ with a high crystal purity[1]. Solid state polymerisation can occur when there is a strong similarity in structure between monomer and polymer lattices. Baughman[5] concluded that polymerisation could occur by ring cleavage, then the chain axis of $(SN)_x$ would develop along what was formerly the a-axis of S_2N_2 (Figure 5.1). There is evidence (an e.s.r. signal with $g = 2.005$ which reaches a maximum after 2 hours and slowly decreases as polymerisation proceeds) for an S_2N_2 radical intermediate, as inferred by this mechanism.

The structure and physical properties of $(SN)_x$ are summarised in Table 5.1.

$(SN)_x$ crystals sublime at 135°C _in vacuo_[10,11] to give a red-purple tetramer believed to be linear $(SN)_4$[12,13]. This can be condensed on a cold-finger (0°C) as a lustrous golden film of $(SN)_x$. Orientated substrates (_e.g._ stretched polythene) can thus be coated with a thin film of $(SN)_x$[10]. Matrix isolation studies of $(SN)_x$ sublimates have shown the presence of

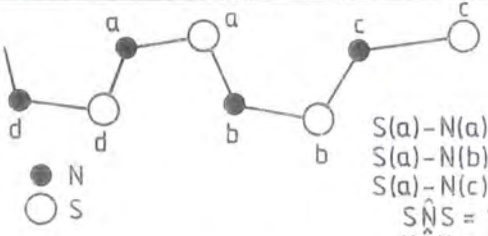
$(SN)_x$

APPEARANCE SHINY METALLIC SOLID. THIN FILMS APPEAR DARK BLUE, THICKER FILMS TAKE ON A BRONZE GOLD COLOUR. WELL FORMED CRYSTALS ARE BRIGHT GOLDEN AND LUSTROUS. FIBRE-ENDS APPEAR BLACK.

SINGLE CRYSTAL

TYPICALLY 2-3 mm. INVARIABLY TWINNED. REFLECTIVITY FROM CRYSTAL FACETS IS ANISOTROPIC. "SINGLE" CRYSTAL CONSISTS OF HIGHLY ORIENTATED PARALLEL FIBRE BUNDLES (~100 Å DIAMETER) WHICH CONTAIN PARALLEL $(SN)_x$ CHAIN (6).

CHAIN STRUCTURE (7,8)



$S(a)-N(a) = 159$ pm
$S(a)-N(b) = 163$ pm
$S(a)-N(c) = 286$ pm
$S\hat{N}S = 119.9°$
$N\hat{S}N = 106.2°$

PROPERTIES

MPT (6) - DECOMPOSES AT 240°C

VAPOUR PRESSURE (9) -
$\ln P = 37.64 - 16351/T$
At 135°C $(SN)_x$ has a pressure of 0.0037 torr

THERMOCHEMISTRY (9) -
$\Delta H^{o}_{vap} = 32.79 \pm 0.99$ Kcal mol^{-1}
$\Delta S^{o}_{vap} = 80.98 \pm 2.48$ Kcal (mol K)$^{-1}$

CRYSTAL STRUCTURE (8)

MONOCLINIC SYSTEM.
SPACE GROUP $P2_1/c$.
TWO EQUIVALENT CHAINS PER UNIT CELL.

a = 415 pm b = 444 pm c = 764 pm β = 109.7°

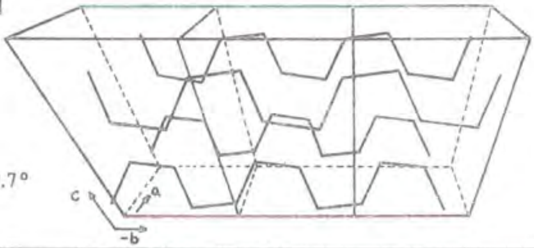


TABLE 5.1 Physical properties of $(SN)_x$

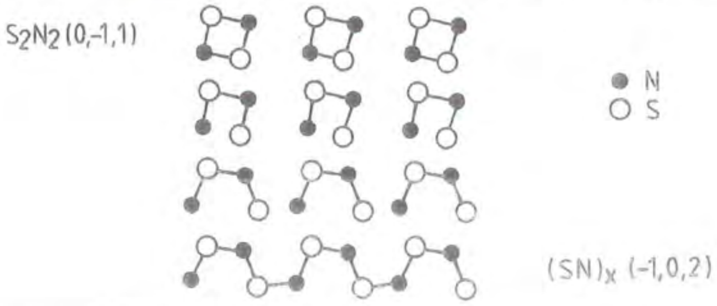


FIGURE 5.1 Solid state polymerisation of S_2N_2

SN (red monomer), S_2N_2, S_4N_4 and other unidentified species[14]. The red monomer has also been observed as a product of the pyrolysis of S_4N_4. It polymerises in several hours at room temperature to give "red"-$(SN)_x$ crystals, the properties of which are similar to normal $(SN)_x$[15]. A third type of polymer, "brown"-$(SN)_x$ has also been documented[15] formed from the monomer, $(SN)_2$. Only impure crystals have, however, been isolated to date.

Band Theory of solids[16]: band-structure of $(SN)_x$

Because of the unusual metallic properties of $(SN)_x$ a large number of band-structure calculations have been reported[17-32].

The energy levels of a free atom (solutions of the Schrödinger equation) are discrete, single levels. However, when a group of identical atoms, widely separated are brought together to form a solid, the electrons interact with each other causing splitting of these energy levels into a range of sub-levels which, with an average separation of 5×10^{-23}eV, are so close together that they form an energy band[16]. The ground state level of a free atom forms the valence band in the solid and the lowest band occupied in the first excited state is known as the conduction band. The lower, fully occupied energy bands are of lesser importance in determining the electronic properties of the solid, just as the core electrons of a free atom are less important than the valence electrons. Band width increases with band energy since the perturbation effect of electrons in neighbouring atoms is greatest on the atomic orbitals furthest from the nucleus. Thus band width increases as the distance between atoms in the solid decreases, up to the equilibrium distance, r_o (Figure 5.2). Energy bands are separated by forbidden energy gaps (that between valence and conduction band is usually denoted, E_g.) and the sublevels are filled (like the energy levels of a free atom) according to the Pauli principle. Solids are classified according to their band structure. An insulator (e.g. diamond) is a solid with a full valence band separated from the

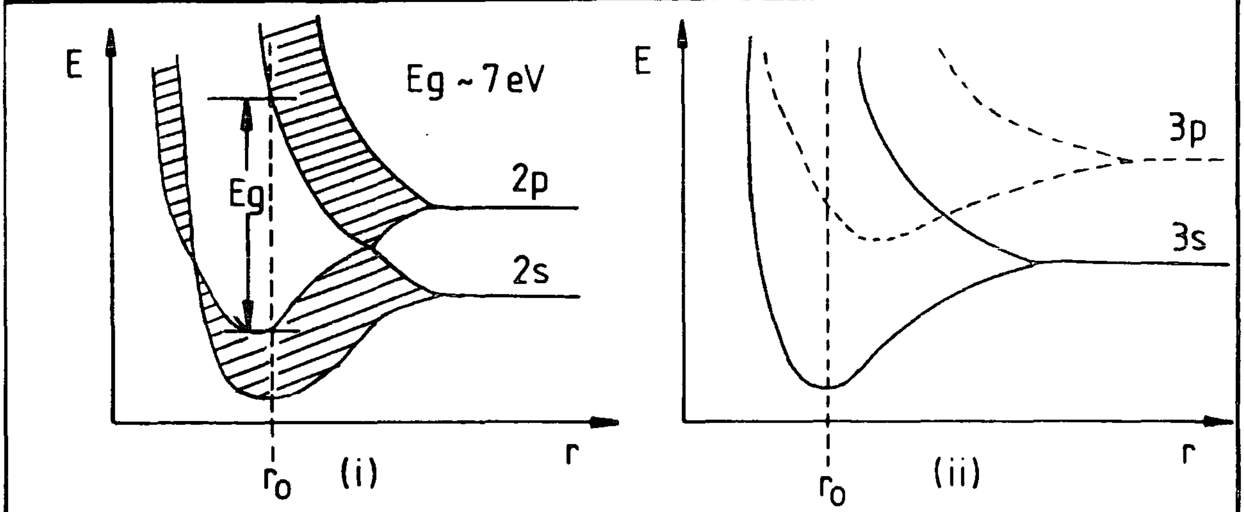
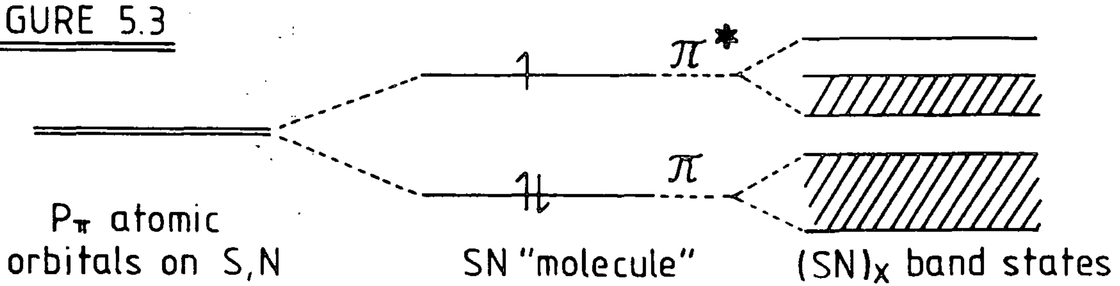


FIGURE 5.2 - Variation of band width with distance for (i) An insulator (diamond) and (ii) A metal (sodium)

conduction band by a large energy gap. Since the conduction band is unpopulated even at high temperatures, application of an electric field causes no current to flow. A solid which has a partially filled valence band, or in which there is partial overlap with the higher energy band (e.g. Na) is known as a metal. Semiconductors have very small band gaps (e.g. Si = 1eV; Ge = 0.07eV) thus valence electrons are thermally excitable to the conduction band even at room temperature.

A simple M.O. model for $(SN)_x$ is described by Walatka[17]. For an SN "molecule" there are bonding and antibonding M.O.s derived from overlap of the p_π atomic orbitals on sulphur and nitrogen. These orbitals hold 3 electrons (2 from sulphur and 1 from nitrogen) with the unpaired electron in the π^* orbital. Walatka considered that when the SN "molecules" polymerised to solid $(SN)_x$ there was a spreading out of these levels into bands, one filled and one half filled (Figure 5.3).

FIGURE 5.3



$(SN)_x$ is best thought of as an anisotropic 3-D semimetal rather than a 1-D metal[33]. This is supported by many band-structure calculations[21,24-26]. If the $(SN)_x$ chains were non-interacting, which is the basis for the 1-D calculations[18-20], then a Peierls distortion would split the energy band at the Fermi level (the boundary between filled and unfilled states) forming an insulating state. The absence of a metal-insulator transition in $(SN)_x$ is taken as evidence for 3-D interaction between the chains in the solid.

Chemical stability

$(SN)_x$ was reported to have a 5-10% hydride impurity[34]. This has been disputed by several workers[35,36] who found that "analytically pure" $(SN)_x$ had a high stability towards moist air. The presence of moisture sensitive intermediates due to incomplete polymerisation of S_2N_2 would explain this anomaly.

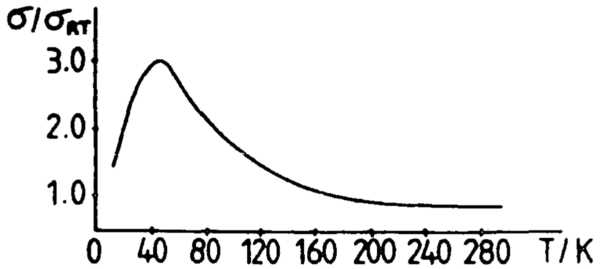
Conductivity and Superconductivity

Table 5.2 summarises information about conductivity and superconductivity in $(SN)_x$. The linear dependence of resistivity on temperature is typical of metallic conductors[40]. Electrical conductivity is dependent on the chemical purity and physical perfection of the $(SN)_x$ crystal examined.

Infra-red and Raman data

Table 5.3 contains infra-red and Raman data on $(SN)_x$. Infra-red frequencies for $(SN)_x$ made by the pyrolysis of S_4N_4 (page 117) were similar to those of Chapman and Warn (for a powdered sample run as a Nujol mull)[43]. Stolz[44] published data for thin films of $(SN)_x$ on various substrates. He found that i.r. and Raman data recorded at room temperature, 77K and 4.2K were essentially the same and concluded that this was consistent with $(SN)_x$ being an anisotropic, 3-D material. Macklin[45] in a far-infra-red and Raman study (using an F.T. spectrometer) considered that absorption measurements on polymeric thin films adequately represented the vibrational characteristics of the bulk material.

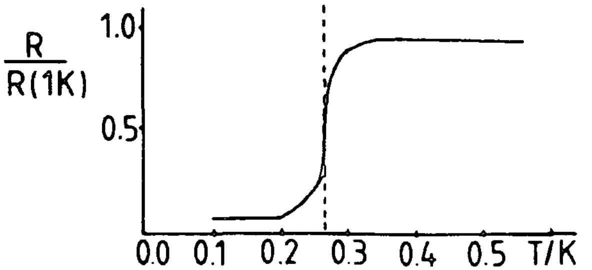
CONDUCTIVITY



Typical conductivity (σ) v temperature graph for $(SN)_x$ (17)

R.T. CONDUCTIVITY		COMMENTS (ref)
$\sigma_{\parallel}$ ($\Omega^{-1}cm^{-1}$)	$\sigma_{\parallel}/\sigma_{\perp}$	
10 - 1730	-	σ dependent on Xtal purity (17)
780-1075	50	Anisotropy observed (37)
600	-	No σ_{max} observed at low temperature (36)
2-4 × 10^3	1000	Pure Xtals by superior growth technique (38,39)

SUPERCONDUCTIVITY



Superconducting behaviour of $(SN)_x$(41)

Transition temperature T_c / K	COMMENTS (ref)
0.26 ± 0.04	Conductivity measured along chain axis (41)
0.33 ± 0.03	T_c and transition width dependent on crystal perfection (38)
0.26 - 0.28	Confirmed phenomenon of superconducting transition (42)

TABLE 5.2-$(SN)_x$

INFRARED				RAMAN	
THIS WORK	(43)	(44)*	(45)	(44)‡	(45)
1400 w	1400m	1400w,br			
		1260m,sh			
1225 w,br	1225s	1220m,br			
1048 vw	1047w	1105 s,br			
1014 mw	1015ms	1017 s,br	1007 V_s A_u	1001 m	1004 m V_s A_g
			918 w	934 m,br	930
		795 m	(812)		
			768 V_{as} B_u	767 m,br	786 V_{as} B_g
685mw	685 w	695m,br	689 V_s A_u	690 sh	700
	657mw		(662 sh)	656s,sh	685 vs V_s A_g
		625 m	629 δ B_u	624 m	627 δ B_g
610 w,br	600m	615m,sh	590 sh		586
		595 sh		580 vw	
			560 sh		
		505w,br	500 δ A_u	503 sh	
		470w,br	(465)	458 m,br	456 vs δ A_g
			(435)		
			(384) (355)		
		280 m	278 γ A_u	290 vw	292 γ A_g

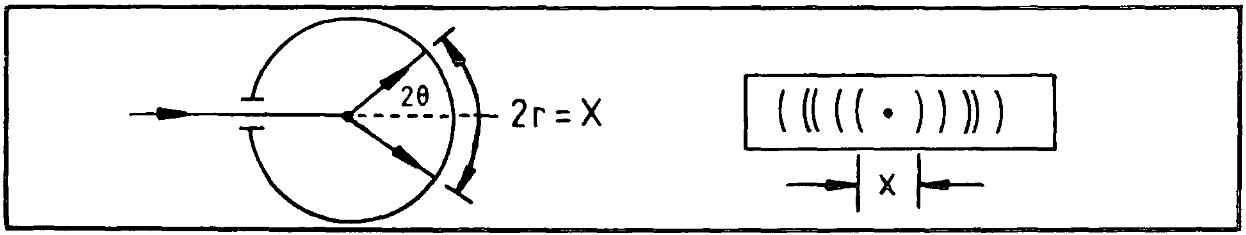
TABLE 5.3-$(SN)_x$

* KBr substrate
‡ Si substrate

Chapman and Warn assigned bands at 1225 and 1015 cm^{-1} to ν_{SN}. According to theoretical correlations, these frequencies would suggest bond lengths in $(SN)_x$ of 148 and 160 pm respectively[43]. Barrow[46] reported the vibrational frequency of gaseous SN (bond length = 149 pm) to be 1204 cm^{-1}. On polymerisation this band would be expected to shift to lower frequency. The bond lengths in $(SN)_x$ are now known from X-ray studies to be 159 and 163 pm respectively. It is likely therefore that only the band at 1015 cm^{-1} represents an S-N stretching vibration. Teichman[14] suggested that the band at 1225 cm^{-1} was due to SN-monomer. Since Macklin reported no band above 1007 cm^{-1}, it is thought that absorptions at 1400 and 1225 cm^{-1} were due to impurities.

X-ray diffraction data

In order to compare our results with those of Becke-Goehring[47] it was necessary to convert the measurement of 2r into values of d-spacing. For this, it was assumed that 2r = X as shown:



There was poor correlation between the two sets of data (Table 5.4). This may have been because the Guinier-de-Wolff fine focussing camera used in the present study scans samples in only 2-D on a translucent window. This would result in less than a true 3-D spatial arrangement of crystallites and the loss of some reflections. Also in our preparation, the process of grinding and spreading out the sample as a smear may have caused plastic deformation of the material, leading to a distribution of cell parameters and consequential formation of broad, diffuse lines.

Mass spectral data

Table 5.5 compares our results with published mass spectral data. Smith[12], using phase angle mass spectrometry, has identified linear $(SN)_4$ as the major species in $(SN)_x$ vapour. A hydride impurity (0.1% H by weight)

TABLE 5.4

X-RAY DIFFRACTION DATA

Becke-Goehring[47]		This Work**		
2r/mm (I/Io)	d-spacing(Å)*	l/mm (I/Io)	θ	d-spacing/Å
23.70 (9)	7.47			
27.20 (10)	6.52			
28.00 (10)	6.34			
31.10 (9)	5.71			
		44.39 (35)≠	11.03	5.06
38.90 (2)	4.57			
39.10 (2)	4.55			
40.80 (4)	4.36			
42.60 (2)	4.18			
44.30 (2)	4.02			
47.00 (<1)	3.79	57.95 (10)	14.39	3.89
49.60 (1)	3.60			
52.00 (1)	3.43	67.96 (35)≠	16.88	3.33
		68.65 (30)≠	17.05	3.30
57.80 (1)	3.09	69.70 (40)≠	17.31	3.25
60.90 (1)	2.94			
65.20 (<1)	2.75			
68.30 (2)	2.63			
71.80 (4)	2.51			
		103.90 (100)	25.81	2.22
		108.10 (70)	26.85	2.14

* Author's calculation

** Fe K_{α_1} Radiation 30 Kv/10mA 10 hours

≠ Broad, diffuse

TABLE 5.5

MASS SPECTRAL DATA

m/e	Relative Intensities (%)			Assignment	(Ref 49)
	This Work	Smith[12,48]	Ueno[49]		
28	54.0			N_2^+	
32	12.9			S^+	
46	100.0	100.0	14.3	SN^+	
48	9.6			SO^+	
64	16.2	4.3		S_2^+	
78	11.1	19.0	7.1	S_2N^+	
92	100.0	60.0	11.6	$S_2N_2^+$	$(SN)_2^+$
94	18.7			$S_2N_2H_2^+$	
110	0.7	0.6	3.0	S_3N^+	
124	2.5	3.0	1.9	$S_3N_2^+$	
138	18.8	63.0	6.0	$S_3N_3^+$	$(SN)_3^+$
156	1.5	0.2	5.7	$S_4N_2^+$	
184	0.5	0.2	1.0	$S_4N_4^+$	$(SN)_4^+$

was detected, which is believed to originate from the slow, solid state polymerisation of S_2N_2 rather than the fast, bimolecular gas phase reaction: $(SN)_4 + H_2O$. The impurity at $^m/e = 63$ (HNSO) was a byproduct of hydrolysis.[34]

5.1.2 Halogenated derivatives of $(SN)_x$

Brominated derivatives of $(SN)_x$ are an additional class of polymeric materials which possess metallic properties. They are prepared by bromination of either $(SN)_x$ or S_4N_4. Sulphur-nitrogen-halogen compounds have been known since 1896 when Clever *et al*[50] reported "$S_4N_4Br_6$" as a product of S_4N_4 bromination. They also isolated "$S_4N_4Br_4$" when bromination was done in carbon disulphide. Becke-Goehring[51] formulated the latter compound as a polymer, $(SNBr)_x$ on the basis of its insolubility in organic solvents. Heal[52] believed that "$S_4N_4Br_6$" was actually $S_3N_2Br_2$ (an analogue of $S_3N_2Cl_2$)[53] and Zborilova[54] concluded it was a mixture of S_4N_3Br and $S_3N_2Br_2$. Clearly bromination of S_4N_4 was more complex than the chlorination and fluorination reactions to give NSCl, $(NSCl)_3$[55] and NSF, $(NSF)_3$ and $(NSF)_4$[56] respectively. Recent work[57-62] has clarified that bromination is strongly dependent on conditions (Table 5.6).

TABLE 5.6

Experimental Conditions					
S_4N_4	$(SN)_x$	Bromine	Solvent	Product(s)	(Ref.)
Solid		Liquid		$S_4N_3Br_3$	(61)
Soln.		Liquid	CS_2	$S_4N_3Br_3/Br + CS_3N_2Br_2$	(62)
Soln.		Liquid	SO_2	$S_4N_3Br_3 + S_4N_3Br$	(62)
Susp.		Liquid	CCl_4	$S_4N_3Br_3/Br/(SNBr_{0.4})_x$	(62)
Solid		Vapour		$(SNBr_n)_x$	(57,58)
	Solid	Vapour		$(SNBr_n)_x$	(59,60)

Brominations of S_4N_4

S_4N_4 reacts quantitatively with refluxing bromine to give yellow crystals of $S_4N_3Br_3$[61]. On heating to 70°C it loses bromine to form S_4N_3Br.

These products were well characterised and i.r. spectra confirmed the presence of the cyclic $S_4N_3^+$ cation. It is likely that the deep red crystals of Clever[50] were really impure $S_4N_3Br_3$. Wolmerhauser suggested[61] that NSBr was a reactive intermediate in the reaction because of the transitory existence of an i.r. absorption at 1319 cm^{-1} (cf. 1372 cm^{-1} for NSF[63] and 1325 cm^{-1} for NSCl[64]) which intensified as S_4N_4 dissolved in the liquid bromine and disappeared as the reaction neared completion. NSBr, the only known S-N compound with bromine directly attached to sulphur, has also been observed in the vapour phase above $(NSBr_{0.4})_x$[65] and its i.r. spectrum (in an argon matrix at 15K) has been published[66].

In carbon disulphide solution, bromination of S_4N_4 gave a mixture of S_4N_3Br, $S_4N_3Br_3$ and $CS_2N_2Br_2$[62]. Formation of the latter, moisture sensitive compound was rationalised by the known tendency of CS_2 to insert into S-N compounds[67]. In inert solvents, only the Br^- and Br_3^- species were formed[62]. Bromination in CCl_4 (in which S_4N_4 is only slightly soluble) produced a combination of solution and solid state bromination products.

Historically, the brominated derivatives of $(SN)_x$ were reported before the S_4N_4 brominations. Smith[59] reported that materials with electrical conductivities greater than $(SN)_x$ could be made by reaction of $(SN)_x$ films or crystals with Br_2, I_2 or ICl. However, Street reported that iodine did not react with either S_4N_4 or $(SN)_x$ at room temperature[57] but produced air sensitive, conducting derivatives at 125°C.

Bromination of $(SN)_x$

Table 5.7 lists the known bromine derivatives of $(SN)_x$. Bromine content is dependent on the conditions of isolation. Akhtar[70] has suggested the following equilibrium:

$$\boxed{(SNBr_{1.5})_x\,(s) \rightleftharpoons (SNBr_y)_x\,(s) + \left[\frac{x(1.5-y)}{2}\right] Br_2\,(g)}$$

where $(SNBr_{1.5})_x$ represented the maximum bromine content. Removal of bromine by heating in vacuo would shift the equilibrium to the right and explain the variation of bromine content in the final product.

<u>TABLE 5.7</u>

COMPOUND (ref)	$(SNBr_{0.4})_x$ *Ŧ (57-60) $(SNBr_{0.5})_x$ Ŧ (59) $\left.\begin{matrix}(SNBr_{0.55})_x\\(SNBr_{0.33})_x\end{matrix}\right\}$ (68-69)	$(SNBr_{0.25})_x$ *Ŧ (58,60) $(SNBr_{0.27})_x$ (68,69)	$\left.\begin{matrix}(SNBr_{0.04})_x\\(SNBr_{0.07})_x\end{matrix}\right\}$ (57)
COMPOSITION RANGE	$(SNBr_{0.3})_x - (SNBr_{0.6})_x$	$(SNBr_{0.16})_x - (SNBr_{0.28})_x$	$(SNBr_{0.04})_x - (SNBr_{0.07})_x$
COLOUR	BLACK	BRONZE	COPPER - BRONZE
TYPICAL PREPARATIONS (ref) From bromination of Ŧ $(SN)_x$ * S_4N_4	$(SNBr_{1.5})_x$ * $\xrightarrow[4h / RT]{10^{-5}\text{ torr}} (SNBr_{0.4})_x$ (58) $S_4N_4 + Br_2(g) \xrightarrow[RT]{10^{-5}\text{ torr}} (SNBr_{0.4})_x$ (57) $\underset{\text{Xtals}}{(SN)_x} + Br_2(g) \xrightarrow{24h / RT} (SNBr_{1.5})_x \xrightarrow[1/2h / RT]{10^{-5}\text{ torr}} (SNBr_{0.4})_x$ (59) $(SN)_x + Br_2(g) \xrightarrow[60\text{ torr}]{1h / RT} (SNBr_{0.04})_x$ (60)	$(SNBr_{0.4})_x$ *Ŧ $\xrightarrow[80°C / 4h]{10^{-5}\text{ torr}} (SNBr_{0.25})_x$ (58)	$(SNBr_{0.4})_x$ * $\xrightarrow[80°C / 18 h]{10^{-5}\text{ torr}} (SNBr_{0.07})_x$ (57) $(SNBr_{0.4})_x$ Ŧ $\longrightarrow (SNBr_{0.04})_x$ (57)

Infra-red and Raman data

Several vibrational studies have been reported for brominated-$(SN)_x$[69,71-72] the most recent by Macklin[45] whose data (for a compound of unspecified composition) is presented in Table 5.8 (cf. Table 5.3, page 103). Of the 24 representations for the unit cell vibrations (based on C_{2h} symmetry) 16 were assigned to the internal frequencies of $(SN)_x$ as follows: $4A_u + 2B_u$ (I.r. active) and $4A_g + 6\ B_g$ (R active). The observed i.r. spectrum of $(SN)_x$ has more bands than can be assigned to six fundamentals thus it is likely that the extra bands are due to non-allowed vibrations which appear because crystal imperfections (e.g. twinning) cause a lowering of the symmetry of the structure. This is supported by the fact that some of these (weaker) bands varied in intensity in spectra of different $(SN)_x$ samples and some of them (particularly at 662 and 465 cm^{-1}) corresponded to the most intense (A_g) vibrations in the Raman spectrum.

After bromination the vibrational spectrum was expected to be essentially that of individual chains (C_s symmetry) thus bands in the i.r. and Raman spectra of $(SN)_x$ with counterparts in $(SNBr_y)_x$ were likely to be fundamentals and were assigned as such[45].

Information as to the nature of bromine in $(SNBr_y)_x$ was gained from the far infra-red and Raman data. Assignment of ν_{Br-Br} to the Raman band at 222 cm^{-1} was consistent with its observed i.r. inactivity and with a decrease in its intensity in materials with a lower bromine content (bromine is removed more easily than Br_3^- under dynamic vacuum)[68]. The Br_3^- assignments also compared well with known standards (e.g. Me_4NBr_3 and $S_4N_3Br_3$)[45].

All the Raman and i.r. data published to date are consistent with a model for brominated-$(SN)_x$[72] in which Br_2 and Br_3^- are both present in different environments, viz. in the $(SN)_x$ lattice and on the outside of the fibres.

INFRARED AND RAMAN (4000 – 350 cm^{-1})(45)					
IR	RAMAN	ASSIGNMENT	IR	RAMAN	ASSIGNMENT
1018	1010	V_s A	550sh		
968 vw			468	480	δ A
830	840	V_{as} B	(434)	420	
688	670	V_s A	(368)	385	δ B
634		δ B	(362)	350	δ B

Figures in parentheses vary in intensity in spectra of samples of different bromine content (45)

FAR-INFRARED AND RAMAN (350 – 100 cm^{-1})				
IR	RAMAN	ASSIGNMENT(45)	RAMAN	ASSIGNMENT(69)
(320)		2 × V_s Br_3^-		
300			305	2 × V_s Br_3^-
	222 vs	V(Br–Br)	230	V(Br–Br) + V_{as} Br_3^-
189 s	190 w	V_{as} Br_3^-		
158	154	V_s Br_3^-	154	V_s Br_3^-
140	130	V_s Br_3^-		

TABLE 5.8

MASS SPECTRA (73)			
m/e	Principal ion	Relative intensity (%)	
		Brominated – $(SN)_x$	Brominated – S_4N_4
46	SN^+	100	100
47	SNH^+	2.1	2.3
64	S_2^+	2.0	1.5
78	S_2N^+	12.4	12.6
79, 81	Br^+	3.3, 3.1	1.8, 1.3
80, 82	HBr^+	1.9, 0.5	1.5, 0.3
92	$S_2N_2^+$	26.0	32.0
93	$S_2N_2H^+$	1.6	1.9
110	S_3N^+	1.0	0.9
111, 113	SBr^+	1.0, 1.0	0.5, 0.5
124	$S_3N_2^+$	1.5	1.8
125, 127	$NSBr^+$	4.4, 4.4	2.1, 2.1
138	$S_3N_3^+$	21.0	20.0
139	$S_3N_3H^+$	1.1	1.2
156	$S_4N_2^+$	0.5	0.5
158, 160, 162	Br_2^+	0.0, 0.0, 0.0	0.0, 0.0, 0.0
184	$S_4N_4^+$	1.0	0.6

TABLE 5.9

Mass spectral data

Like polythiazyl, brominated-$(SN)_x$ can be sublimed to produce thin films[7b,10,17,36,41]. Table 5.9 presents mass spectral data of the vapour species from $(SNBr_y)_x$[73]. The volatiles from brominated-$(SN)_x$ and brominated-S_4N_4 products were identical, consisting of Br_2, NSBr and $(SN)_4$ with lesser amounts of HBr and S_2Br_2[73,74].

X-ray diffraction data

In general broad, diffuse lines were obtained, indicating poor sample crystallinity[75]. Further evidence was provided (Table 5.10) that the compounds produced by bromination of $(SN)_x$ and S_4N_4 are identical. The two sharp peaks at 2.30 and 2.15 Å occur only in the sample of $(SNBr_{0.25})_x$ made from S_4N_4 and were probably due to an impurity. The absence of a line at 3.68 Å in the pattern of $(SNBr_{0.4})_x$ indicated that there are significant structure differences between compounds of differing bromine content.

Conductivity and superconductivity

Yoshino[76] reported an order of magnitude increase in electrical conductivity when $(SN)_x$ was doped with bromine. Furthermore conductivity was greater across the temperature range 0-300K. Superconductivity in $(SNBr_y)_x$ systems was investigated by Green[77] who demonstrated an increase in transition temperature (T_c) (0.32K) and a decrease in transition width in these materials. A tentative explanation is that the transition width becomes sharper because of increased coupling between fibres after bromination (despite the apparently increased disorder suggested by X-ray diffraction). In other words the brominated material is a more 3-D like superconductor. The physical origin of this increased coupling is not understood, partly because the exact structure of brominated-$(SN)_x$ materials is unknown (no crystal studies have been possible to date). $(SNBr_{0.4})_x$ is still a highly anisotropic material despite the increased coupling between fibres.

As mentioned above, some bromine may be present in the lattice as Br_3^-.

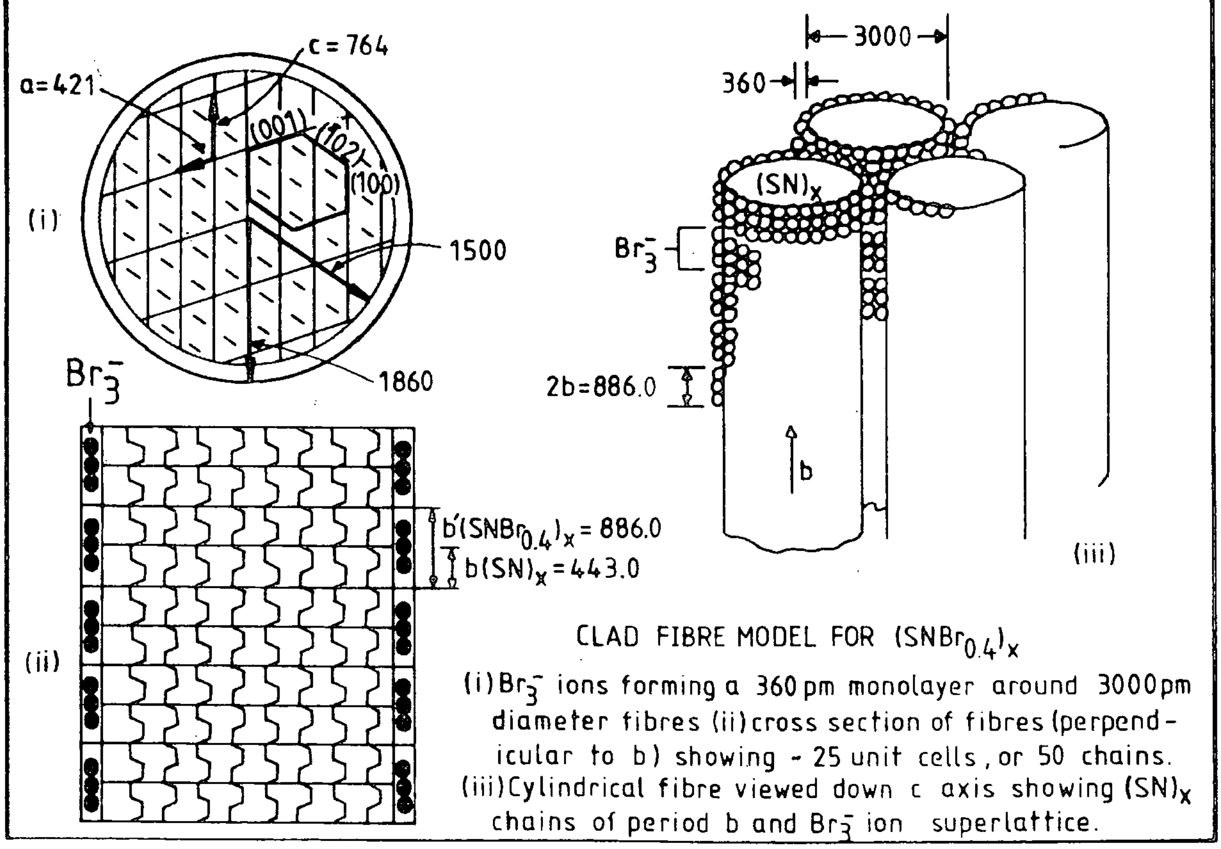
TABLE 5.10

X-RAY DIFFRACTION DATA[75] [d-spacing(Å)≠]

$(SNBr_{0.25})_x$*	$(SNBr_{0.25})_x$**	$(SNBr_{0.4})_x$**
3.66 s,br	3.68 s,br	3.35 w
3.16 s,br	3.18 vs,br	3.18 s,br
2.82 ms,br	2.84 ms,br	
2.43 vvw,br		
	2.30 w	
	2.15 w	
2.08 vvw,br	2.08 w,br	2.09 w,br
2.00 vvw		
1.90 w,br		
1.75 vw,br		
1.58 w,br	1.58 vw,br	
≠ Cu K_α radiation	* From $(SN)_x + Br_2$	** From $S_4N_4 + Br_2$

FIGURE 5.4

PROPOSED STRUCTURE FOR $(SNBr_y)_x$[72]



CLAD FIBRE MODEL FOR $(SNBr_{0.4})_x$

(i) Br_3^- ions forming a 360 pm monolayer around 3000 pm diameter fibres (ii) cross section of fibres (perpendicular to b) showing ~ 25 unit cells, or 50 chains. (iii) Cylindrical fibre viewed down c axis showing $(SN)_x$ chains of period b and Br_3^- ion superlattice.

If this is so, there must be a small transfer of charge from the $(SN)_x$ chain towards bromine. For example, for $(SNBr_{0.4})_x$ if all the bromine were present as Br_3^-, then the net charge transfer would be 0.13 electrons per SN unit, $(SN)_x^{+0.13}$ $Br_{0.4}^{-0.13}$. This transfer would have the effect of decreasing the Fermi energy of $(SN)_x$ and increasing the population of the conduction band. Such a perturbation of the Fermi surface would explain the increase in room temperature conductivity on bromination.

Possible structure for $(SNBr_{0.4})_x$

Figure 5.4 shows a possible model for the structure of $(SNBr_{0.4})_x$[72]. Such a simplistic model (assuming bromine to be present purely as Br_3^-) must be open to doubt in view of recent work discussed above[45]. In reality the fibres of $(SN)_x$ are heavily twinned and not cylindrical. More work is necessary before the structure of these materials is fully understood.

5.1.3 Recent advances (1980-81)

A comparison of the properties of polythiazyl and polyacetylene and their derivatives has been published[78]. Other reviews and dissertations included electrical conductivity of polymers[79], the effect of impurities on superconductivity in $(SN)_x$[80], superconducting diamagnetism[81], surface studies and chemical modification of $(SN)_x$ electrodes[82], metallic covalent polymers[83], conjugated $(SN)_x$[84] and $(SN)_x$ and its derivatives[85].

Patents were filed concerning applications of $(SN)_x$ in amorphous solar cells (as the barrier material)[86-88], information recording materials (using lasers)[89], light rechargeable silver-halogen batteries[90] and as an electrical conductor[91].

More academic studies included determination of electronic structure by X-ray fluorescent spectroscopy[92], a simple chemical synthesis[93], further investigation of conductivity and superconductivity[94-97] and a gas phase/ solid state ESCA study of derivatives containing the repeating SN unit[98].

In a Raman study of $(SN)_x$ modified by iodine[99] evidence was presented for a charge transfer complex in which iodine enters the interfibre regions of the $(SN)_x$ lattice as I_5^- or I_3^- linked to distorted I_2 units. Materials of composition $(SNI_{0.02})_x$ to $(SNI_{0.14})_x$ were obtained by exposure of $(SN)_x$ crystals to iodine vapour (20 torr/350K/2-12 hours). It is clear that these iodinated materials are similar in nature (although formed by a different route) to the polymer described in sections 5.2.3 and 5.3.3. Our work, and the subsequent paper[100] predated the study by Tubino[99] by several months.

5.2 Experimental

It was shown in Chapter 3 that small traces of $(SN)_x$ were formed in the following systems:

I $S_3N_2Cl + NaI \xrightarrow{MeOH}$

II $S_4N_3Cl + NaH_2PO_2 \xrightarrow{aq}$

Since S_4N_4 was the major product of these reactions, it was decided to attempt to produce $(SN)_x$ by combined vapour phase reduction and catalytic cracking (III):

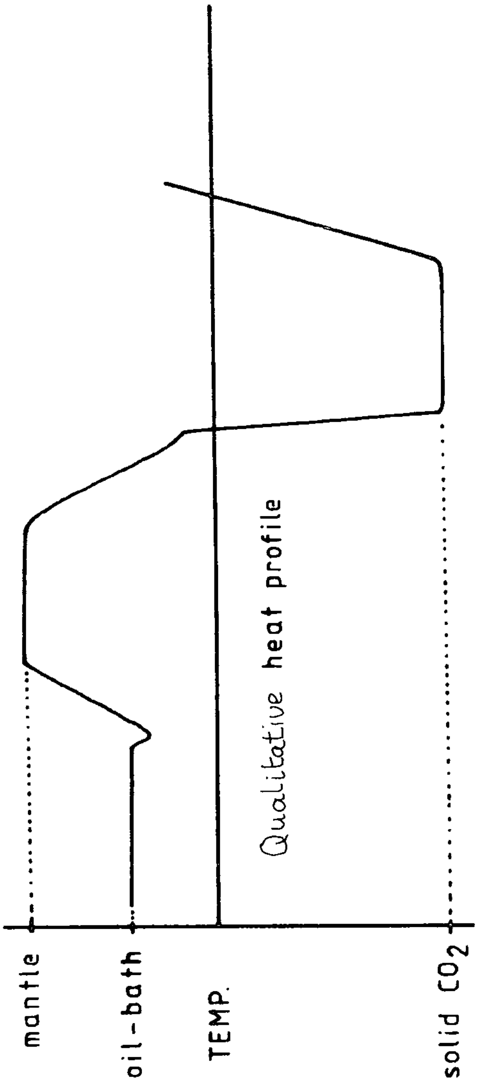
III $S_4N_3Cl + \text{reducing agent} \longrightarrow (S_4N_4) \xrightarrow{\text{catalyst}} (SN)_x$

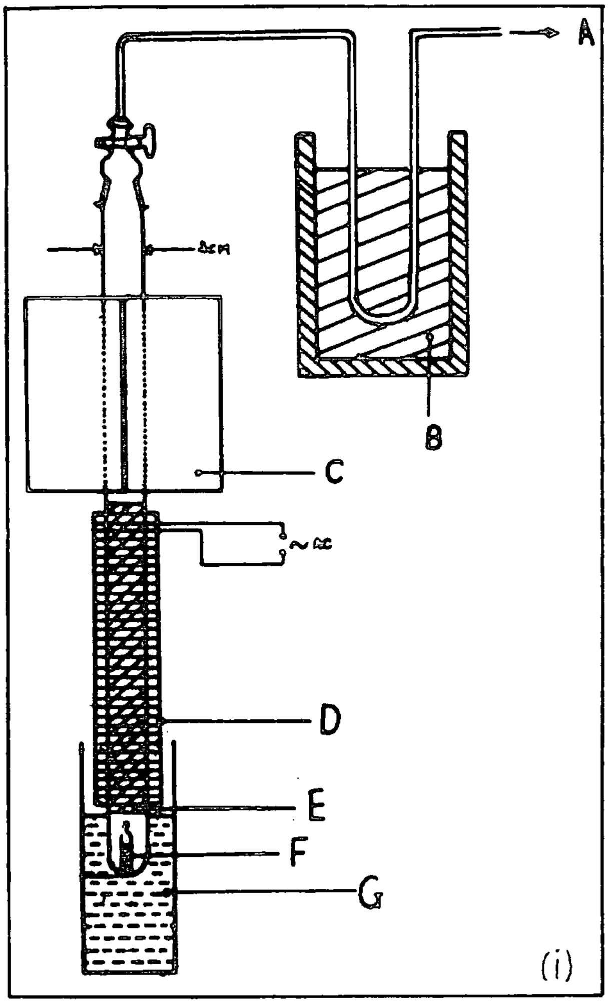
Hypophosphites decompose violently on heating (250°C) so only reaction I above was suitable for vapour phase study. S_4N_3Cl was substituted for S_3N_2Cl because of its greater stability to moisture.

Attempts to produce $(SN)_x$ from vapour phase reactions involving metal thionitrosyls and the chloro- and tetrachloroferrate salts of pentathiazyl ($S_5N_5^+$) were also investigated.

5.2.1 Apparatus design

The basic apparatus (used in sections 5.2.2 and 5.2.3) was designed to allow thiazene vapours to interact with a hot catalytic surface and any volatile products to condense in a cold zone. It consisted (Figure 5.5) of a pyrolysis tube (50 x 3 cm) connected via a liquid nitrogen coldtrap (B) to a vacuum line (with rotary and mercury diffusion pumps). The glass bucket (F) which contained the starting material had a hook to facilitate placement in, and removal from, the tube. The starting material was heated





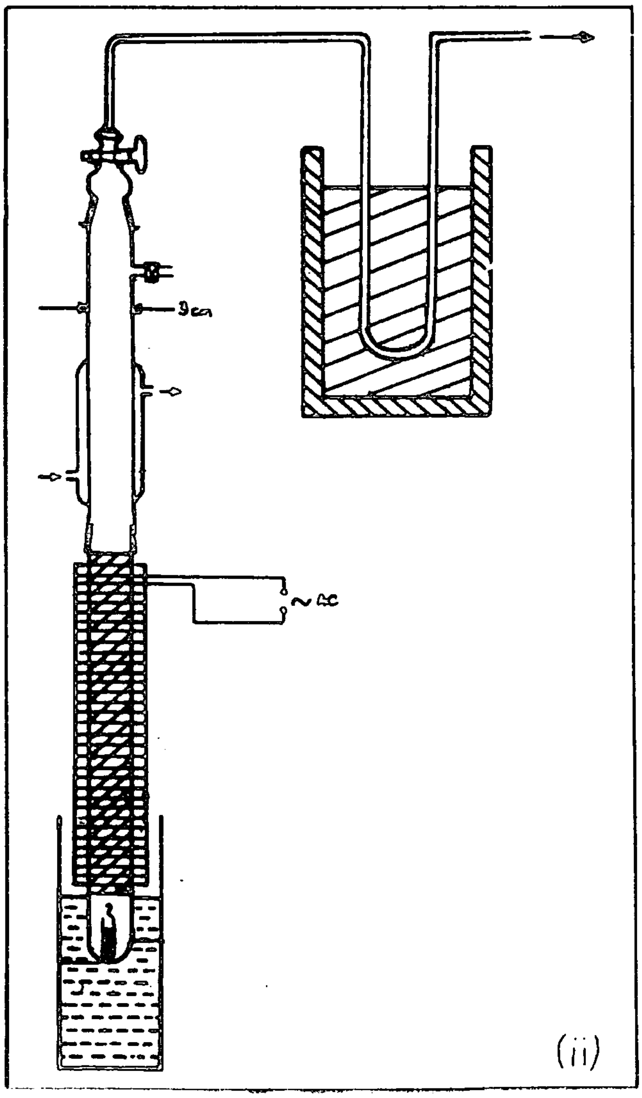


FIGURE 5.5

(i)Pyrolysis apparatus and idealised heat profile.
(ii)Modified apparatus.

by immersion in a silicone oil bath (G). The quartz wool support (E) (later replaced by glass wool for health safety reasons) was surrounded by an electric mantle (D). This was built (from an original design by Dr. Z.V. Hauptman) by winding nichrome wire onto a glass former and cementing this element concentrically inside a glass tube. The mantle had the following specifications:

Diameter of glass former	3.00 cm
Radius of former, r	1.50 cm
Length of former, L	24.00 cm
Surface area, $2\pi rL$	226.19 cm^2
Volume of heater, $\pi r^2 L$	169.65 cm^3
Circumference of former, $2\pi r$	9.43 cm
Spacing of loops	~ 2 mm
Length of nichrome wire[101]	11.03 m
Resistance of winding	282 Ω

Calibration graphs (Figure 5.6)show that the design had a temperature stability of ±1°C over the central 8 cm of the heater. Temperature was measured using a Cr/Al thermocouple with a Comark electronic thermometer (type 1602). A qualitative heat profile for the pyrolysis tube is shown in Figure 5.5. Using a Cenco hotplate and efficient stirring of the oil bath, a level temperature gradient with good thermal stability (± 1°C) was obtained.

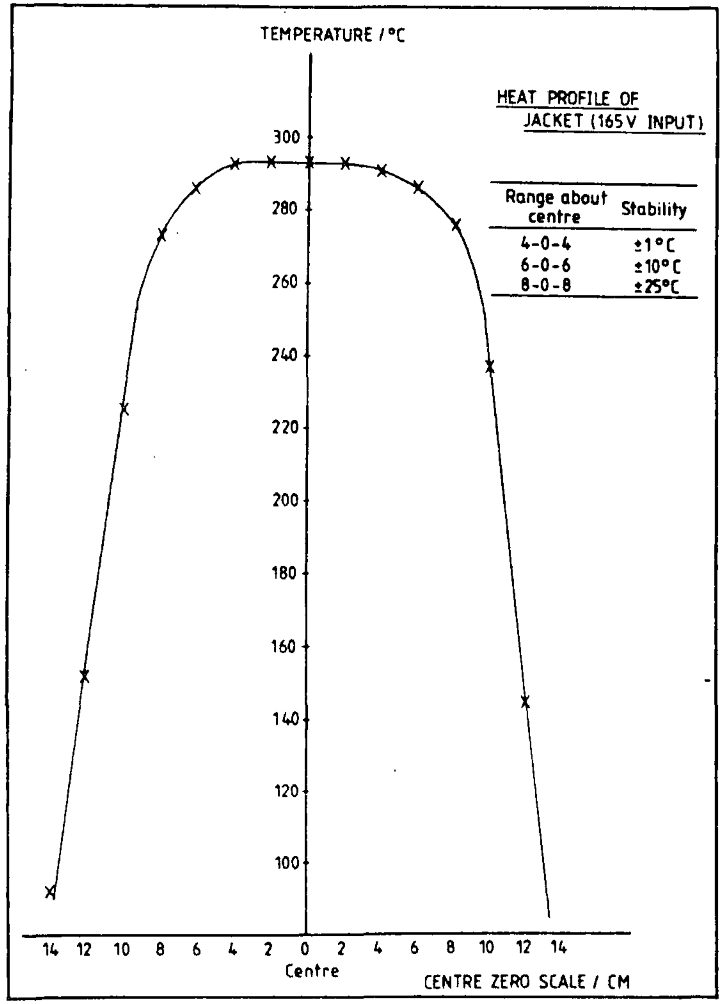
In the early experiments the cooling zone consisted of a hinged polystyrene box (C) containing solid carbon dioxide (-77°C). Modifications to this basic design are described in later sections.

In all experiments the glass apparatus was flame dried and cooled in a dry nitrogen atmosphere prior to use.

5.2.2 Vapour phase pyrolysis of S_4N_4

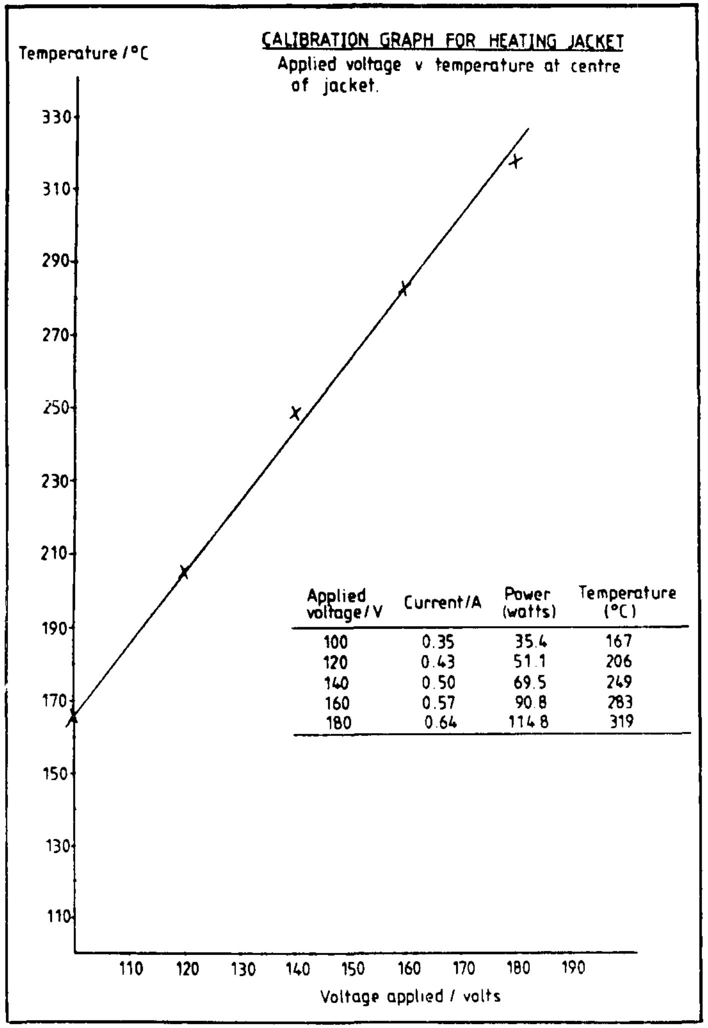
S_4N_4 (0.4g, 2.2 mmol) was placed at the bottom of the pyrolysis tube. The tube was packed with quartz wool (2.5g, fibre diameter 3-5μ) previously

FIGURE 5.6



HEAT PROFILE OF JACKET (165V INPUT)

Range about centre	Stability
4-0-4	±1°C
6-0-6	±10°C
8-0-8	±25°C



CALIBRATION GRAPH FOR HEATING JACKET

Applied voltage v temperature at centre of jacket.

Applied voltage/V	Current/A	Power (watts)	Temperature (°C)
100	0.35	35.4	167
120	0.43	51.1	206
140	0.50	69.5	249
160	0.57	90.8	283
180	0.64	114.8	319

dried in vacuo (350°C, 10 hours). The system was evacuated slowly to a pressure of 10^{-3} mm Hg, the quartz wool heated (220°C) and the polystyrene box filled with solid CO_2. Finally the oil bath was heated to a maximum of 90°C. After 8 hours a thin blue, streaky film had formed in the cold zone. Orange crystals of S_4N_4 condensed in the zone between the heaters and above the catalyst. About 70% of the starting material remained after this time.

The reaction was repeated with several modifications:

(i) The oil bath and electric mantle temperature were raised, to 100 and 250°C respectively, and the distance between the heat sources reduced.

(ii) The surface area of quartz wool was increased.

(iii) A glass rod (0.8 cm diameter x 15 cm) was suspended in the cooling zone and

(iv) The experiment was continued for 13 hours until most of the S_4N_4 had been vaporised.

Scrapings from zones A-D (Figure 5.7) gave the i.r. absorptions listed in Table 5.11.

5.2.3 Reaction between S_4N_3Cl and NaI

(i) Initial experiments

Apparatus and experimental techniques were described in section 5.2.2 with the following exceptions:

(a) S_4N_3Cl (1.0 g, 4.8 mmol) was pyrolysed at 130°C.

(b) The reactive surface (sodium iodide on glass fibre) was heated to 250°C. It was prepared as follows. Dried glass wool (24 hours, 350°C, 10^{-3}mm Hg) was saturated with a solution of dry sodium iodide (1.0 g, 6.67 mmol) in dry methanol (10 ml). The mixture was then evaporated to dryness leaving sodium iodide distributed evenly throughout.

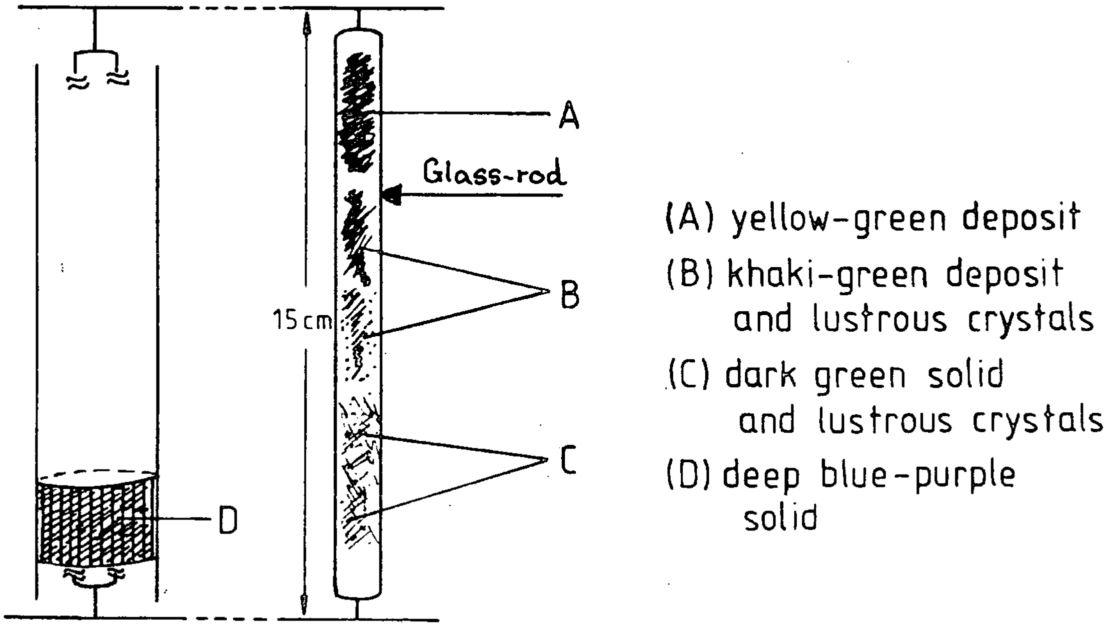
TABLE 5.11

INFRA-RED DATA ON SAMPLES A-D

A	B	C	D	Assignment
			3150 br	ν_{NH}
1400 w		1400 w	1400 m	δ_{NH}
		1225 m,br	1231 mw	$(SN)_x$
	1199 w		1199 mw	ν_{SO}
		1050 w	1045 w	$(SN)_x$
1000 w,br		1014 mw	1009 m	$(SN)_x$
929 w	924 w	927 m	925 s	S_4N_4
	885 mw		885 mw	
	765 w		765 w	
727 w	725 mw	727 mw	726 ms	S_4N_4
690 mw,br		699 ms	698 s	S_4N_4
	685 mw,br	685 sh	685 sh	$(SN)_x$
		665 sh		$(SN)_x$
610 w,br	610 w,br	610 mw	600 mw	$(SN)_x$ ν_{SO}
553 mw	550 w,br	550 ms	548 s	S_4N_4
		345 m	345 s	S_4N_4

FIGURE 5.7

Representation of apparatus after reaction (modified procedure)



The apparatus was evacuated and heated for 3½ hours. During this time a black solid with a metallic lustre formed in the cold zone. An orange-yellow product condensed in the region between the heaters, which gave i.r. absorptions (Nujol mull) at 1165 (w,br), 1000(w), $\underline{\text{928(s)}}$, 770(w,d), $\underline{\text{728(ms)}}$, $\underline{\text{699(s)}}$, 670(sh), 620(w), $\underline{\text{550(s)}}$, $\underline{\text{340(s)}}$, and was characteristic of an S_4N_4/S_4N_3Cl mixture (S_4N_4 absorptions underlined).

The black solid had i.r. absorptions (KI disc) at 3150(w), 1390(m), 1190(w), 1110(mw), 923(ms), 820(w,br), 705(ms,br), 610(ms), 563(m), 460(w,br), 384(m) cm^{-1}. Similar absorptions were obtained in experiments 2-5 below. Elemental analysis of the black product is reported in Table 5.12. It gave the following mass spectrum, $^m/_e$ (relative intensity %):

46(100)-SN^+; 48(2)-iSN^+,SO^+; 63(8)-$HNSO^+$; 64(35)-$S_2{}^+$,$SO_2{}^+$;
78(24)-S_2N^+; 92(83)-$S_2N_2{}^+$; 96(3)-$S_3{}^+$; 110(7)-S_3N^+; 124(5)-$S_3N_2{}^+$;
127(22)-I^+; 128(10)-HI^+,$S_4{}^+$; 138(58)-$S_3N_3{}^+$; 156(4)-$S_4N_2{}^+$;
160(5)-$S_5{}^+$; 184(8)-$S_4N_4{}^+$; 192(3)-$S_6{}^+$; 254(62)-$I_2{}^+$; 256(6)-$S_8{}^+$
(i = isotope).

The ratio of Cl^- to I^- detected in the quartz wool after the reaction was 1.4:1.0 and the amount of Cl^- (0.13 g) represented 75% of the total available from S_4N_3Cl.

In experiment 2, to avoid S_4N_4 and S_4N_3Cl condensing below the catalyst, the distance between the heat sources was reduced and the catalyst packing was loosened. A polythene disc (1.5 cm diameter) and a low temperature thermometer were suspended in the cold zone. The disc was degreased (in hexane) and had eight stainless steel pins arranged in a cross matrix in order to facilitate four-probe conductivity measurement of the deposited layer. Other experimental conditions were as in experiment 1. After 7 hours the S_4N_3Cl residue (ca. 5%) was brick-red. The temperature of the cold zone was -85°C; the black solid layer deposited was ca. 0.5 mm thick and had a bright metallic lustre. Scrapings of this material (1.5 g) smelled strongly of iodine and storage in sample bottles resulted in discolouration of the plastic tops.

TABLE 5.12

ANALYTICAL DATA FOR BLACK PRODUCT													
Experiment	1	2	3						CS_2 Washing	4			
Element			A1	A2	Av.	B1	B2	Av.					
N	12.10	11.63	15.90	15.27	15.59	11.00	11.10	11.05	13.82	11.10	11.00	13.20	12.60
S	36.10	40.50	49.90	49.90	49.90	34.47	33.10	33.78	37.27	41.50	41.50	38.30	43.30
I	47.30	46.27	34.02	35.00	34.51	55.10	56.30	55.70	29.60	41.00	47.20	48.60	42.30
TOTAL	95.50	98.40	99.82	100.17	100.00	100.57	100.50	100.53	80.69	93.60	99.70	100.10	98.20
Empirical Formula	$S_3N_{2.30}I$		$S_3N_{2.15}I_{0.53}$*			$S_3N_{2.25}I_{1.25}$*				$S_3N_2I_{0.80}$*			

* based on average

The coating on the suspended polythene disc was thin and uneven and the room temperature d.c. resistance was high (2-5 x 10^5 ohm measured with an Avometer). With a high voltage mega-tester a transient low resistance was observed (ca. 200Ω) which increased rapidly to 5 x $10^7\Omega$.

Table 5.13 compares mass spectra of the black materials obtained from this experiment (I) and from the solution reaction between S_3N_2Cl/NaI (Chapter 3, Table 3.7) (II).

Flakes of the black solid remained lustrous indefinitely when stored in a sample bottle, however, exposure to moist air caused hydrolysis (2-3 days) to a grey, powdery residue.

The back-scattered electron image photographs (Figure 5.8) are of a fresh fracture surface at several magnifications. One photograph was taken with an optical microscope (x 15).

X-ray powder diffraction data were difficult to obtain on the black material; even after 48 hours exposure to Fe $K_{\alpha 1}$, radiation, the diffraction lines were of very low intensity, with d-spacings (Å): 4.78, 4.57, 4.36, 3.92, 3.87, 3.28, 3.24, 3.16, 3.13, 3.06 and 3.01.

(ii) Modified apparatus (Experiments 3 and 4)

The hot and cold sections of the modified pyrolysis apparatus (Figure 5.5) were separated by a greaseless O-ring joint. A glass jacket with circulating coolant provided a variable temperature cold zone below the polystyrene box. In experiment 3, products were condensed at 10°C and -77°C. Each fraction (A and B respectively) was analysed (Table 5.12). ESCA data (Table 5.14) were obtained on the thin layer of product deposited on a glass slide (1.5 x 0.5 cm) suspended in the 10°C zone.

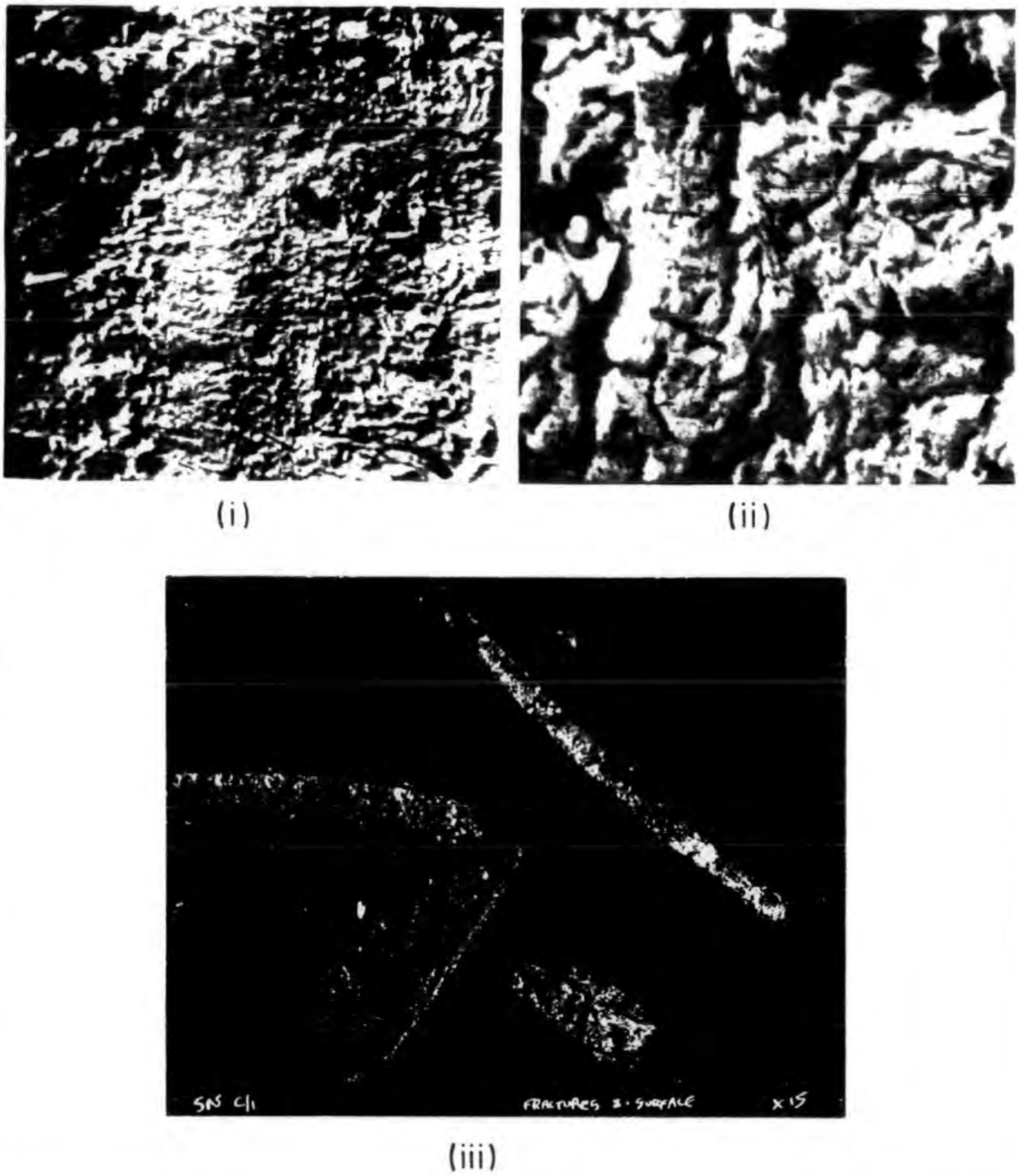
Extraction of the black material (-77°C fraction) with dry carbon disulphide produced a deep violet solution and even after several extractions the washings remained pale violet. After this treatment some flakes had a bronze-gold lustre and were deeply pitted. Elemental analysis (Table 5.12) confirmed a decrease in iodine content.

TABLE 5.13

m/e	Fragment	Relative Intensity (%)	
		I	II
46	SN^+	100	100
48	SO^+, iSN^+	91	9
63	$HNSO^+$	35	6
64	S_2^+, SO_2^+	233	111
78	S_2N^+	16	36
92	$S_2N_2^+$	99	93
96	S_3^+	13	13
110	S_3N^+	3	6
124	$S_3N_2^+$	3	3
127	I^+	12	-
128	HI^+, S_4^+	29	31
138	$S_3N_3^+$	33	109
156	$S_4N_2^+$	1	3
160	S_5^+	20	28
184	$S_4N_4^+$	9	21
192	S_6^+	9	11
254	I_2^+	25	9
256	S_8^+	19	39

TABLE 5.14

Compound	B.E(ev)/(Relative Intensity)							
	$I(3d)_{3/2}$			N(1s)			$S(2p)_{av}$	
Black Solid	631.0 (41)	632.8 (14)		398.8 (55)	400.3 (22)	401.8 (10)	164.0 (73)	166.1 (22)
$Ph_2I^+PF_6^-$			635.2					
$Ph_2I^+ I^-$	631.4	632.2	635.1					
$NH_4 I$	631.3					401.9		



(i) (ii)

(iii)

Figure 5.8. Back-scattered electron images (i) x 175, (ii) x 500 and optical photograph, (iii) x 15 of freshly fractured surface.

In experiment 4 a Fisons Haake-F2C bath circulator (with methanol coolant) was used to condense a product at -15°C. Other modifications included reducing the glass wool column to 10 cm in length (with only the central 6 cm impregnated with sodium iodide) and reducing the temperature of the zone to 220°C. The yield of black product was 0.7 g (from 1.0 g S_4N_3Cl) and four scrapings were analysed (Table 5.12).

(iii) Effect of heat on the black material (Experiment 5)

A flame-dried Pyrex tube (16 x 1.2 cm O.D) containing black material (80.3 mg) was evacuated to 10^{-6} mm Hg (2 hours, 23°C). The iodine which condensed under these conditions was quantitatively determined using 0.02 M sodium thiosulphate. In this way, 0.6 mg (2.4 μmol) was detected.

The tube was then sealed at 10^{-6} mm Hg. After 48 hours some evolution of nitrogen had occurred (deduced from a change of discharge colour, pale yellow to violet). Heating the tube at 50°C (12 hours) caused a bronze-brown thin layer, several crystals of iodine and some S_4N_4 to condense at the cold end. The brown-black residue (31.3 mg, 39%) gave a complex X-ray diffraction pattern: d-spacing/Å (relative intensity %): 6.34(35), 6.08(25), 5.78(20), 4.75(100), 4.64(95), 4.40(45), 4.35(40), 4.07(30), 3.94(25), 3.89(20), 3.86(90), 3.73(50), 3.60(15), 3.57(15), 3.50(25), 3.45(75), 3.40(45), 3.35(60), 3.23(70), 3.17(40), 3.13(65), 3.10(45), 3.06(15), 3.03(20), 3.00(15), 2.90(30), 2.86, 2.82, 2.79, 2.77, 2.75, 2.70(50), 2.67, 2.63, 2.60, 2.43, 2.37, 2.32, 2.29, 2.25, 2.21, 2.18(15-20), 2.15, 2.12, 2.10, 2.02, 1.96, 1.95 (Assignments, ____ S_4N_4, cf Chapter 1, page 6; _ _ _ S_8). The heat treated residue gave i.r. absorptions (KBr disc) at 1390(mw), 1190(m), 1110(s), 928(s), 725(w), 699(s), 620(w), 550(ms), 350(mw) cm^{-1} (S_4N_4 absorptions underlined) and the following mass spectrum, $^m/e$ (relative intensity %): 46(100)- SN^+; 48(36)-iSN^+,SO^+; 63(9)-$HNSO^+$; 64(100)-S_2^+; 78(79)-S_2N^+; 92(100)-$S_2N_2^+$; 96(81)-S_3^+; 110(18)-S_3N^+; 124(18)-$S_3N_2^+$; 127(11)-I^+; 128(100)S_4^+,HI^+; 138(100)-$S_3N_3^+$; 156(19)-$S_4N_2^+$; 160(100)-S_5^+; 184(55)-$S_4N_4^+$; 192(38)-S_6^+; 224(5)-S_7^+; 254(28)-I_2^+; 256(98)-S_8^+ (underlined fragments were of decreased intensity compared to the corresponding ones in Table 5.13 (I). The remainder were increased).

A pressed pellet (6 x 4 mm diam) of the untreated material was cemented with conducting silver paste between copper wires (20 swg). Its resistance, measured with an Avometer was 10-100Ω. After 2-3 days its resistance increased to 200 MΩ. A similar, unmounted pellet exhibited some conductivity (ca. 1 KΩ) even after a year. Pressed pellets of the heat treated residue showed low conductivity (resistance 1-2 MΩ).

5.2.4 Vapour phase pyrolysis of $S_5N_5FeCl_4$

Research by Dr. Z.V. Hauptman concurrent with that described in the previous section, showed that $(SN)_x$ formed when S_4N_3Cl vapour was passed through a hot silver catalyst[102]. It was similarly formed from $S_5N_5FeCl_4$[103,104]. Whilst investigating the latter system, results were obtained which provided an insight into the mechanism of the pyrolysis. Experimental details are summarised in Table 5.15 where reference is made to Figure 5.9 (apparatus design) and the notes below.

(1) Catalyst

The silver wire (B.D.H. 99.9%, 50 μm diameter) was coiled into plugs (7 mm diameter), degreased and washed (in hexane and concentrated ammonia) and dried in vacuo. In experiments 3, 4, 7, 8, 9 and 10 these plugs were flattened before use (3-4 mm thick). In experiment 8 the catalyst was powdered silver sulphide on zirconia fibre (1-2 mm) and in experiments 9 and 10 a mixture of silver and silver sulphide.

(2) Substrate Preparation

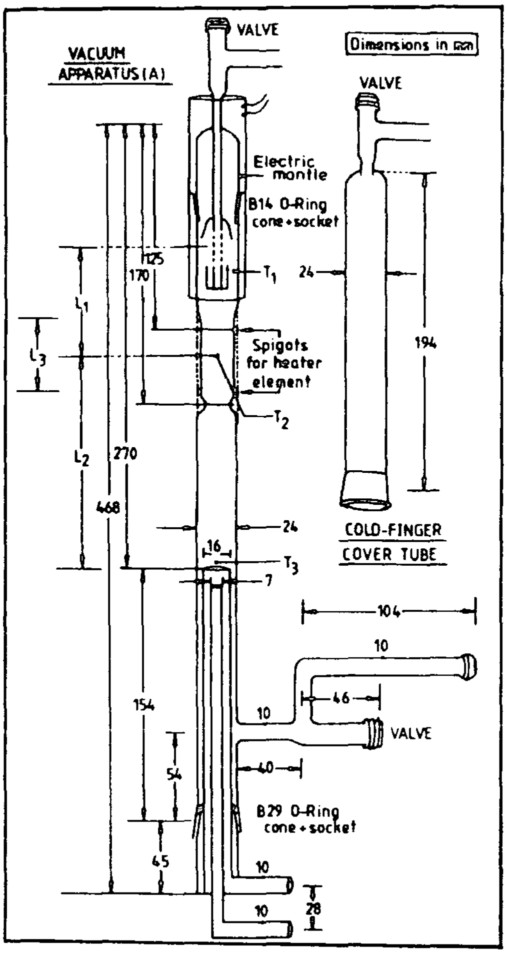
Zinc sulphide and selenide crystals supplied by Dr. Alan Thomas (Dept. of Applied Physics, Durham) were polished, etched (in bromine) and mounted in indium foil.

Glass and gold fragments were treated with hot chromic acid and the ruby crystal (3% Cr_2O_3 - basal plane 0001) washed with ethanol/caustic potassia solution. They were then rinsed with distilled water and oven dried.

TABLE 5.15

EXPT	APPARATUS	EXPERIMENTAL CONDITIONS													RESULTS	COMMENTS
		L_1	L_2	L_3	T_1	T_2	T_3	P	W_s	W_c*1	ΔW_c	t_1	t_2	Substrate*2		
1	A	6.5	11.5	1.5	120	200	25	10^{-4}	0.17	0.20	0.01	4	6	ZnSe, Ruby and glass chips	Ag blackened, ZnSe untouched Ruby and glass had slight blue film. $S_5N_5FeCl_4$ partially melted.	Ag : $S_5N_5^+$ ratio too high. Residue ir analysed.*3 Heat profile too steep near $S_5N_5FeCl_4$.
2	A modified	6.5	11.5	1.5	120	200	30	10^{-3}	0.26	0.13	-	2	24	Glass, ruby and ZnSe	Faint blue coatings on substrates. Nodules on catalyst - EPMA*4 PTFE sleeve partially coated.	Bad thermal contact of substrates with cold-finger. Apparatus too complex.
3	B	13	5	0.2	140	230	10	10^{-3}	0.41	0.38	-	6	17	-	0 - 6h Ag blackened 6 - 12h Blue gold film on cold-finger 12 - 17h Gold dulled and Xtals deposited.	Good yield $(SN)_x$, some S_4N_4. Microscope examⁿ and colour photographs. *5
4	B modified	13	2	0.5	120	210	5	2×10^{-3}	0.49	0.49	-	-	12	Gold*6, ZnS	Better thermal contact*7 good deposition on substrates. Some S_4N_4 formed after 10 hours.	Catalyst problems (section 5.3.4). EPMA*6 on gold.
5	B modified	13	2	1.2	120	210	15	10^{-3}	0.49	0.47	-	8	16	Gold, ZnS	$S_5N_5FeCl_4$ used as fine powder but rate of vaporisation too rapid.	Substrates poorly coated. S_4N_4 formed
6	C	11	4	0.7	130	240	15	10^{-3}	0.98	0.50	-	2	10	Gold	Vaporisation started at 80°C instead of RT. Blue-black coating and S_4N_4 crystals.	Brittle coatings on gold chipped off. Cold-finger annealed by heating*8 Substrate hard to remove intact from cement.
7	D	15	2	1.3	130	230	25	10^{-3}	0.23	0.25	-	-	12	Glass	No $(SN)_x$ only S_4N_4 crystals	
8	C	11	4	0.7	140	250	10	10^{-3}	0.47	Ag_2S 0.43	-	-	8	Glass	No $(SN)_x$ only S_4N_4 crystals on niobium	Interference colours due to attack on niobium surface.
9	D	15	2	0.3	135	250	10	10^{-3}	0.42	Ag_2S (0.26) 0.17	-	4	20	Glass	Blue film and S_4N_4 crystals	Substrates uncoated
10	C	10	3	0.2	135	250	25	5×10^{-3}	1.05	0.17 on Ag_2S (0.28)	-	3	18	Glass	Thin blue film and S_4N_4	

* see notes in text



L_1, L_2, L_3 = Apparatus geometry / cm
T_1 = Temp. of vaporisation / °C
T_2 = Temp. of catalyst zone / °C
T_3 = Temp. of cold-finger / °C
P = Pressure / mm Hg
W_S = Wt. of starting material / g
W_C = Wt. of catalyst / g
ΔW_C = Wt. inc. of catalyst / g
t_1 = Time to onset of blue film / Hr
t_2 = Time to completion / Hr

VARIABLES LISTED IN TABLE 5.15

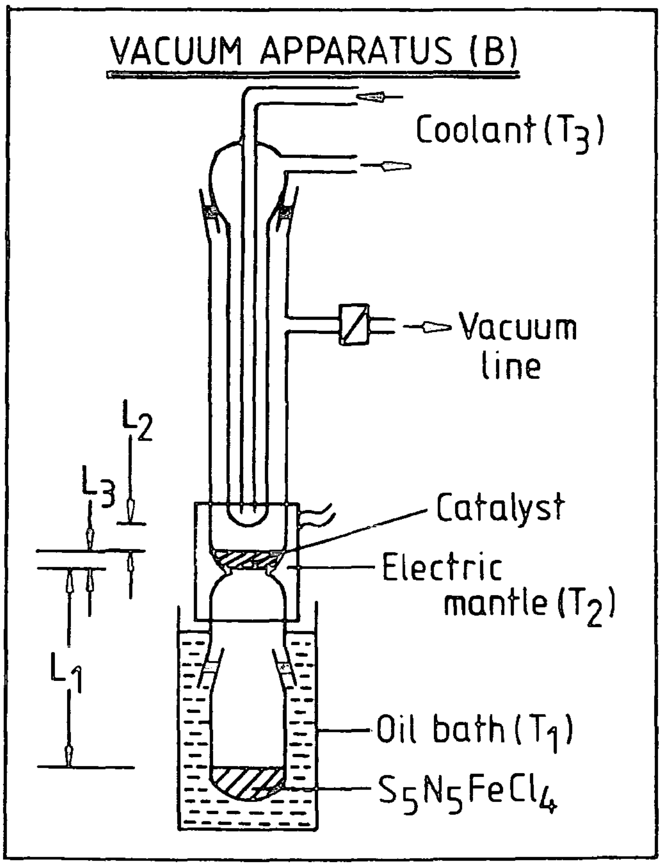


FIGURE 5.9

Pyrolysis apparatus designs

FIGURE 5.9 (cont'd)

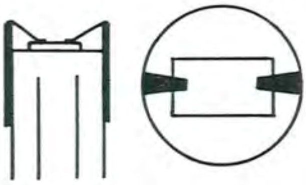
SUBSTRATE ATTACHMENT

In apparatus A the substrates were held on the coldfinger with an organic resin. In the modified apparatus, a PTFE sleeve was fitted to the coldfinger in order to concentrate volatiles above the coating surface (i).

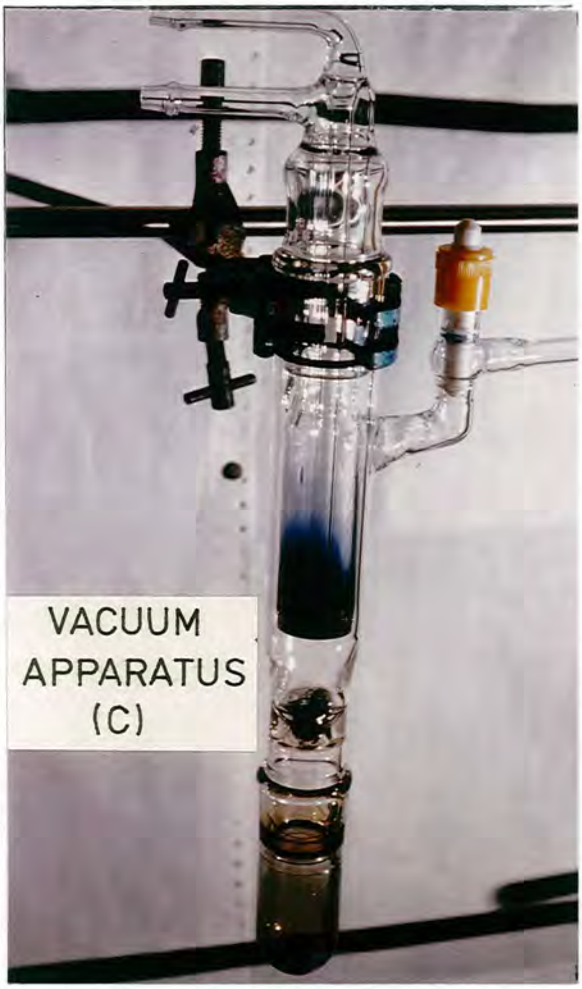
Apparatus B (modified) had a Pyrex disc (25 mm diam. x 2 mm) welded to the end of the coldfinger, to which substrates were cemented using a silver colloid paste (ii). In experiments 7 and 8 (apparatus C and D) a niobium sheath with spring clips was constructed to hold the substrates in place (iii).

(i)

(ii)

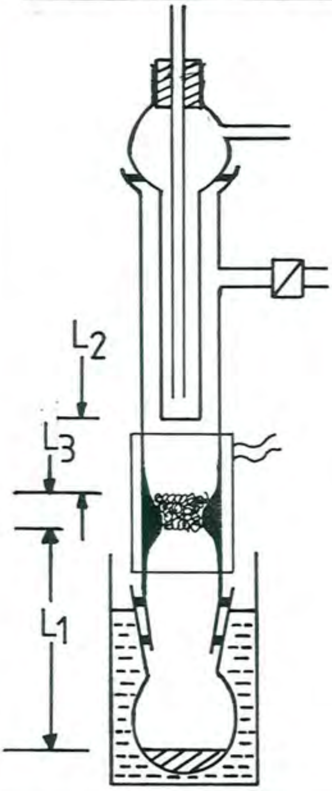


(iii)



VACUUM APPARATUS (C)

VACUUM APPARATUS (D)



(3) Infra-red spectrum of residue

After pyrolysis, the yellow-brown residue (typically 50-70% of the original bulk of $[S_5N_5][FeCl_4]$) had i.r. absorptions at 1168(vs), 1132(s), 1025(vs), 699(vs), 565(vs), 476(vs), 364(s) cm^{-1}, *cf*. $S_4N_3FeCl_4$[105].

(4) EPMA - back scattered electron images

The reacted silver wool was examined with an optical microscope (x 20). The fibres were covered with a grey-black material which formed, in places, nodule-like growths suggestive of partial melting. A cluster of fibres was embedded in resin (Araldite), sectioned to reveal some nodules, metallographically polished and examined with the light-optical system of an electron probe microanalyser (Geoscan Instruments, Cambridge). All the cross-sectioned fibres showed clearly an unaltered silver core separated from the reacted layers by a sharp but rugged boundary. In Figure 5.10, the back-scattered electron image (i) and concentration profiles of four elements (ii) revealed extensive inhomogeneity of the reacted zone.

(5) Microscopic examination

The colour photographs (Figure 5.11) depict the coldfinger after experiment 3 (Magnification x 9.3). They were taken on Pan F (50 ASA) slide film with an Exacta camera and No.1 and 2 extension tubes. Relief lighting from a 16W focussed beam tungsten lamp and 60 W anglepoise gave exposure times of *ca*. 45 seconds at full aperture.

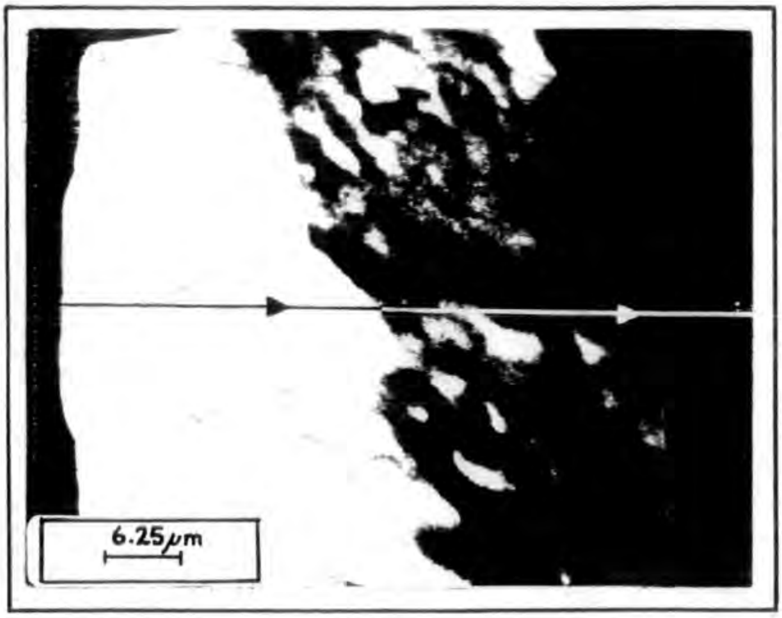
They show that the coldfinger was covered with a hard, purple-blue thin film (0.2-0.3 mm) and a compact layer of golden microcrystals. Some crystals were 2-3 mm long and had longitudinal striations. Material scraped from the coldfinger showed strong absorptions at 928, 725, 698 and 550 cm^{-1}, plus a few weak, broad ones at 1025 and 620 cm^{-1}.

The larger crystals were spongy and did not mull in Nujol.

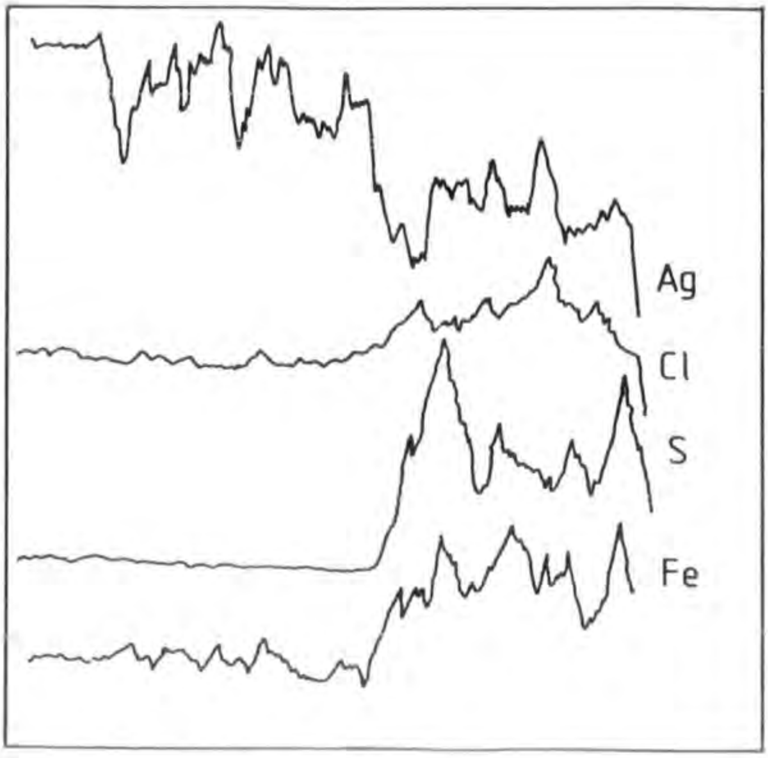
(6) EPMA on gold substrate

The gold substrate from experiment 4 was embedded in a perspex disc (3 cm diam.) and examined by EPMA technique (instrumentation as described

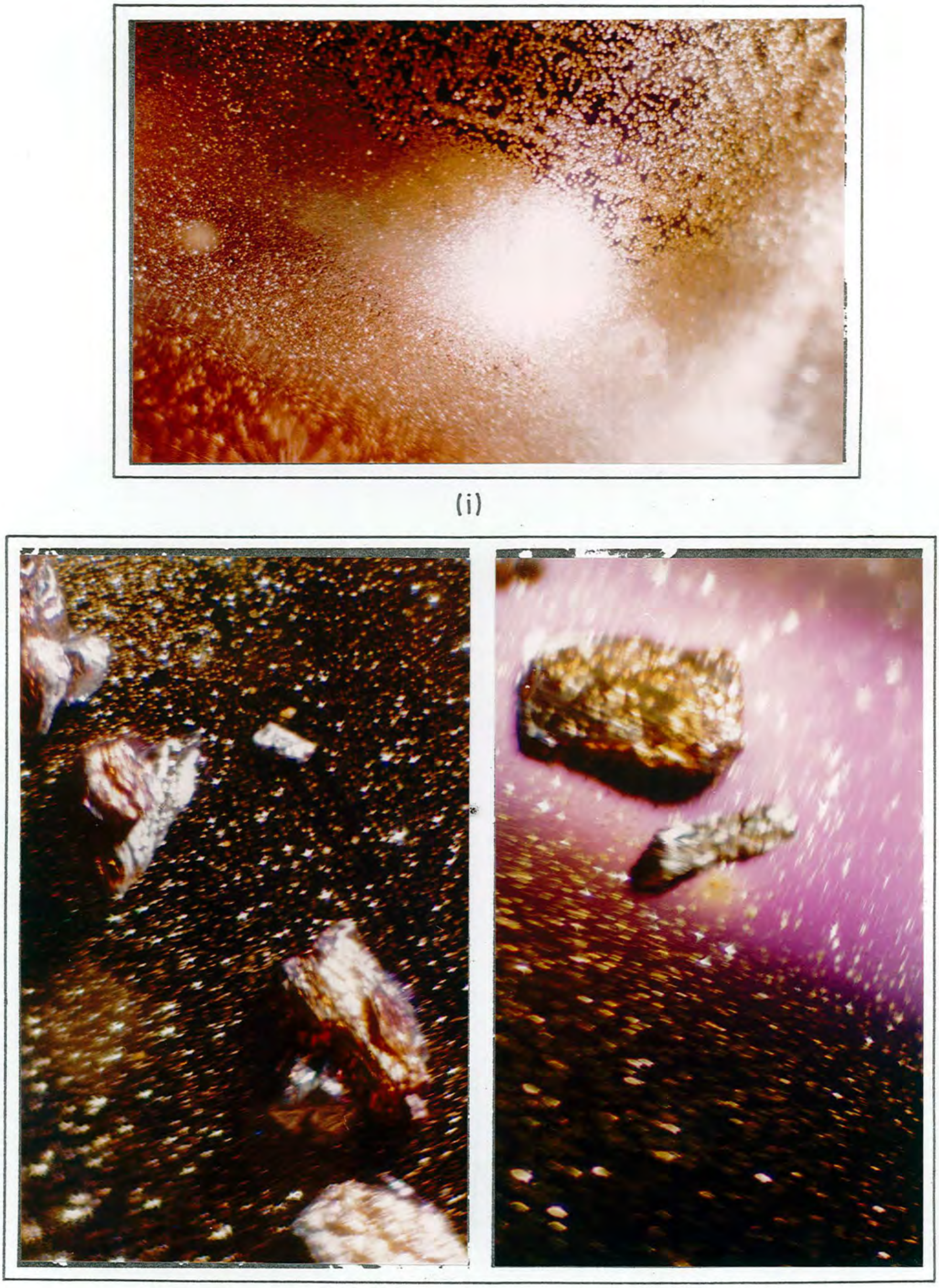
FIGURE 5.10 Back-scattered electron images



(i)



(ii)

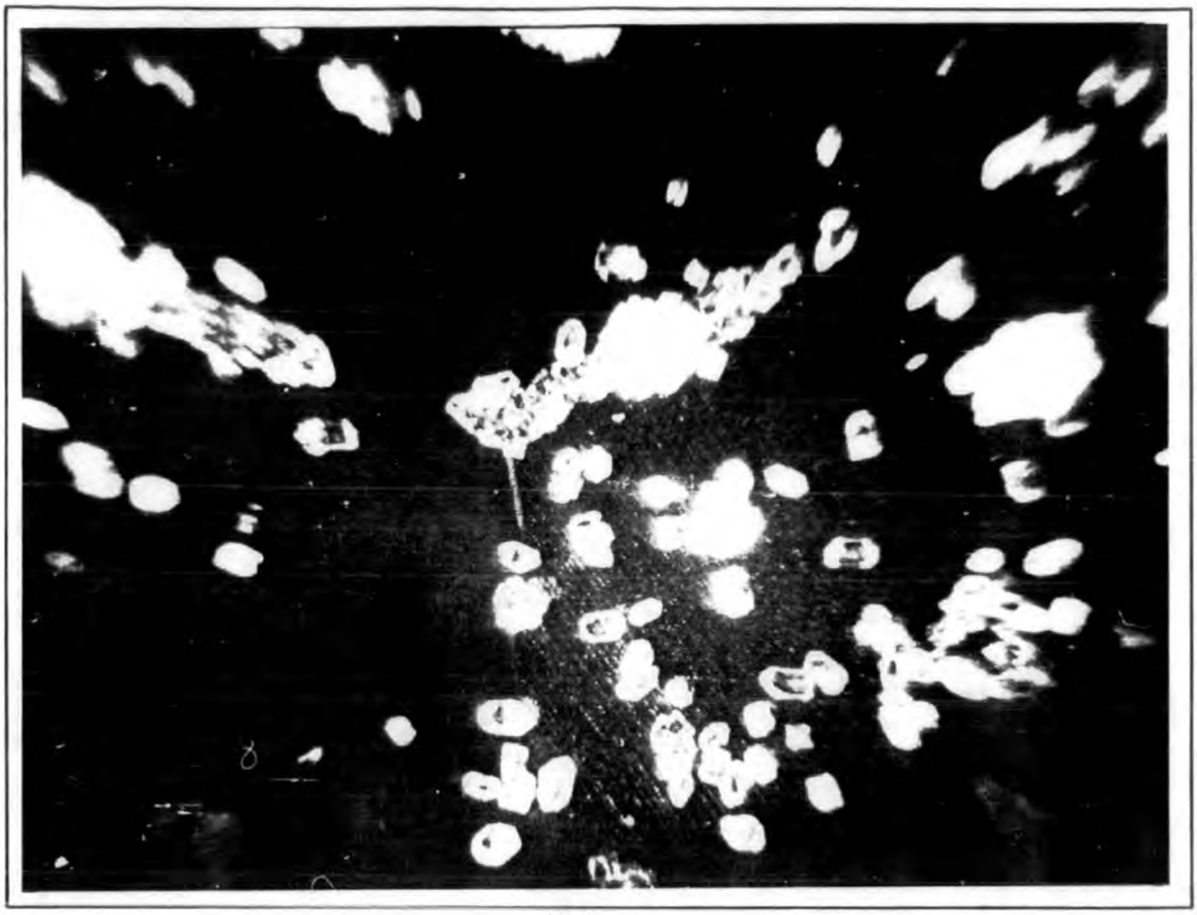


(i)

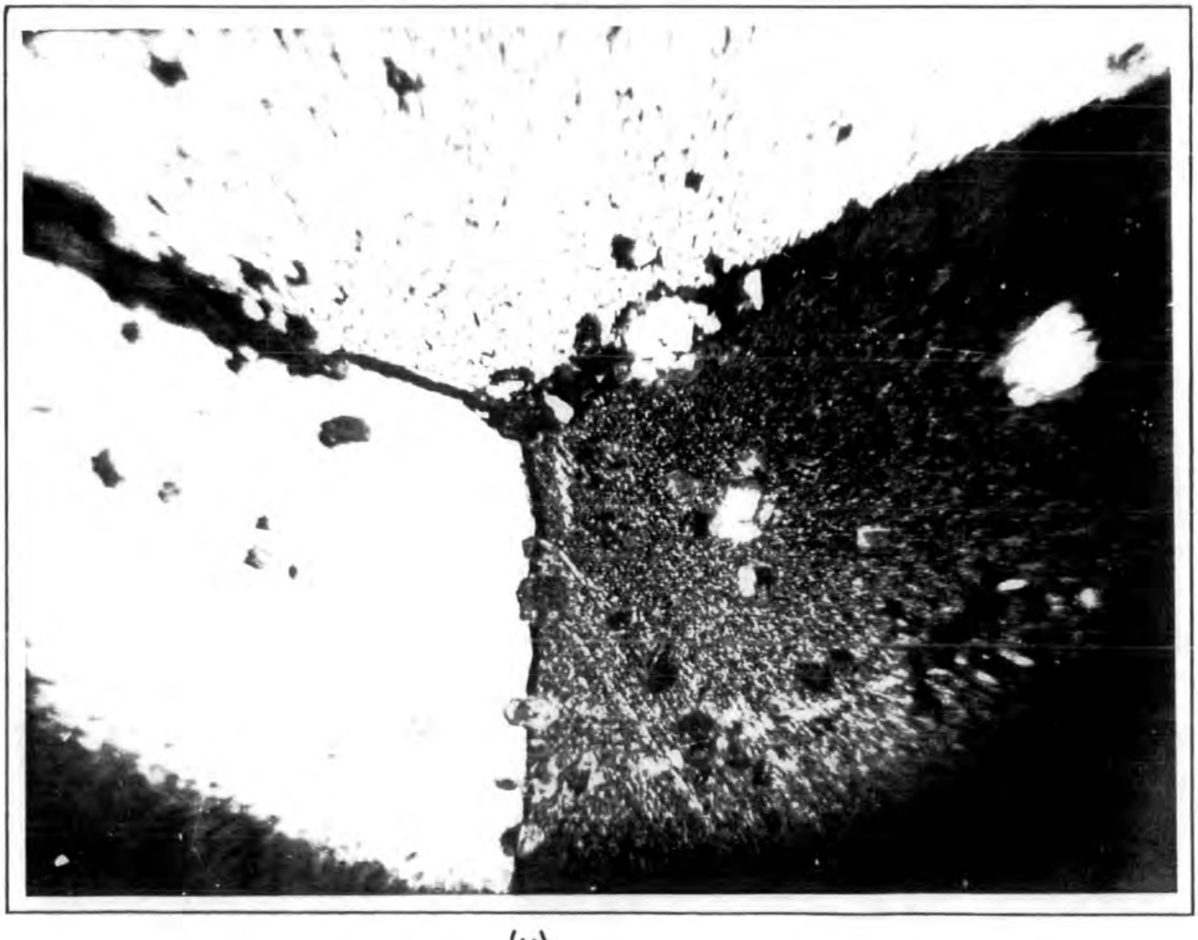
(ii)

(iii)

FIGURE 5.11 (i – iii) Colour photographs of cold-finger after experiment 3 (see note 5)



(iv)



(v)

FIGURE 5.11 (cont'd) Microscope pictures of ZnS substrate under normal illumination (v) and between crossed polars (iv).

above). The gold had a thin but fairly even blue-gold coating and a deposit of lustrous micro-crystals. Results showed that the thin layer contained sulphur and chlorine in the weight ratio (based on counts) 25:7 and that it contained 1% iron. The microcrystals contained sulphur but no iron or chlorine.

(7) Attachment of substrates to coldfinger

A major problem was encountered in attempts to deposit thin films of the vapour species on substrates attached to the coldfinger, since volatiles preferentially condense on the coldest surface and the substrates would typically be several degrees warmer than the coldfinger. It was necessary therefore to obtain the best possible thermal contact between substrate and coldfinger and various methods were tried (Figure 5.9). The setup of experiment 4 (using silver cement) was most successful, however it was important to use the cement sparingly when mounting substrates because the thin coatings were extremely brittle and easily chipped off (Table 5.15, experiment 6).

The black and white photographs (Figure 5.11) depict a microscopic examination (x 10) of a zinc sulphide crystal coated in experiment 4. The surface has three large grains meeting essentially at the centre of the die. Deposition of S_4N_4 crystals in the latter stages of the reaction was observed in experiment 3 (Table 5.15) and is believed to be due to poisoning of the catalyst (see section 5.3.4). This phenomenon is also noticeable in the photographs (particularly the one taken between crossed polars) where deposition is heaviest on one grain and on the grain boundaries.

(8) Annealing the thin layer

In experiment 6 an attempt was made to sublime the S_4N_4 deposits from the coldfinger and substrates, thus improving the quality of the polythiazyl thin film. After 12 hours (at $40^oC/10^{-3}$ mm Hg) most of the microcrystalline growth had been removed and the substrate had an increased golden lustre.

5.2.5 Pentathiazyl chloride, S_5N_5Cl

(i) Preparation of S_5N_5Cl

$(NSCl)_3$ (0.7 g, 2.86 mmol) was ground to a fine powder in a dry box and placed in a Schlenk tube. S_4N_4 (1.39 g, 7.57 mmol) was ground (in small portions on an open bench), intimately mixed with the $(NSCl)_3$ and heated, under nitrogen, at 75°C for ½ hour. The dark red melt was allowed to cool and the solid pulverised and washed with dry benzene until the extracts were colourless. The red-orange crude product (1.5 g) had i.r. absorptions (Nujol mull) at 3150(w,br), 1405(mw,br), 1120(s), 622(ms) and at 1169(w,br), 1155(m,br), 1067(ms), 1042(s), 1000(vw), 962(ms), 941(ms), 722(w), 668(s), 546(vs), 465(ms), 415(vs) and 348(s) cm^{-1}.

(ii) Attempted recrystallisations of S_5N_5Cl

Formic Acid Crude S_5N_5Cl (1.2 g) was dissolved in warm formic acid (20 ml, 99%). The orange solution formed was filtered and evaporated to low volume, however no crystallisation occurred. On further evaporation to dryness, the residue turned black. Analysis found C, 1.36; Cl, 15.10; N, 24.64; S, 44.80; H, 2.75. S_4N_4 and some hydrolysis product were detected in the i.r. spectrum. Soxhlet extraction of the black residue (0.3 g) with benzene (100 ml) gave a grey-black residue (characterised as $(NH_4)_2SO_4$) and an orange solution from which S_4N_4 was recovered (0.13 g). Similar results were obtained when vacuum distilled formic acid (dried over boric oxide for 3-4 weeks) was used.

Thionyl chloride (12.5 g) was vacuum distilled onto crude S_5N_5Cl (0.9 g). The solution became red-orange when warmed to 50°C. Filtration isolated a pale yellow-orange solid with i.r. absorptions (cm^{-1}) at 1164(ms), 1000(s), 685(m), 568(m), 471(ms), 455(m)-(S_4N_3Cl) at 1070(w,br), 1045(w,br), 965(w), 945(w), 668(m), 540(s)-(S_5N_5Cl) and at 3100(w,br), 1402(m), 1120(w,br), 620(w,br)-(hydrolysis product). S_4N_4 was isolated by evaporating the filtrate to dryness.

S_4N_4 was also the major product from nitromethane and phosphoryl chloride solutions in attempted recrystallisations from these solvents.

Acetonitrile A sample of crude S_5N_5Cl (0.5 g) was Soxhlet extracted with acetonitrile (80 ml). After 3 hours the insoluble residue was shown to contain S_4N_3Cl and $(NH_4)_2SO_4$ and S_4N_4 was recovered from solution (0.16 g).

Sulphur dioxide Liquid SO_2 (16.8 g) was condensed onto crude S_5N_5Cl (2.09 g) in an SO_2-reaction vessel[106]. The mixture was filtered at room temperature, then the SO_2 returned to dissolve more S_5N_5Cl from the mixture. This procedure was repeated twice and the SO_2 pumped away to give a bright red solid. This solid ignited explosively and burnt with a blue flame when the vessel was opened with a hot glass-cutter in a N_2-filled glove box. Analysis found Cl, 12.5; N, 25.9; S, 60.1. S_5N_5Cl required Cl, 13.4; N, 26.3; S, 60.3. I.r. absorptions (KBr disc) characterised the solid as a mixture of S_4N_3Cl, S_4N_4 and S_5N_5Cl (Table 5.16). Essentially the same absorptions (though with different relative intensities) were recorded for a KCl disc.

(iii) Pyrolysis of crude S_5N_5Cl

The apparatus was as described in section 5.2.4 (Apparatus C) with the following conditions (Figure 5.9): $L_1 = 11.0$; $L_2 = 4.0$; $T_1 = 100$; $T_2 = 230$; $T_3 = 10$; $P = 10^{-3}$; $W_s = 0.05$; $W_c = 1.18$. Sulphided silver wool was used as the catalyst. After 4 hours the entire coldfinger was coated with a magenta thin film (which intensified towards the bottom). A thicker brown-green solid condensed over the bottom 5-8 mm. Unfortunately on cooling the apparatus overnight, an O-ring joint (J. Young scientific apparatus) shattered, causing hydrolysis of the magenta compound. From its i.r. spectrum, the brown-green solid appeared to be largely S_4N_4. A broad, weak band at 1015 cm^{-1} may have been due to polythiazyl. The S_5N_5Cl was almost completely vaporised - the residue (ca. 10% by volume) was sticky and would not mull in Nujol.

In a later experiment the effect of passing S_5N_5Cl vapour through heated silver wool ($200^{\circ}C/10^{-6}$ torr)(in apparatus similar to that described by Dr. Z. V. Hauptman[102]) was investigated. With T_1 = room temperature, a blue thin film formed at a constriction in the tube, however no thickening of the layer occurred when T_1 was raised to $45^{\circ}C$. Instead a yellow solid

TABLE 5.16

Peak	Assignment	Intensity (cm)		Ratio (I:II)	
		KCl	KBr	KCl	KBr
I) 1164	S_4N_3Cl (X)	1.20	1.65	0.50	0.53
II) 1000		2.39	3.11		
I) 1042	S_5N_5Cl (Y)	2.33	2.09	1.44	1.38
II) 960		1.62	1.52		
I) 699	S_4N_4 (Z)	4.82	4.32	0.97	0.96
II) 345		4.99	4.51		
X(I): Y(I): Z(I)		1.0:1.9:4.0	1.0:1.3:2.6		

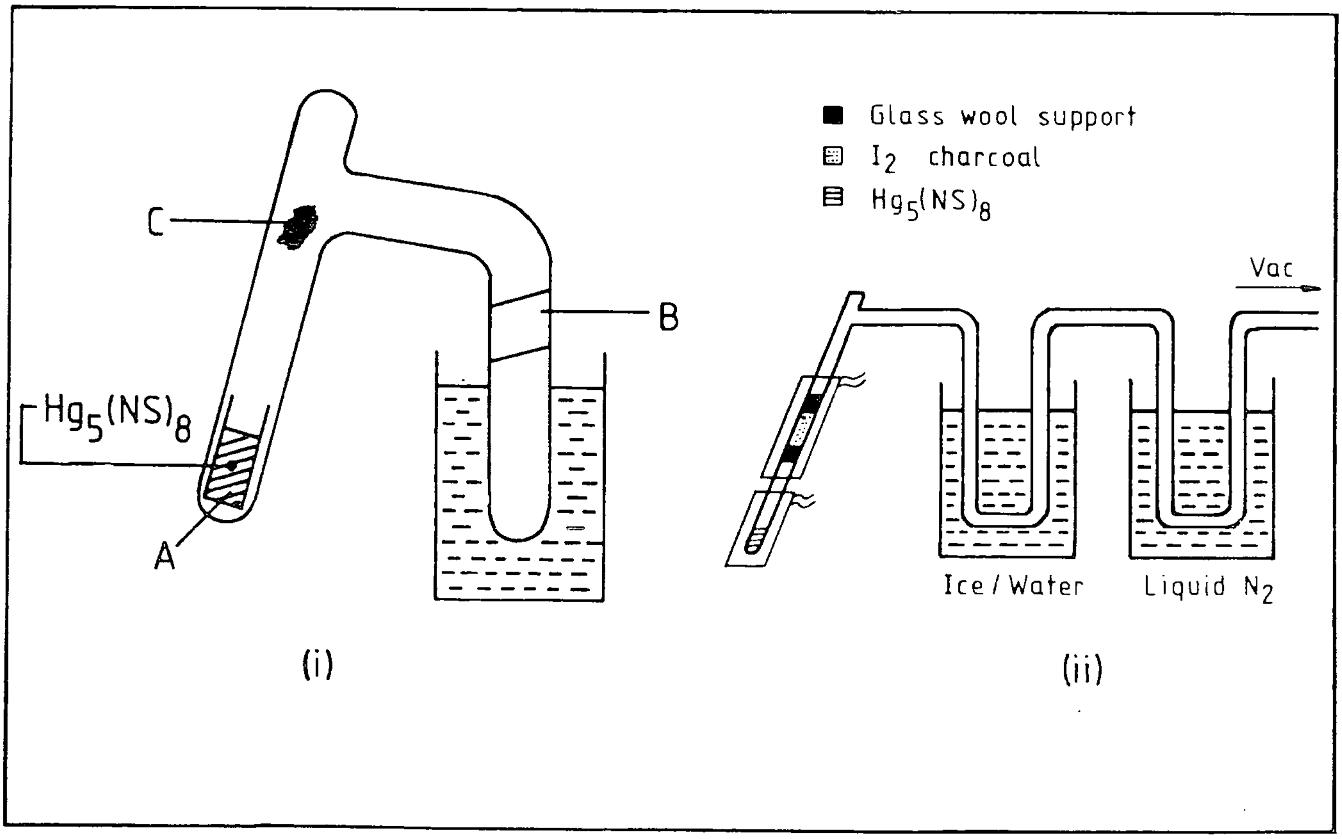


FIGURE 5.12. (i) Pyrolysis tube after 5 hours, (ii) Modified apparatus

(identified as S_4N_4) condensed and the pressure increased to 10^{-5} torr. A further pressure increase (to 10^{-4} torr) occurred at $T_1 = 60^{o}C$. After 3 hours the pressure returned to 2×10^{-6} torr. A thin, yellow-white band of volatiles trapped at -196°C was thought to be $(NSCl)_3$.

5.2.6 Pyrolysis of mercury thionitrosyl, $Hg_5(NS)_8$

The apparatus consisted of glass tubing (12 mm O.D) as shown in Figure 5.12 with one limb containing $Hg_5(NS)_8$ (114.5 mg).

The tube was sealed at 10^{-2} mm Hg and the compound heated to 120°C using the electric mantle described in section 5.2.1. The other limb was immersed in liquid nitrogen. At 70°C, a thin orange film condensed in the cold zone, and at temperatures above 90°C mercury vapour was produced(C). Heating was continued at 70°C for 5 hours. When the golden-orange film (B) was heated gently it changed to a blue-green colour. No i.r. data were obtained on this material because of its low concentration. The green-black residue (A) gave infra-red absorptions at 1051, 921, 683, 604, and 437 cm^{-1} (cf. $Hg_5(NS)_8$, Chapter 2, page 33).

In a repeat experiment, a mercury scavenger, iodine charcoal[107] was incorporated into a modified form of the apparatus (Figure 5.12(ii)). Two electric mantles were used to heat (i) the mercury thionitrosyl at 50-90°C and (ii) the iodine charcoal at 180-200°C. There were two cold traps (0°C and -196°C). The experiment was run for 6 hours at 5×10^{-2} mm Hg. As before the mercury thionitrosyl darkened and deposition of an orange substance (plus silvery-grey bands of mercury) occurred in the first trap. Some iodine (and mercury) condensed in the second trap. An i.r. spectrum of the thionitrosyl residue was similar to that quoted above. A sample of ground iodine charcoal gave a blank spectrum in the region 1050-450 cm^{-1}. There was some fine structure in the region 450-250 cm^{-1} with peaks at 435(sh), 420(br) 390, 379, 360(br), 345, 339, 330(ms), 319, 308(ms), 292(ms), 285(ms) and 270(m) cm^{-1} (unidentified). Analysis found (thionitrosyl residue); Hg, 78.7; N, 0.8; S, 13.3; and (iodine charcoal); Hg, 3.60; N, 0.00; S, 0.00. The orange thin film faded to pale brown after 10-12 hours.

5.2.7 Other thionitrosyls

(i) $Ag_5S_4N_4$ Silver metal (637.7 mg) was refluxed in a solution of S_4N_4 (148.7 mg) in CCl_4 (50 ml) for 12 hours. The mixture was left to stand for 3-4 weeks, but no attack on the silver surface was apparent.

(ii) $Cu_7S_4N_4$ Strips of copper metal (742.1 mg) were similarly treated with a solution of S_4N_4 (203.3 mg) in CCl_4 (50 ml). After 48 hours the metal surface had blackened and a fine black precipitate formed. Analysis found: Cu, 65.9 ; N, 5.4; S, 7.5 (78.8%). $Cu_7S_4N_4$ required Cu, 70.53; N, 8.96; S, 20.51 (100.0%).

In a final attempt to produce the copper thionitrosyl, copper powder (1.84 g, 28.9 mmol) was refluxed for 2 hours with S_4N_4 (0.78 g, 4.2 mmol) in CCl_4 (100 ml). The solution was filtered at room temperature and the solid extracted with CH_2Cl_2 (120 ml) to remove any solid S_4N_4. The insoluble, fine black powder (1.88 g) was pumped dry. Analysis found: Cu, 87.5; S, 5.3; N, 2.6 (95.4%). The CCl_4 and CH_2Cl_2 solutions were analysed for S_4N_4 using U.V. spectroscopy. The total amount of unreacted S_4N_4 (X + Y, see Table 5.17) was 0.54 g (70% of the original quantity).

TABLE 5.17

STANDARD SOLUTIONS			
Concentration (mole L^{-1})		Absorbance	
CCl_4	CH_2Cl_2	CCl_4(275 nm)	CH_2Cl_2(253 nm)
1.75×10^{-4}	6.33×10^{-5}	1.06	1.43
8.76×10^{-5}	3.16×10^{-5}	0.69	0.91
4.38×10^{-5}	1.58×10^{-5}	0.39	0.44
2.19×10^{-5}	0.79×10^{-5}	0.24	0.22
$\varepsilon = 6812$	$\varepsilon = 26,666$		
UNKNOWN SOLUTIONS			
(X)/100	(Y)/100	1.47	1.79
(X)/200	(Y)/200	0.81	1.06
(X)/400	(Y)/400	0.40	0.56
X = 21.6 mmol L^{-1}	Y = 6.71 mmol L^{-1}		

5.3 Discussion

5.3.1 Apparatus design

The apparatus, described in section 5.2.1, was designed with the emphasis on simplicity. It was then tested using a known system (i.e. the vapour phase pyrolysis of S_4N_4).

5.3.2 Pyrolysis of S_4N_4

A recent alternative preparation of $(SN)_x$[108], avoiding intermediate S_2N_2, involved condensing the volatiles (mostly $(SN)_4$) obtained by passing S_4N_4 vapour through quartz wool.

In section 5.2.2 the blue film observed in the cold zone was due to a thin layer of $(SN)_x$. Viewed in reflected light, films of $(SN)_x$ appear golden-bronze and often display interference colours. Formation of S_4N_4 above the catalyst and between the heat sources suggested respectively that the catalyst surface area was too small and that the trough in the heat profile (Figure 5.5) was too deep. These problems were partially overcome in the repeat experiment. Although $(SN)_x$ and S_4N_4 were both products of this experiment, the proportion of $(SN)_x$ was greatest in the zone in direct contact with the coolant. I.r. absorptions recorded for $(SN)_x$ compared well with those of Warn[43].

5.3.3 Reaction between S_4N_3Cl and NaI

The major product from experiments 1 - 4 was a black solid, with a metallic lustre which could be scraped from the pyrolysis tube as brittle flakes, and which was shown to contain an iodinated poly(sulphur nitride). The surface of the product from experiments 1 and 2 (high iodine content) tarnished rapidly over 2-3 days when exposed to moist air. Samples of lower iodine content remained lustrous even after a year, thus it was either decomposition of a moisture sensitive impurity or release of surface adsorbed iodine which caused the surface deterioration.

Composition of the iodinated polymer

The composition of the product varied widely (Table 5.12) indicating that it contained a mixture of species. Analytical data for experiments 1 and 2 were unreliable as the percentages totalled less than 100%. In this case it is believed that hydrolysis of a moisture sensitive impurity caused low analysis of S, N and I. The high consistency achieved in experiment 3, for separate scrapings of the same fraction, indicated that this product was largely homogeneous.

The amount of iodine in the polymer depended on the temperature of condensation. In experiments 1 and 2, the low temperature ($-85^{o}C$) resulted in co-condensation of the polymer and (the more volatile) iodine. Differential cooling zones were therefore used in experiment 3. Table 5.12 showed that fraction A (which condensed at $10^{o}C$) contained less iodine (0.17 mole per mole of sulphur instead of 0.42 mole at $-85^{o}C$). The S:N ratio however remained the same at the two temperatures (3:2). The empirical formula $S_3N_{2.15}I_{0.53}$ represents either a mixture of species, or a polymer with an irregular combination of different structural units. The latter possibility is more likely in view of the greater degree of variation in the S:N ratio observed in experiment 4 (for four scrapings).

Surface iodine was readily extracted by CS_2 and the subsequent bronze lustre was probably indicative of the true nature of the polymer. Analysis indicated that hydrolysis had occurred during the extraction (Table 5.12). Under the microscope the surface of the extracted polymer appeared pitted because of the slow leaching of iodine from the solid on prolonged extraction.

Infra-red data

I.r. spectra showed that the black solid contained S_4N_4 and some hydrolysis product (absorptions at 3150 and 1390 cm^{-1} were assigned to ν_{NH} and δ_{NH} respectively). Because S_4N_4 absorptions are characteristically strong whilst polymeric materials give weak absorptions, the i.r. spectrum of a polymeric material containing a small S_4N_4 impurity often suggested that the mixture was mostly S_4N_4. S_4N_4 could be present either (i) as a product of the reaction (less likely - see mechanistic discussion) or (ii) due to decomposition of the polymer itself or a moisture-sensitive component of the mixture.

The remaining absorptions, at 1190, 1110, 820, 610 and 460 cm^{-1} were within the typical range of SN absorptions (viz. 1200 - 350 cm^{-1})[109] but did not correspond to $(SN)_x$ (page 103).

Those at 820 and 460 cm^{-1} had counterparts in the spectrum of $(SNBr_y)_x$ (page 110) and were therefore assigned to S-N fundamentals in $(SNI_y)_x$.

Structural nature of the polymeric mixture

The photographs (page 124) and microscopic examination revealed that the solid flakes had an irregular, pitted surface and showed no sign of a fibrous or crystalline structure. The absence of strong lines in the X-ray pattern confirmed the amorphous nature of the material. The lack of crystallinity was probably due to rapid condensation of the product. Calculated d-spacings did not correspond to those for sulphur or solid iodine[110], neither was there evidence for the presence of S_4N_4. This confirmed that the S_4N_4 detected in the i.r. spectrum was small in quantity and present because of hydrolysis or decomposition.

The X-ray data (page 122) were obtained on a sample with a high iodine content and suggested a highly disordered system. D-spacings at 3.24, 3.28 and 3.87 Å correlated with those of 3.25, 3.30 and 3.89 in $(SN)_x$ (page 105). This suggested that, in the iodinated material (cf. $(SNBr_y)_x$[75])the $(SN)_x$ lattice had remained partly intact, for example, there had been no expansion of the lattice along the chain axis.

Compositional range

It is likely that an equilibrium (below) exists for the iodinated polymer. A similar equilibrium has been reported for the brominated polymers[70]:

$$(SNI_{1.5})_x\,(s) \rightleftharpoons (SNI_y)_x\,(s) + \frac{x(1.5-y)}{2}\,I_2\,(g)$$

The actual composition of $(SNI_y)_x$ found would depend on the temperature of condensation and on the degree of displacement of the equilibrium to the right. As with the brominated systems, there are likely to be several discrete compositional ranges.

Conductivity

A high resistance was measured for the coated polythene disc (experiment 2) because the layer was thin and too uneven. In contrast the compact flakes and pressed pellets showed much greater conductivity. Resistance was also measured with a low voltage ohmmeter, in order to check that the conductive pathways in the material were not broken down by the high voltage megatester. The measurements made on pressed pellets were the most reliable because of good electrical contact. Estimated conductivity (on the basis of the lowest resistance measured) would be $0.5\,\Omega^{-1}\ \mathrm{cm}^{-1}$ which was compared with various standards(110b) (Table 5.18).

TABLE 5.18

Material	Conductivity (298K) $\Omega^{-1}\mathrm{cm}^{-1}$	Class
Polythene	$\sim 10^{-14}$	Insulators
Glass (99.5% SiO_2)	$\sim 10^{-6} - 10^{-7}$	
Iodine	$\sim 10^{-7}$	
Si	$\sim 10^{3} - 10^{5}$	Semiconductors
$(SN)_x$	$\sim 10^{3}$	
Pb	$\sim 10^{8}$	Metals
Al	$\sim 10^{11}$	

The increase in resistance of the pellet after 2-3 days was probably caused by the silver cement reacting to give an insulating layer of silver sulphide and/or iodide between the electrical contacts. The effect of heat treatment on conductivity (experiment 5) is discussed below.

Mass spectral data

The mass spectral data (page 123) were typical of the general breakdown of an S-N ring or chain. The fragments $(SN)_n^+$ (where n = 1-4) and $S_xN_y^+$ $(x > y)$ are found in the mass spectra of many S-N compounds[111]. No fragment with $n > 4$ has been observed (Table 5.5), which is compatible with the observation that $(SN)_x$ dissociates to give linear $(SN)_4$ in the vapour phase[12].

Peaks at $^m/e$ 48, 63, 64 and 128 due to SO^+, $HNSO^+$, SO_2^+ and HI^+ respectively were assigned to breakdown of a hydrolysis product, since their relative intensities varied widely from sample to sample. Sulphur fragments S_n^+ (n = 1-6,8) were observed in low intensity. Evidence for a sulphur impurity was obtained by comparing these intensities with those in pure sulphur run under identical conditions (Table 5.19).

The absence of peaks such as SNI^+ ($^m/e$ 173) and $S_2N_2I^+$ (219) indicated that either these species were too shortlived to be recorded or the polymer decomposed under the probe conditions, so that the observed spectrum was of decomposition products: S_4N_4, S_8 and I_2 (which would explain the contradiction of mass spectral and X-ray data concerning a sulphur impurity).

TABLE 5.19

Fragment	Sulphur	S_3N_2Cl/I^- (solution)	Black solid from Expt.	
			1	2
S_2	81	111	35	233
S_6	33	11	3	9
S_5	30	28	5	20
S_4	20	31	10	29
S_3	13	13	3	13
S_8	8	39	6	19
S_7	4	-	-	-

Comparison of the data in Table 5.13 showed that there was a strong similarity between the polymeric products produced in solution (Chapter 3) and in the vapour phase.

Heat treatment

The polymeric material decomposed in vacuo to give S_4N_4. This was evident from the diffraction pattern of the heat treated residue (which also showed the presence of sulphur) and from the mass spectrum, since the intensity of iodine-containing fragments had decreased, whilst that of SN fragments increased. The heat treated residue was non-conducting as would be expected for an S_4N_4/sulphur mixture. Iodine and S_4N_4 crystals were observed in the cold zone of the apparatus. The decomposition can be summarised simplistically as:

$$S_3N_{2.15}I_{0.53} \xrightarrow[10^{-6}\,\text{mm Hg}]{12\,\text{h}\,/\,50\,°\text{C}} S_4N_4 + 0.25\,S_8 + 0.53\,I_2 + 0.15\,N_2$$

ESCA data

(i) Iodine, I(3d)

Table 5.14 showed that iodine was present in the polymer, both as I^- (cf. band at 631.0 with that for the standards $[Ph_2I]I$ and NH_4I) and neutral iodine, in approximate ratio 3:2. This does not rule out the possibility of higher iodides (such as I_3^-); confirmation would require further ESCA studies. ESCA data on the brominated polymer[112] have similarly shown the presence of Br^-. No comparison of the ESCA data with Br_3^- standards was reported. The possibility of Br_3^- being present in $(SNBr_y)_x$ was, however, not excluded.

(ii) Nitrogen, N(1s)

B.E.s have been measured for many inorganic and organic nitrogen-containing compounds[113-115] and correlations exist between these and net atomic charges. Hendrickson[115] obtained a linear correlation using charges computed by CNDO and Extended Hückel methods.

A similar correlation using charges computed by an MNDO method[116] was done (Table 5.20) in order to put into context the present N(1s) data for the iodinated $(SN)_x$. Compounds were chosen to give a spread of data points in the range 397 eV (highly electron rich) to 408 eV (highly electron deficient nitrogen) and ESCA data from two sources were used. Although Hendrickson's values[115] were between 0.1 and 1.4 eV higher than Jolly's, the sequence in each case was the same.

MNDO calculations were necessarily made on isolated ions, e.g. CN^-, NH_4^+ (bracketed in Table 5.20), since the programme cannot make corrections to allow for the effect of neighbouring ions on the crystal field. When considerin core electronic levels, this effect might be expected to be small because of screening by the valence electrons. Indeed it has been reported that the expected differences in crystal potentials do not appear in measured B.E.s (for example in the S_{2p} energies of a series of sulphates)[115]. This conclusion can also be deduced from the data for ammonium and sodium nitrates (Table 5.20), although Folkesson detected a difference of 1.3 eV between them. Folkesson rationalised his result by considering Na^+ to be more highly polarising than NH_4^+ - leading to a greater electron density at the (nitrate) nitrogen in NH_4NO_3 and therefore a lower B.E. A similar situation was reported for the tetramethyl ammonium halides:

Compound	B.E.	(Ref)
$[Me_4N]Cl$	402.1	(121)
$[Me_4N]Br$	401.2	(122)

Here the effect of a more highly polarisable anion (Br^-) causes an increase in electron density at the nitrogen atom and a lowering of the N_{1s} B.E. It is concluded therefore that, in some systems, the crystal field may significantly affect the net atomic charges, and because the potential is not included in the MNDO calculations, this must be considered as a contributing factor to the pronounced scatter usually associated with correlations of this kind. Even with this limitation the correlations are qualitatively useful.

Input geometries for the calculations are shown in Table 5.21. Atomic charges were also calculated for a computer optimised geometry and, in each case, good agreement with actual geometry was obtained. A least squares analysis (developed with Dr. R. S. Roberts for a Sinclair ZX81 personal computer with 16k RAM) was used to calculate the best straight line for each set of data points (Table 5.22). Less scatter was obtained using Hendrickson's ESCA data and Correlation 2 (Figure 5.13) was used to estimate the net atomic charge on nitrogen in various S-N compounds (Table 5.23).

TABLE 5.20

ION	MNDO CHARGE		N(1s) BE (Ref)		BE
	I	II	(114)	(115)	(115)-(114)
K[C$\underset{\sim}{N}$]	-0.54	-0.56	398.2	399.0	0.8
Na[$\underset{\sim}{N}$N$\underset{\sim}{N}$]	-0.63	-0.63	398.8	399.3	0.4
[$\underset{\sim}{N}H_4$]NO_3	+0.05	+0.06	400.9	402.3	1.4
Na[N$\underset{\sim}{N}$N]	+0.27	+0.26	403.0	403.7	0.7
NH_4[$\underset{\sim}{N}O_3$]	+0.67	+0.65	406.0	407.2	1.2
Na[$\underset{\sim}{N}O_3$]	+0.67	+0.65	407.3	407.4	0.1

I — Actual Geometry II — Optimised Geometry

TABLE 5.21

Species	Geometry			
	Parameter	Actual (Ref)	Trial	MNDO Optimised
C(1)-N(2)	C-N	1.13 in KCN (117)	1.13	1.18
N(1)-N(2)-N(3)	N-N NNN	1.16 in NaN_3 180.00 (118)	1.16 180.00	1.67 180.00
H(3) H(1)-N(2)—H(4) H(5)	N-H $H\hat{N}H$ ϕ_{4231}	1.03 in NH_4Cl 109.00 (119) 120.00	1.03 109.00 65.00	1.02 109.50 120.00
O(3) O(1)-N(2) O(4)	N-O $O\hat{N}O$ planar	1.22 in $NaNO_3$ 120.00 (120) 180.00	1.22 120.00 180.00	1.24 120.00 180.00

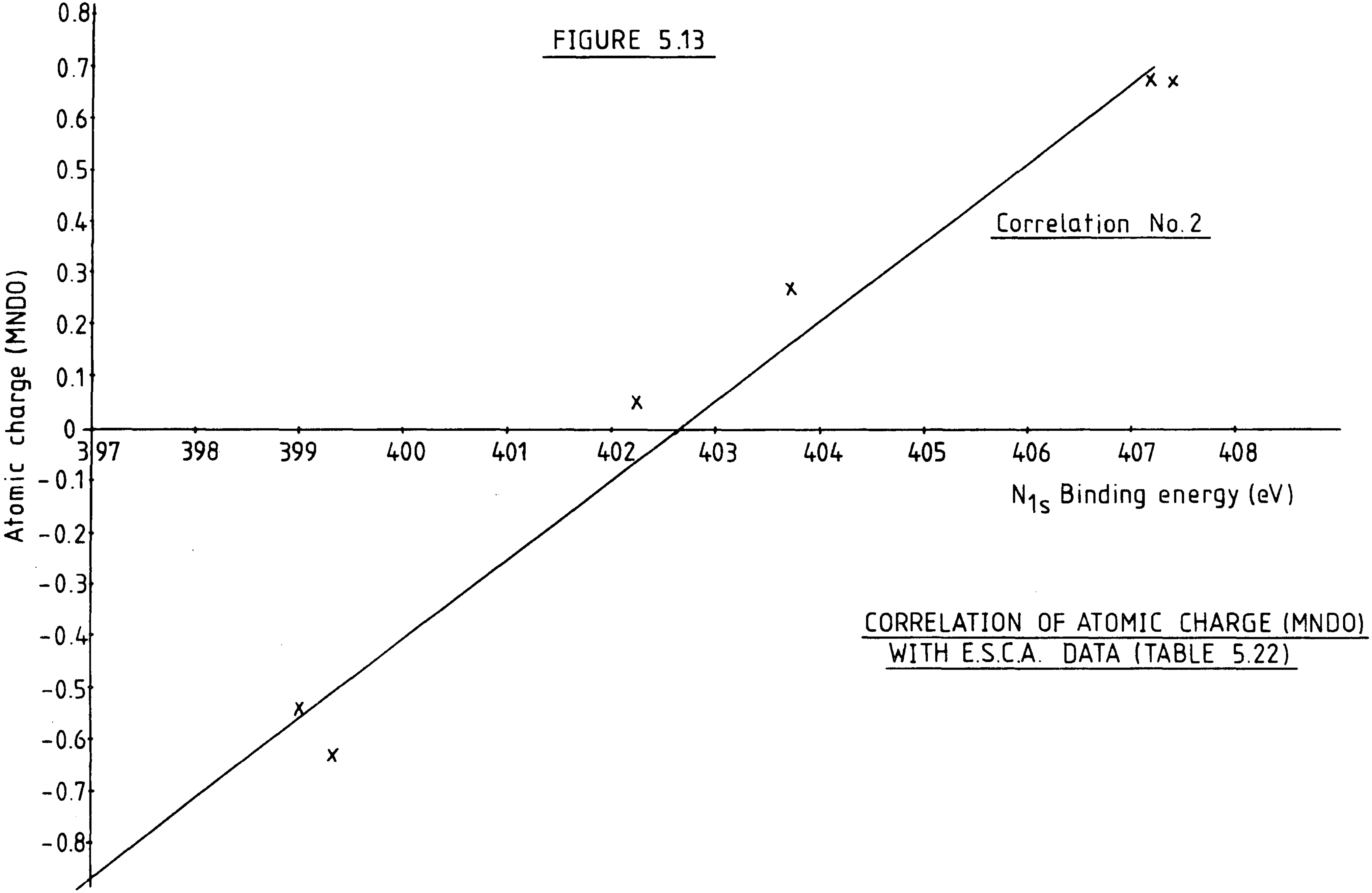
TABLE 5.22

Correlation			Data	Intercept of best straight line on	
No.	Geometry	ESCA	Points	X-axis	Y-axis
1	II	115	6	402.65	-0.86
2	I	115	6	402.61	-0.86
3	II	114	6	401.88	-0.72
4	I	114	6	401.83	-0.71

TABLE 5.23

Compound	B.E.	(Ref)	At. Charge Correlation 2	Compound	B.E.	(Ref)	At. Charge-Correlation 2
S_2N_2	399.1	(123)	-0.54	$(SNI_y)_x$	398.8	(100)	-0.59
					400.3		-0.36
S_4N_4	397.9	(124)	-0.73		401.8		-0.13
	399.2	(112)	-0.53				
				$[S_3N_2Cl]\ FeCl_4$	401.6	(127)	-0.16
$(SN)_x$	398.3	(124)	-0.66		400.5		-0.33
	397.3	(125)	-0.82				
	401.4	(126)	-0.19	S_4N_3Cl	401.0	(127)	-0.25
$(SNBr_y)_x$	400.3	(112)	-0.36	$[S_5N_5]\ FeCl_4$	400.4	(127)	-0.34
	403.2		+0.08				

FIGURE 5.13



CORRELATION OF ATOMIC CHARGE (MNDO) WITH E.S.C.A. DATA (TABLE 5.22)

Since B.E.s reported for $(SN)_x$ vary significantly (up to 3 eV), discussion of the results for the iodinated material must necessarily be speculative.

Two of the ways in which the halogen molecules might interact with $(SN)_x$ are as follows:

(a) There could be charge transfer from $(SN)_x$ to the halogen, in which case the chain might be considered as "partially oxidised", or

(b) the intercalated halogen molecules might reduce the sulphur-sulphur interaction between chains (responsible for the anisotropic properties of $(SN)_x$) with the effect of increasing the electron density in the chain (predominantly at the nitrogen atoms).

The first possibility would therefore lead to higher, and the second one lower, N(1s) and S(2p) B.E.s compared with pure $(SN)_x$.

Table 5.23 showed that the iodinated polymer contained nitrogen in three different environments with approximate atomic charges ranging from -0.59 to -0.13. The most likely assignments are argued as follows:

(i) Sharma[112] reported that the peak at 403.2 eV was due to NH_4^+, an "invariable contaminant of the brominated polymer". This is reasonably consistent with Hendrickson's value of 402.3 for NH_4NO_3[115] but suggests that the value for NH_4I (Table 5.14) and Folkesson's result for NH_4NO_3[114] are too low.

(ii) Acceptance of (i) would suggest that the value for $(SN)_x$ of 401.4 eV (determined at Durham on a sample of high purity) is not unreasonably high. The peak at 401.8 eV in the iodinated polymeric mixture could therefore also be due to the presence of some unchanged $(SN)_x$. It is conceivable that the peak at 398.8 was due to S_4N_4, <u>cf</u>. values at 398-399 eV[112,124] the possible presence of which was discussed above (page 141).

(iii) The peak at 400.3 eV could therefore be assigned to $(SNI_y)_x$ suggesting that the net charge on the nitrogen atoms was similar in both halogenated derivatives. Comparison of the B.E.s for $(SN)_x$, $(SNBr_y)_x$ and $(SNI_y)_x$ (below) therefore favours the second model discussed (<u>i.e</u>. intercalation of iodine with reduction of S-S interactions between chains).

$(SN)_x$	401.4
$(SNBr_y)_x$	400.3
$(SNI_y)_x$	400.3

Furthermore, if the increase in electron density at nitrogen were caused by intercalated halogen atoms, then the greatest effect should be observed when comparing $(SN)_x$ with $(SNHal)_x$ - replacing bromine by iodine would not significantly alter this increase.

(iii) Sulphur, S_{2p}

In general the S(2p) state gives a broad band (in the range 160 - 170 eV) which can be resolved into spin states ($^3/2$ and $^1/2$). An average is, however, usually quoted for the S(2p) B.E. Table 5.24 compares S(2p) B.E.s for $(SN)_x$, $(SNBr_y)_x$ and $(SNI_y)_x$ with some sulphur-containing standards. Linear correlations between S(2p) B.E. and calculated atomic charge have been reported[128] which are generally better than those for N(1s)[129]. The charges in Table 5.24 were estimated from Siegbahn's correlation[128].

Comparison of the band at 164.0 eV in the iodinated polymeric mixture with our value of 167.5 eV for the S(2p) band in $(SN)_x$ showed the same trend towards greater electron density along the chain that was evident from the N(1s) data. This trend can also be observed in the S(2p) B.E. reported for $(SNBr_y)_x$[112] although the actual value (166.9 eV) is somewhat higher than our result for $(SNI_y)_x$.

The higher B.E. (166.1 eV) observed in our iodinated polymeric mixture was probably from sulphur bonded to oxygen (due to hydrolysis). The electron-withdrawing effect of oxygen is demonstrated in Table 5.24 (cf. B.E.s for Ph_2S and Ph_2SO).

There is an apparent contradiction in the ESCA results for $(SNI_y)_x$ in that, the I(3d) data suggested the presence of iodide (and therefore a "partially oxidised" SN-chain) whilst both the N(1s) and S(2p) data suggested greater

TABLE 5.24

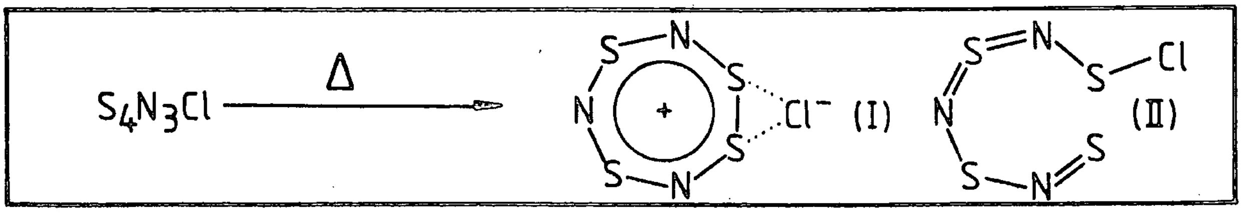
Compound	B.E. (Ref.)	Charge (128)	Compound	B.E. (Ref.)	Charge (128)
PbS	160.6 (130)	-0.32	S_4N_4	165.3 (124) 165.8 (112)	+0.61 +0.66
$Na_2\underline{S}SO_3$	161.4 (131)				
			Na_2SO_3	165.8 (128)	
Ph_3PS	162.2 (132)				
			Ph_2SO	165.8 (131)	+0.66
S_8	162.2 (128) 163.8 (131)	0.00 +0.28	$(SNBr_y)_x$	166.9 (112)	+0.90
Ph_2S	163.0 (131)	+0.12	$Na_2S\underline{S}O_3$	167.5 (131)	+1.01
PhSSPh	163.8 (131)	+0.28	$(SN)_x$	167.5 (126) 164.0 (125) 164.9 (124)	+1.01 +0.32 +0.51
$(SNI_y)_x$	164.0 } 166.6 } (100)	+0.32 +0.76			
			$Fe_2(SO_4)_3$	168.9 (131)	+1.28
Thiophene	164.1 (131)				

electron density along the chain compared with $(SN)_x$. It looks as if the major effect on N and S core levels was due to reduced sulphur-sulphur interaction between chains as described earlier. $(SN)_x$ has a secondary level of structure (see section 5.1.1, page 99) in which fibre bundles are orientated parallel to each other. It is possible that iodide (or triiodide) ions take up interfibrillar positions and that stabilisation occurs by partial charge transfer from the fibre bundles. This process would have only a minimal effect on the N- and S- core levels in the $(SN)_x$ chains.

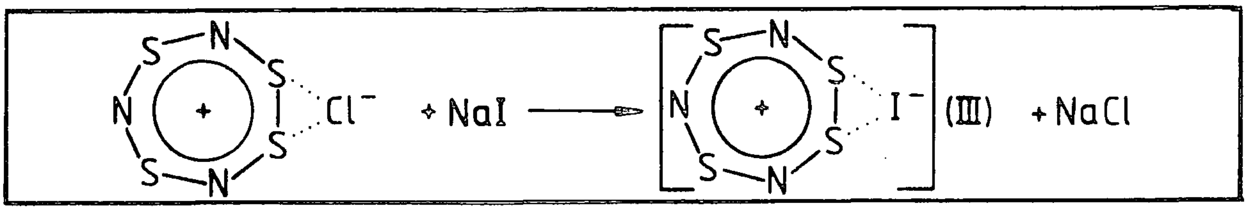
The presence of interfibrillar (tribromide) ions has already been postulated[72] to explain i.r. and Raman data on the brominated polymer (see section 5.1.2, page 112).

Mechanistic discussion

A possible mechanism for the gaseous reaction would be as follows. Initial formation could occur of $S_4N_3^+Cl^-$ ion pairs (I) and/or open chain S_4N_3Cl (II) in the vapour phase:



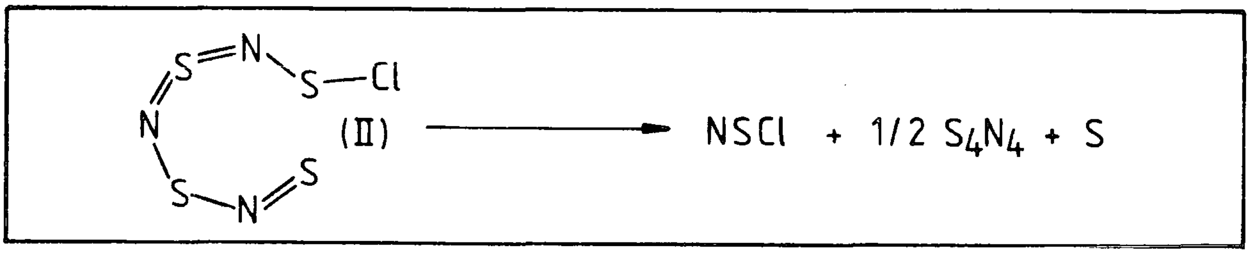
In the case of species (I) reaching the hot surface then halogen exchange might take place with the sodium iodide. The presence of Cl^- in the glass wool was demonstrated in experiment 1.



Compound (III) can be made[66] but it is thermally unstable at room temperature. Under the conditions prevalent at the hot surface therefore, such a species would have a transitory existence, probably decomposing to S_4N_4, I_2 and S_8:

$$\underset{(\mathrm{III})}{4S_4N_3I} \longrightarrow 3S_4N_4 + 2I_2 + 1/2\,S_8$$

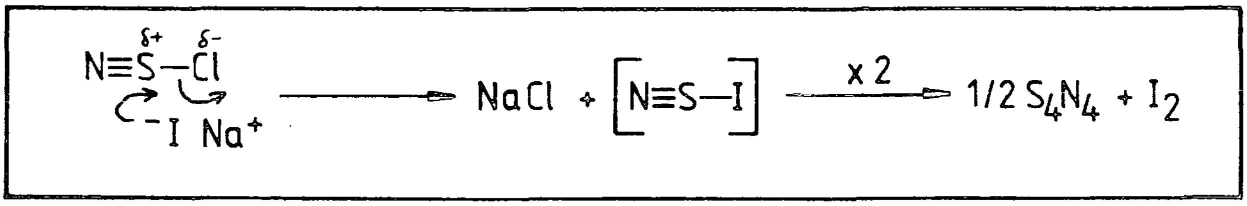
Species (II), if formed, would probably break down as follows:



Indeed, Peake and Downs[66] observed that controlled pyrolysis of S_4N_3X (where X = Cl,Br) would yield the thiazyl halide (NSX), S_4N_4 and sulphur.

(The species NSCl can exist at temperatures of 100-200°C as it is postulated as the building unit for $S_3N_2Cl_2$ in refluxing S_2Cl_2[133]. At temperatures below ca. 50°C it associates to form $(NSCl)_3$).

Once again halogen exchange might be expected at the hot surface:



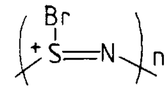
$$N{\equiv}\overset{\delta+}{S}{-}\overset{\delta-}{Cl} \;\; {}^{-}I\ Na^+ \longrightarrow NaCl + [N{\equiv}S{-}I] \xrightarrow{x\,2} 1/2\,S_4N_4 + I_2$$

NSI however has not been observed by Peake and Downs in matrix isolation studies and other evidence for the instability of S-N-I fragments was obtained from the absence of such peaks in our mass spectral data (page 123). The first hypothesis, involving species (I), might therefore seem more likely.

In summary, the products after reaction at the hot surface are likely to be S_4N_4, I_2 and sulphur. Street et al[57] have observed that S_4N_4 and I_2 react at temperatures higher than ca. 125°C to give a conducting solid, whereas no reaction occurs at room temperature. It is likely therefore that interaction between S_4N_4 and I_2 occurred at the hot surface to form iodinated poly (sulphur nitride) which then condensed in the cold zone. At the hot surface, S_4N_4 vapour would be highly activated towards attack by iodine and a vapour phase iodination is postulated similar to the solid state bromination which S_4N_4 undergoes in the presence of bromine. Since S_4N_4 would decompose explosively at 180°C, it is probable that it has only a short lifetime. It may already be present as highly reactive, linear $(SN)_4$ which was discussed in section 5.1.1 (page 104).

The possible nature of the iodinated polymer has already been discussed (page 150). The overall picture of a stacked lattice of "partially oxidised" macrocyclic donor molecules and small anion acceptors (such as iodide or triiodide) would be similar to the iodinated metal bis(dioximates), $M(dpg)_2^{\delta+}\ I_3^{\delta-}$ reported by Marks[134]. These compounds are golden-olive in colour and are conducting.

In these "partially oxidised" species the donor should be unidimensional and have a stacked lattice whilst the acceptor should be polarisable and sufficiently compact to fit into narrow channels in the donor lattice. It is possible that the halogenated derivatives of $(SN)_x$ belong to such a class of compounds.

There is no support in the literature for a structure in which bromine exists covalently bonded to sulphur in $(SNBr_{0.4})_x$ i.e.  $\left(\overset{+}{\underset{}{\overset{Br}{S}}}{=}N\right)_n$ and this is even less likely for the iodinated derivative. Although no structural data are yet available on brominated systems, the sulphur-bromine interaction will probably be shown to be electrostatic, rather than a covalent bonding one.

Further Work

The iodinated poly (sulphur nitride) described in this chapter was not studied further. Clearly, like the brominated-$(SN)_x$ polymers, this new derivative has similar physical properties to polythiazyl itself. If and when applications (in semiconductor or other devices) are found for $(SN)_x$ then further study of this system (especially purification and characterisation) might be worthwhile.

5.3.4 Pyrolysis of $S_5N_5FeCl_4$

Traditionally $(SN)_x$ has only been prepared by the slow polymerisation of S_2N_2 (section 5.1.1). Even the recent new method from S_4N_3Cl/Ag[102] involved S_2N_2. Clearly the synthesis from $S_5N_5FeCl_4$, which avoids S_2N_2, involves a different mechanism.

Since S_4N_4 was produced as a major by-product many experiments were attempted (Table 5.15) in order to find optimum conditions for preparation of pure $(SN)_x$ layers. Several designs were tried for the pyrolysis tube and results showed that the geometry of the apparatus was critical for formation of $(SN)_x$. (e.g. apparatus A produced hardly any $(SN)_x$).

The important geometrical variables of the apparatus (Figure 5.9) were L_1 (the distance travelled in vacuo by the vapour species from the solid to the catalytic hot zone), L_2 (the distance travelled by the reactive species from the hot zone to condensation on the cold finger) and L_3 (the thickness of the catalyst layer). Better layers were obtained when $L_1 > L_2$. L_1 and L_2 should not be so great that crystalline S_4N_4 forms below the catalyst hot zone, or rearrangement of the reactive species occurs prior to condensation on the cold finger. They were 13 cm and 2-5 cm respectively in the experiments which produced the best yield of $(SN)_x$. L_3 was varied between 0.2 and 1.5 cm (keeping the surface area constant). It was found that the greatest ratio of $S_4N_4:(SN)_x$ was obtained at both extremes. This can be explained since for $L_3 < 0.5$ cm (approx) a high proportion of vapour species would pass through the catalyst unchanged whilst for $L_3 > 0.5$ cm (approx) the probability of the reactive species formed at the catalyst surface being decomposed by further collisions would become greater.

Other important variables considered were

(i) the temperatures, of vaporisation (T_1), of the hot zone (T_2), and of the cold finger (T_3).

(ii) the pressure of the system(P).

(iii) the ratio of $S_5N_5FeCl_4$:catalyst.

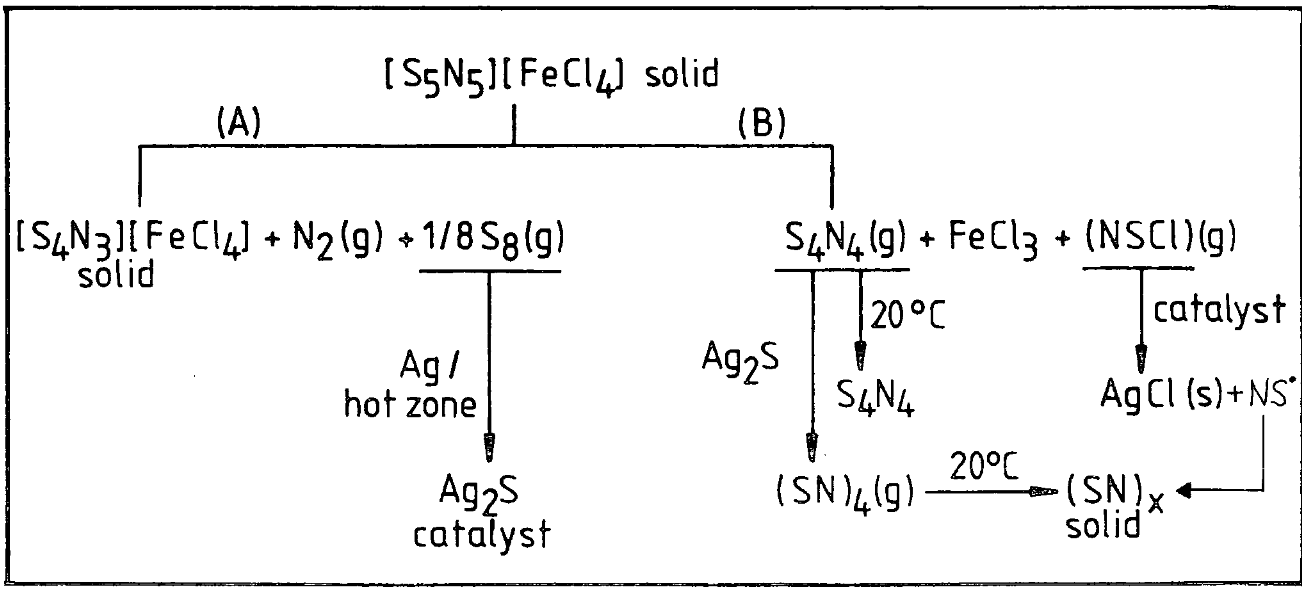
(iv) the time taken for formation of a blue film (t_1) which indicated the onset of stage 2 (see proposed reaction mechanism) and

(v) the time taken for complete reaction (t_2) which indicated the end of stage 2.

The highest yield of $(SN)_x$ came from experiments 3 and 4 (Table 5.15) although even these products were contaminated with S_4N_4.

Proposed reaction mechanism

The following scheme represents a possible rationale for the reaction. It is proposed that there are two competing decomposition pathways of the $S_5N_5^+$ salt, (A) and (B):



Reaction (A) is a solid state ring contraction to form the thermodynamically more stable salt, $S_4N_3FeCl_4$ (i.r. spectroscopy showed that, after pyrolysis, the residue was mainly this compound). It also produces gaseous sulphur and nitrogen. The former reacts with the hot silver surface to form black silver sulphide. Slow liberation of nitrogen was particularly noticeable during the first few hours of pyrolysis. Reaction (B) produces the vapour species S_4N_4, $FeCl_3$ and NSCl. It is believed that decomposition (A) is preferred over (B) at lower vaporisation temperatures (T_1), but that the situation is reversed when T_1 = 120 - 140°C. Furthermore, the silver sulphide produced in the hot zone during the first stage of the pyrolysis acts as a catalyst for the conversion of cyclic S_4N_4 to linear $(SN)_4$. The reactive species, linear $(SN)_4$ then polymerises by condensation on the cold-finger. Smith[12] has reported that acyclic $(SN)_4$ is the vapour phase precursor to poly (sulphur nitride) thin films from $(SN)_x$ crystals.

The concentration profiles depicted in figure 5.10 (page 131) clearly show that the surface layers of the silver catalyst fibres had been attacked by sulphur, iron and chlorine. The surface layers therefore probably contained an inhomogeneous mixture of silver sulphide and silver and iron chlorides. This suggested that the reaction was mainly controlled by diffusion along the grain boundaries of the silver fibres. The nodules did not seem to contain any unreacted silver and were generally richer in iron.

In simple terms the reaction took place in three stages.

STAGE	1	2	3
TIME/h	0-6	6-12	12-18
	Reaction (A) predominates. Formation of Ag_2S catalyst and $\left.\begin{matrix}FeCl_3\\AgCl\end{matrix}\right\}$ poisons.	Reaction (B) predominates. Formation of $(SN)_x$. Concentration of poisons increases.	Catalyst deactivated. S_4N_4 major product.

In stage 1, reaction (A) appeared to predominate since during this time the only visible signs of reaction were a blackening of the silver wool and a very slight deposition of S_4N_4 on the cold finger. The build-up of iron, chlorine and sulphur on the silver fibres during stages 1 and 2 eventually inhibited the formation of silver sulphide by retarding the diffusion of silver from inside the fibres.

After approximately 6 hours, the concentration of silver sulphide (plus higher temperature of vaporisation, T_1) began to favour reaction (B), and $(SN)_x$ began to form on the cold finger. Thereafter (in stage 2) the catalyst was slowly deactivated through build-up of the surface poisons. After approximately 12 hours the only product being produced on the cold finger was S_4N_4.

The "spongy" crystals deposited on the cold-finger during the latter stage of the reaction, which are depicted in the colour photographs (note 5, page 130) were shown to be S_4N_4, probably partially coated with $(SN)_x$. The black and white photographs of a zinc sulphide crystal (note 7) also show the heavy deposition of S_4N_4 on top of a thin film of $(SN)_x$. Note that the $(SN)_x$ layer is amorphous and appears dark between crossed polars. Description and further discussion of the significance of these photographs appeared in section 5.2.4. Some of the micro crystalline deposits of S_4N_4 were removed by annealing the thin film and substrate at $40^{\circ}C/10^{-3}$ mm Hg (note 8). This resulted in a slight improvement of the quality of the polythiazyl layer.

Difficulty was found in obtaining good characterisation of the polymeric thin films. With $(SN)_x$ this is a material science and applied physics problem since the usual probes available to the synthetic organic/inorganic chemist, e.g. i.r. and mass spectroscopy, chemical analysis etc. are not very informative with polymeric materials. Evidence for the presence of $(SN)_x$ came mainly from visual observation (layers of $(SN)_x$ are visually quite distinctive) and i.r. spectroscopy. ESCA is a useful technique for probing solid surfaces especially of polymeric materials, however attempts made to cover gold and glass substrates with thin films for evaluation by ESCA were unsuccessful because coatings could not be obtained which were thick or even enough to satisfy the requirements of the ESCA laboratory. This was basically an apparatus design problem. Because this reaction was so strongly dependent on apparatus geometry and produced only a low yield of $(SN)_x$ and since concurrent research by Dr. Z.V. Hauptman had found other rapid methods of forming thin films of $(SN)_x$ (using a better catalyst, silver selenide), it was decided not to continue research on this system. The process does however stand on its own as a remarkably simple demonstration experiment and has been published as such in an educational journal[103].

5.3.5 Pentathiazyl chloride, S_5N_5Cl

In view of the role that iron and silver chlorides played in poisoning the catalyst in the vapour phase decomposition of $S_5N_5FeCl_4$, S_5N_5Cl[135] was considered to be a more promising starting material because of its lower chlorine content and absence of iron.

The preparation described by Zborilova[135] was attempted, however, problems were encountered when repeating the recrystallisation from formic acid. The crude solid was extremely soluble in formic acid and crystallisation could not be induced by evaporating the solvent to low volume. Instead, on evaporation to dryness, a black solid formed which was shown to contain S_4N_4 and some hydrolysis products (including $(NH_4)_2SO_4$). This hydrolysis occurred even after the solvent had been scrupulously dried with boric oxide, hence it is believed that the water was being produced by the decomposition of formic acid under reduced pressure:

$$HCOOH \rightleftharpoons CO + H_2O$$

Another possibility was that hydrolysis occurred by reaction with formic acid, however, this would not explain why the black solid only formed when the formic acid was present in low concentrations.

Strong absorptions at 1155, 1067, 1042, 962, 941, 668, 546, 465, 415 and 348 cm^{-1} were observed in the i.r. spectrum of the crude product obtained after heating S_4N_4 and $(NSCl)_3$ together, and these were assigned to S_5N_5Cl. No i.r. data have been reported by Zborilova for this compound.

S_5N_5Cl is believed to contain the pentathiazyl cation[135] (which is consistent with the observation of high solubility in ionizing solvents such as H.COOH). Consequently it would have a similar i.r. spectrum to $S_5N_5{\cdot}FeCl_4$ except that some shifting would occur of bands associated with fundamental ring vibrations, because of the greater cation-anion interaction in S_5N_5Cl.
A comparison of the S_5N_5Cl absorptions (above) with those recorded for $S_5N_5FeCl_4$ (Chapter 2, page 34) showed that the peaks at 1150, 1067, 1042, 668, 546, 415 and 348 cm^{-1} had possible counterparts in the spectrum of the tetrachloroferrate salt.

Recrystallisation was investigated from other high polarity solvents such as thionyl chloride, nitrobenzene, phosphoryl chloride and acetonitrile. Results showed that the crude S_5N_5Cl was actually a mixture of S_4N_4, S_4N_3Cl and S_5N_5Cl. This was demonstrated by the analysis of i.r. absorptions (Table 5.16). The intensities of pairs of absorptions (I and II) were measured in each of two separate samples (one run as a KBr and the other as a KCl disc). The ratio I:II showed that in each case these absorptions belonged to the same component of the mixture. When the relative intensities of the I-absorptions for S_4N_3Cl, S_5N_5Cl and S_4N_4 were compared, a different value was found for each disc. If these absorptions had belonged to the same compound the ratios would have been the same.
Liquid SO_2 was not a good recrystallisation solvent since S_4N_4, S_4N_3Cl and S_5N_5Cl were all quite soluble in it.

Two attempts were made to synthesise $(SN)_x$ from S_5N_5Cl. In the first, a magenta coloured and moisture sensitive thin film was formed in low yield which may have been an oligomeric sulphur-nitride similar to the product formed from the pyrolysis of mercury thionitrosyl (see section 5.3.6). In this attempt there was no evidence for the presence of $(SN)_x$.

In the second attempt $(SN)_x$ was produced in low yield. When the vaporisation temperature was raised to 45°C, S_5N_5Cl decomposed to form, predominantly, S_4N_4.

5.3.6 Pyrolysis of mercury thionitrosyl

Because the yield of $(SN)_x$ was low from vapour phase pyrolysis of $S_5N_5^+$ salts, it was decided to investigate a different type of S-N starting material: the metal thionitrosyls.

These are generally difficult to synthesise and, to date, have been little studied. If the sulphur-nitrogen ligands of a metal thionitrosyl could be removed by pyrolysis, then condensation of the volatile species might produce $(SN)_x$ or oligomeric sulphur nitrides.

Younger[136] investigated metallated salts of $S_4(NH)_4$ such as $Li_4(NS)_4$ and $Na_4(NS)_4$ which contain the $S_4N_4^{4-}$ ion. Similar salts of $S_3N_3^-$ [137] and $S_4N_5^-$ [138] are also known.

These ionic compounds tend to be thermally unstable and not amenable to gas phase study. Li^+, Na^+, K^+, etc. are Class A (hard acid) metals. The ions are small, highly electropositive, have low polarisabilities and form essentially ionic compounds. However, sulphur, S^{2-} is a soft base and tends to form covalent compounds with soft acids (Class B metals) such as Cu, Ni, Hg, Fe and Co. Most thionitrosyls reported in the literature involve these metals (Table 5.25). Much of this work was done 30 years ago and recent attempts to repeat some of it have been unsuccessful[139]. The mercury thionitrosyl (believed to be a mixture of $3Hg(II)(NS)_2 + Hg_2(I)(NS)_2$) was easily prepared from $S_4(NH)_4$ [147] and used for initial vapour phase experiments. Chemical analysis indicated that pyrolysis caused almost complete decomposition to black mercury (II) sulphide, HgS. The residue was ca. 95% HgS (Table 5.26).

Absorptions in the i.r. spectrum were assigned to unreacted $Hg_5(NS)_8$ (cf. Chapter 2, page 33) and HgS would not be expected to give absorptions in the range 4000-400 cm^{-1}.

TABLE 5.25

Compound	(Ref)	Compound	(Ref)
$Cu_7S_4N_4$	(140)	FeS_4N_4	(144,145)
$Cu(NS)_x$, CuS_2N_2	(141)	CoS_4N_4	(146)
$CuX_2S_2N_2$	(142)	$Hg_5(NS)_8$	(147)
NiS_4N_4	(143)	$Ag_5S_4N_4$	(140)
$Ni(S_2N_2H)_2$	(143)	Review	(148)

TABLE 5.26

Experimental		Theoretical	
	Residue	$Hg_5(NS)_8$	HgS
N	0.8	8.2	-
S	13.3	18.7	13.8
Hg	78.7	73.1	86.2

Decomposition of the mercury thionitrosyl also produced mercury vapour. A commercial mercury scavenger,"Iodine charcoal"was used in an attempt to trap this vapour. However, its efficiency was low, and under experimental conditions it released traces of iodine. Analysis of the charcoal after pyrolysis indicated that its surface had not retained any sulphur nitrides, though it had absorbed traces of mercury.

The orange-gold thin film was probably a sulphur-nitride (not $(SN)_x$ because thin films of this material appear blue), and the blue-green colour formed on gentle heating may have been due to a mercury adsorbate. Unfortunately the yield of the sulphur nitride was very low and its formation not reproducible. The reaction was not studied further, but useful spectroscopic information could be obtained in future by condensing the species directly into an infra-red gas cell.

5.3.7 Other thionitrosyls

It was mentioned in the previous section that attempts to repeat published preparations of metal thionitrosyls have not been very successful. This was largely the case for "$Cu_7S_4N_4$" and "$Ag_5S_4N_4$" reported by Padma and Vasudeva-Murthy [140]. The $Ag_5S_4N_4$ preparation could not be repeated. The copper thionitrosyl was apparently formed from Cu and S_4N_4 in carbon tetrachloride. However in the first attempt (using copper strips) chemical analysis (3 elements) of the black precipitate totalled only 79% and the N:S ratio was 1.6:1 (not 1:1 as in $Cu_7S_4N_4$). When copper powder was used, analysis totalled 95% and the corresponding N:S ratio was 1.1:1. However the Cu:N:S ratio was 8.4:1:1 as opposed to the 1.8:1:1 required for "$Cu_7S_4N_4$". It is believed that a copper thionitrosyl was formed but that the empirical formula "$Cu_7S_4N_4$" represents a copper thionitrosyl with excess copper. It is possible that the compound formed is polymeric, with the formula, $Cu(NS)_x$ [141].

Thionitrosyls such as $Ni(S_2N_2H)_2$ [143] and $(Cp)CoS_2N_2$ [150] have been prepared and characterised recently and these might be promising materials for vapour phase reaction with suitable catalyst surfaces.

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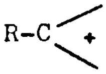
PART II

SOME ASPECTS OF THE CHEMISTRY OF THE RCN_2S_2 RING SYSTEM

II.1 Introduction

The sulphur-nitrogen ring cations, $S_5N_5^+$ and $S_4N_3^+$ are termed electron rich species[1-3] since they cannot be adequately represented by canonical forms, and are best described as containing a σ-framework of 2-coordinate S and N atoms and a π-system to which S donates two, and N one electron. If the number of π-electrons equals 4n + 2 (where n is an integer) e.g. S_2N_2(6π), $S_4N_3^+$(10π) and $S_5N_5^+$(14π), then the species are termed "Hückel species", and, like their organic analogues (e.g. benzene) they exhibit planarity.

Introducing 3-coordinate carbon (with 1 π-electron) into the S-N ring results in a series of C-S-N heterocycles, some of which are expected to be stable Hückel species (Table II.1). For example, the dithiadiazolium ring system (Chapters 6 and 7) can be considered as the 6π species S_2N_2, with insertion of the fragment, 

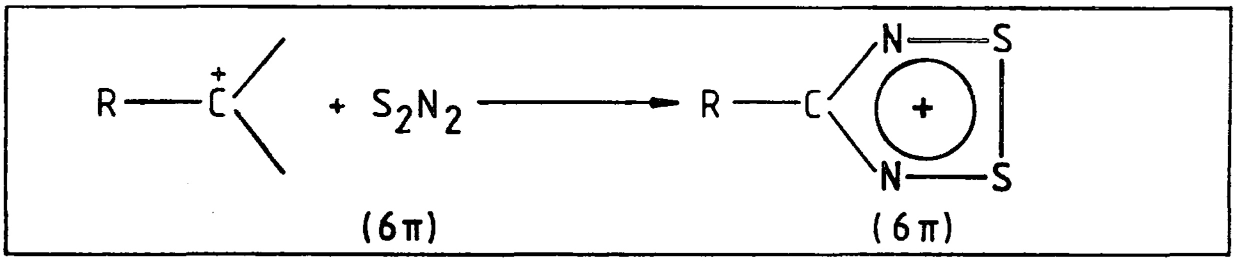


Table II.1. C-S-N Heterocycles

No. of Atoms			Ring	πe^-
C	S	N		
1	1	1	3	4
1	2	1	4	6
1	1	2	4	5
1	2	2	5	7
2	1	1	4	5
2	1	2	5	6
2	2	1	5	7
2	2	2	6	8
3	1	1	5	6
1	3	1	5	8
1	1	3	5	6
3	1	2	6	7
3	2	1	6	8
2	1	3	6	7
2	3	1	6	9
1	2	3	6	8
1	3	2	6	9

Table II.1 (cont...)

No. of Atoms			Ring	πe^-
C	S	N		
3	2	2	7	9
2	3	2	7	10
2	2	3	7	9
3	3	2	8	11
3	2	3	8	10
2	3	3	8	11
3	3	3	9	12
3	3	1	7	10
3	1	3	7	8
1	3	3	7	10
4	1	1	6	7
1	4	1	6	10
1	1	4	6	7
4	1	2	7	8
4	2	1	7	9
1	4	2	7	11
2	4	1	7	11
1	2	4	7	9
2	1	4	7	8
4	2	2	8	10
2	4	2	8	12
2	2	4	8	10
4	2	3	9	11
4	3	2	9	12
2	3	4	9	12
3	2	4	9	11
2	4	3	9	13
3	4	2	9	13
4	3	3	10	13
3	4	3	10	14
3	3	4	10	13
4	3	4	11	14
4	4	3	11	15
3	4	4	11	15
4	4	4	12	16
4	3	1	8	11
4	1	3	8	9
1	4	3	8	12
3	4	1	8	12
1	3	4	8	11
3	1	4	8	9
4	4	1	9	13
4	1	4	9	10
1	4	4	9	13
4	4	2	10	14
4	2	4	10	12
2	4	4	10	14

The following summary includes nomenclature, structural examples and references to the vast literature of known C-S-N heterocycles.

(1) Four-membered rings

Ring	πe^-	Cation	Neutral	Anion
CSN_2	5			6 π
CS_2N	6		6π	
C_2SN	5			6 π

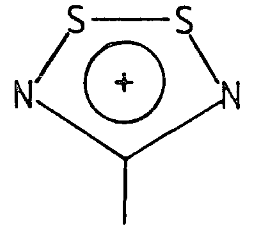
These strained (and as yet, unknown) rings would be unlikely to be stable as anions because the increased electron density on sulphur would destabilise the d-orbitals believed to participate to a small extent in bonding^4.

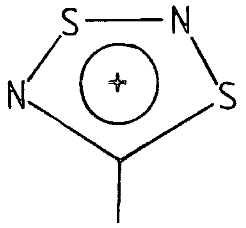
(2) Five-membered rings

Ring	πe^-	Cation	Neutral	Anion
CS_2N_2	7	DITHIADIAZOLIUM(a)		
C_2SN_2	6	THIADIAZOLIUM(b)	THIADIAZOLE(d)	
C_2S_2N	7	DITHIAZOLIUM(c)	DITHIAZOLE(c)	
C_3SN	6	THIAZOLIUM(b)	THIAZOLE(e)	
CS_3N	8			
CSN_3	6	THIATRIAZOLIUM(b)	THIATRIAZOLE(f)	THIATRIAZOLIDE(f)

Most of the five-membered C/S/N heterocycles are known either as neutral molecules or cations.

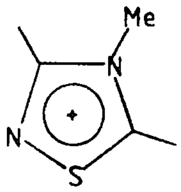
(a) Two isomers of the DITHIADIAZOLIUM system are known but little chemistry of the compounds has been reported to date.

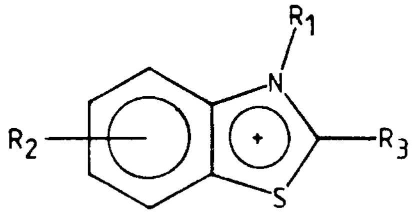

1,2,3,5 - Dithiadiazolium (5-7)

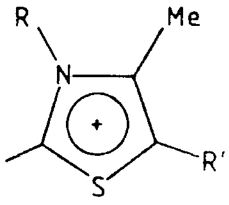

1,3,2,5 - Dithiadiazolium (8)

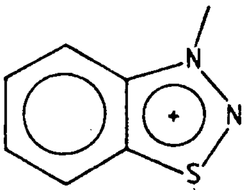
Several derivatives of the 1,2,3,5-isomer have been made, varying the 4-substituent (Ph,CCl_3,Bu^t)$^{5-7}$ and the stabilising anion ($SbCl_6^-$, $CF_3SO_6^-$, $N(SO_2F)_2^-$, BF_4^- and PF_4^- ^{7,8}. Hey recently extended this list of anions to include Br^-, I^-, BCl_4^- and $SnCl_6^=$ ^{9}.

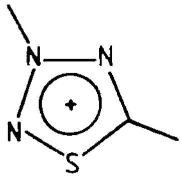
(b) The THIADIAZOLIUM, THIAZOLIUM and THIATRIAZOLIUM systems all have one 3-coordinate N involved in the ring, formally contributing a π-lone pair to the delocalised π-M.O.'s. As cations therefore they can be considered as 6π Hückel species.


1,2,4-Thiadiazolium (10)

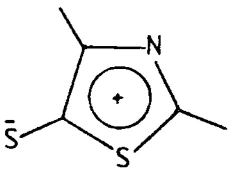

1,3-Benzothiazolium (11)

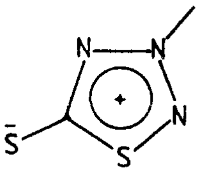

1,3-Thiazolium (12)

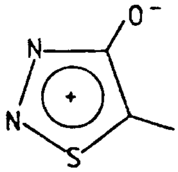

1,2,3-Benzothiadiazolium


3-sub-1,2,3,4-Thiatriazolium

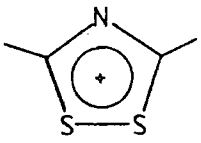
Some "meso-ionic" heterocycles involving these ring skeletons are also known, for example:


1,3-Thiazolium-5-thiolate (13,14)

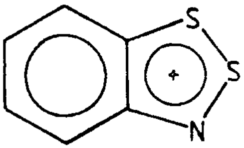

1,2,3,4-Thiatriazolium-5-thiolate (15)


1,2,3-Thiadiazolium-4-olate (16)

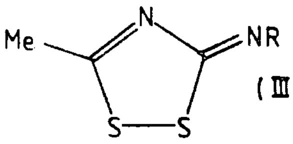
(c) A large range of 3,5-substituted 1,2,4-DITHIAZOLIUM compounds (I) are known[17] which have found industrial uses as sterilizers[18], male contraceptives[19] and photographic development accelerators[20]. Herz compounds (II) have found applications in the dyestuffs industry[21,22]. A great many neutral 1,2,4-DITHIAZOLES (III) are also known.


(I)

1,2,4-Dithiazolium cation

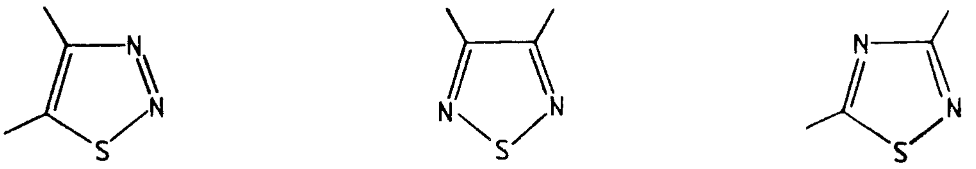

(II)

1,2,3-Benzodithiazolium cation


(III)

5-imino-3-methyl-1,2,4-dithiazole

(d) Many THIADIAZOLES have been synthesised and these are well reviewed by Barton and Ollis[23]. Some examples are:



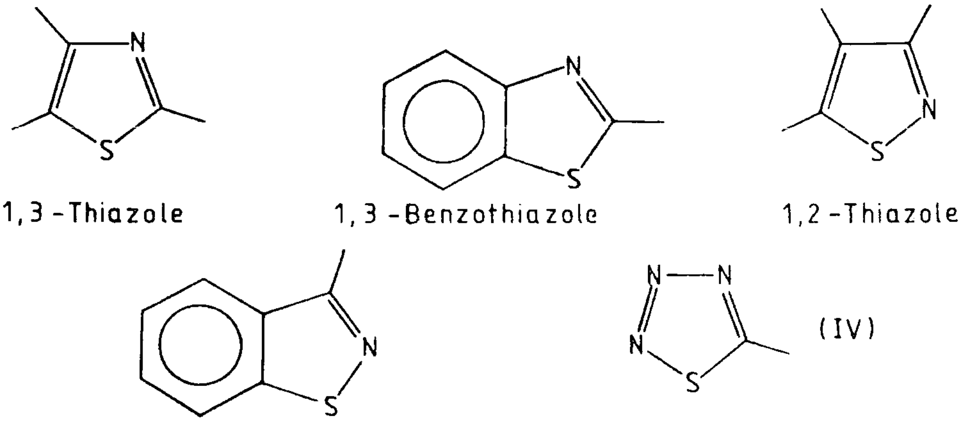
1,2,3-Thiadiazole 1,2,5-Thiadiazole 1,2,4-Thiadiazole

Once again the thiadiazoles (particularly the 1,2,4 isomer) have important analytical, industrial and pharmacological uses[24]. Physical, theoretical and spectroscopic properties of the thiadiazoles have been reviewed as follows:

Isomer	Reference	Isomer	Reference
1,2,4-	(24,26c,27)	1,3,4-	(30,31c)
1,2,3-	(25-29)	1,2,5-	(30,31)

Although the thiadiazoles are usually drawn with localised structures (above) according to microwave spectroscopy they have substantial π-electron delocalisation which decreases in the order 1,2,5-thiadiazole > thiophene > 1,3,4-thiadiazole.

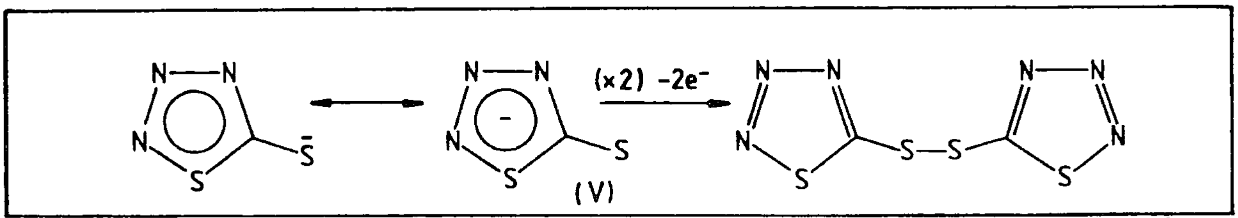
(e) There are also many THIAZOLES and these have been reviewed and their physical properties summarised in Specialist Periodical Reports[31] and other sources[32-35]. Recent industrial uses of thiazoles include anti-oxidants[31b] and photochromics[31a,c] and many thiazoles are pharmacologically active.[36] Some examples include:



1,3-Thiazole 1,3-Benzothiazole 1,2-Thiazole

1,2-Benzothiazole 1,2,3,4-Thiatriazole (IV)

(f) Rings containing more than two atoms of either sulphur or nitrogen are not generally known except for THIATRIAZOLES (IV). These compounds are mentioned in a recent review by Roesky.[37] The CN_3S_2 anion (V) is found in salts of most alkali metals[38]. They are however very sensitive to mechanical shock. The exocyclic sulphur atom probably helps to stabilise the anion as shown below. Evidence for this comes from the susceptibility of the anion to oxidation, resulting in formation of the disulphide[39].



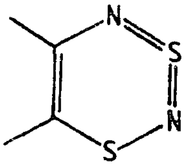
As well as the ring heterocycles there are many benzo-fused systems[40–42] some of which were mentioned above (sections b, c and e).

(3) Six-membered rings

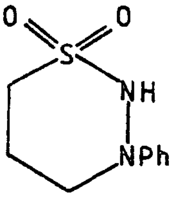
Ring	πe⁻	Cation	Neutral	Anion
$C_2S_2N_2$	8		DITHIADIAZINE(g)	
C_3SN_2	7	THIADIAZINIUM(h)	THIADIAZINE(h)	
C_3S_2N	8		DITHIAZINE(j)	
C_2SN_3	7	THIATRIAZINIUM(k)		
C_2S_3N	9			10π
CS_2N_3	8		DITHIATRIAZINE(k)	
CS_3N_2	9			10π
C_4SN	7	THIAZINIUM(l)	THIAZINE(l)	THIAZINIDE(l)
CSN_4	7	6π		
CS_4N	10		10π	

(g) The only isomer known of the DITHIADIAZINE system is the 1,3,2,4 compound (VI) which has not been widely studied. The compound has a localised structure with S(IV) and S(II).

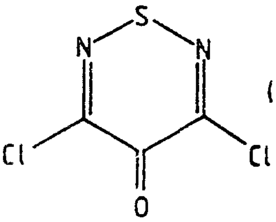
(h) Representatives of all six possible isomeric THIADIAZINES are known[43] (e.g. Structures VII - IX). The tetrahydro compound (VII) is non aromatic and contains fully saturated sulphur and nitrogen.


(VI)

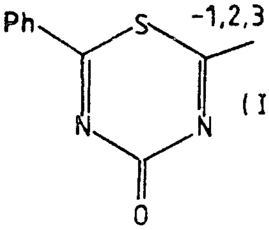
1,3,2,4-Dithiadiazine


(VII)

Tetrahydro-3-phenyl-1,2,3-thiadiazine-1,1-dioxide (44)


(VIII)

3,5-Dichloro-1,2,6-thiadiazine-4-one (45)

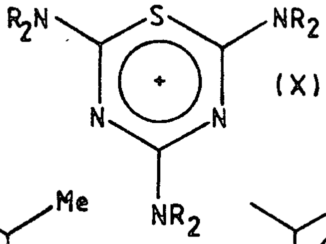

(IX)

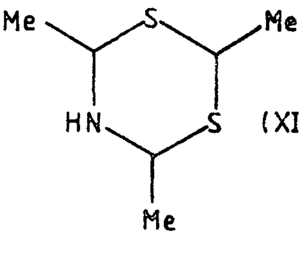
2-phenyl-1,3,5-thiadiazine-4-one (46,47)

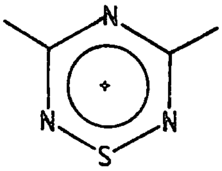
The THIADIAZINIUM cation (X), a 6π Hückel species has also been prepared[48].

(j) Representatives of five of the six isomeric DITHIAZINES are known[49] an example being thialdine (XI), which was identified as being responsible for the flavour of beef broth. Other 1,3,5-dithiazines have been proposed as flavour enhancers.

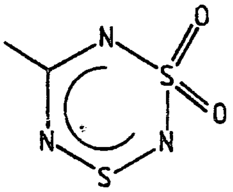
(k) The THIATRIAZINIUM and DITHIATRIAZINE systems are known but very little work has been reported on their uses and chemistry (e.g. Structures XII and XIII).


(X) 2,4,6-Triamino-1,3,5-thiadiazinium


(XI)

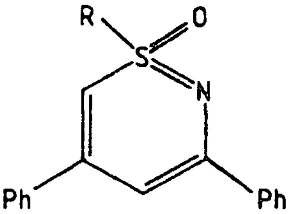

(XII)

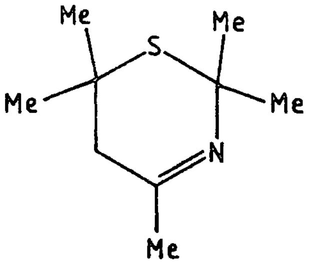
1,2,4,6-Thiatriazinium

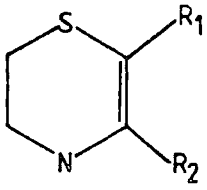

(XIII)

1,3,2,4,6-Dithiatriazine-3,3-dioxide

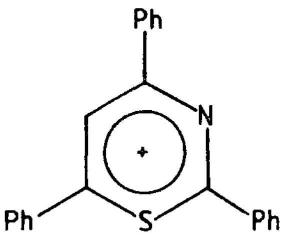
(l) 1,2-, 1,3-, and 1,4-THIAZINES are all known and widely studied having pharmaceutical and fungicidal uses[50,51]. Some examples are:


3,5-Diphenyl-1,2-thiazine-1-oxide (52)

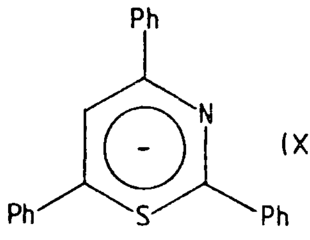

5-Dihydro-2,2,4,6,6-methyl-1,3-thiazine (53)


5,6-Dihydro-2,3-diaryl-1,4-thiazine (54,55)

THIAZINIUM salts, for example the 2,4,6-triphenyl substituted -1,3-thiazinium (XIV) are also known[56]. The 8π -thiazinide anion (XV) is prepared by reduction of (XIV) with sodium borohydride followed by proton abstraction with butyl lithium. The anion is unstable however and readily decomposes to form pyrrole anions (sulphur extrusion)[57].

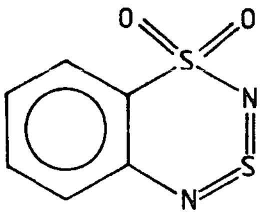


(XIV)

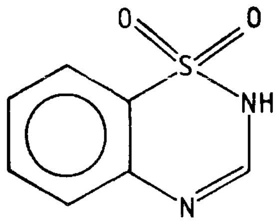


(XV)

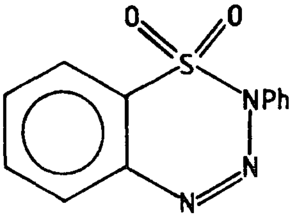
As with the five-membered heterocycles, there are a great many six-membered benzo-fused systems, for example:



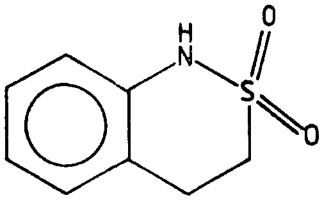
2,4-didehydro-1,3,2,4-benzodithiadiazine-1,1-dioxide (58)



Benzo-1,2,4-thiadiazine-1,1-dioxide (59)



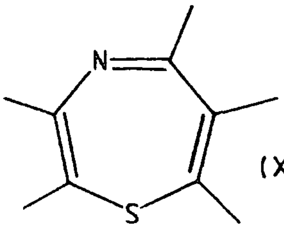
2-Phenyl-1,2,3,4-benzothiatriazine-1,1-dioxide (58)



3,4-dihydro-2,1-benzothiazine-2,2-dioxide (50,51)

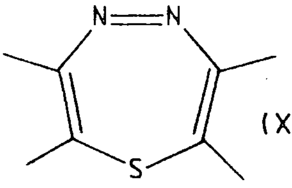
(4) Larger sized ring-heterocycles

There are a few heterocycles with a ring size greater than six; in general these have at least one site of unsaturation (e.g. Structures XVI and XVII).



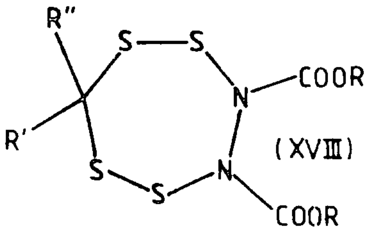
(XVI)

1,4-Thiazepine



(XVII)

1,4,5-Thiadiazepine



(XVIII)

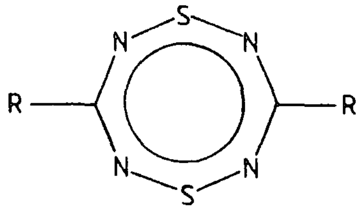
Table II.2 lists those seven-membered and eight-membered rings which might be stable Hückel aromatics.

CS_4N_2 has recently been reported[60] but as a neutral ring (XVIII) with saturated carbon and nitrogen. X-ray analysis has shown that the ring is not linear like $S_4N_3^+$ but exists in a twist conformation[61,62].

As the ring size increases, it might be expected to buckle, and structures containing localised double bonds (such as the thiazepines) and/or sulphur (IV), (VI) and nitrogen (III) would be more likely. However a remarkable new heterocycle has been reported by Ernst *et al*,[63] a 1,5-dithia-2,4,6,8-tetrazocine (XIX). The ring was shown to be planar, and bond lengths, electronic spectra, *etc*. suggested that it was a 10π-delocalised Hückel aromatic species.

Table II.2. Seven and eight membered rings

Ring	πe^-	Cation	Neutral
$C_2S_3N_2$	10		✓
C_3S_3N	10		✓
CS_3N_3	10		✓
CS_4N_2	11	✓	
C_2S_4N	11	✓	
$C_3S_3N_2$	11	✓	
$C_3S_2N_3$	10		✓
$C_2S_3N_3$	11	✓	
$C_4S_2N_2$	10		✓
$C_2S_2N_4$	10		✓
C_4S_3N	11	✓	
CS_3N_4	11	✓	



(XIX)

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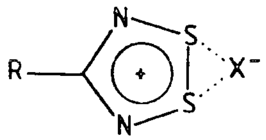
CHAPTER 6

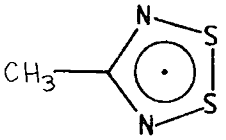
PREPARATION OF SOME DITHIADIAZOLIUM SALTS WITH ALIPHATIC SUBSTITUENTS

6.1 Introduction

Several aliphatic dithiadiazolium salts (I) are already known and their synthetic routes are summarised in Table 6.1.



(I)



(II)

Specific aims of the work described in this chapter were:

(i) to improve the SCl_2/NH_4Cl route to alkyl dithiadiazolium compounds

(ii) to find a higher yield synthesis of 4-methyl dithiadiazolium chloride so that reduction to the 7π free radical (II) (analogous to $PhCN_2S_2{}^{\bullet}$) could be investigated (Chapter 8) and

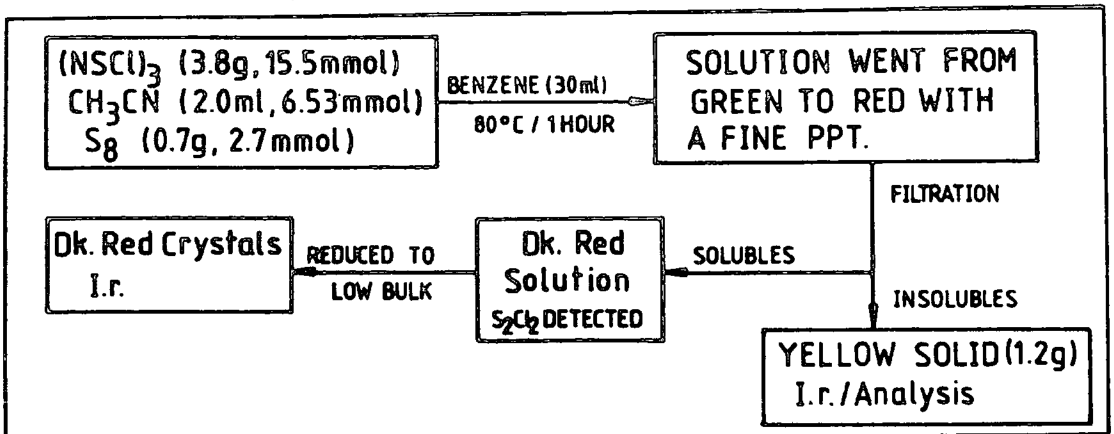
(iii) to attempt synthesis of novel double dithiadiazolium salts from dinitriles.

TABLE 6.1

R-	Route	(Ref)	Comments
CH_3-	$CH_3CN/S_2Cl_2/MN_3$	(1)	Very low yield
Cl_3C-	$Cl_3CN/(NSCl)_3$	(2a)	Good analysis/IR
	$C_2Cl_4/(NSCl)_3$	(3)	
	$Cl_3CN/NH_4Cl/SCl_2$	(3)	
$(CH_3)_3C$-	$Bu^tCN/(NSCl)_3$	(2b, 4-6)	

6.2 Experimental

6.2.1 Reaction of CH_3CN with $(NSCl)_3$ and sulphur



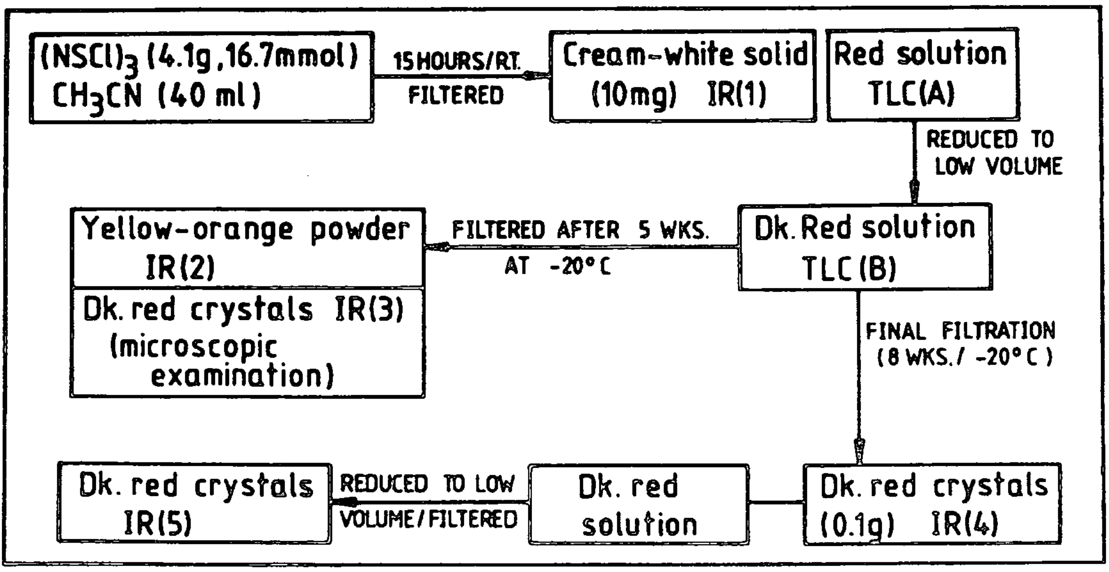
(i) Infra-red spectroscopy

Infra-red absorptions at 1163(m), 1000(s), 679(m), 562(m), 469(ms), and 452(m) cm^{-1} identified the yellow solid as S_4N_3Cl. The dark-red, benzene soluble crystals had the following infra-red spectrum: 1169(m,br), 1015(mw), 935(s,br), 725(s,br), 582(m), 462(m) and 405(ms) cm^{-1}. (cf. $S_3N_2Cl_2$, Chapter 1). On evaporation of the dark red solution an orange liquid (containing benzene and S_2Cl_2) was condensed in the cold trap. From this on warming to RT a pale yellow solid precipitated, which had strong ν_{NH} and δ_{NH} absorptions (at 3130 and 1405 cm^{-1} respectively), a broad absorption at 1760 cm^{-1} and several weak absorptions in the region 1000-800 cm^{-1} with a stronger one at 1170 cm^{-1}.

(ii) Analysis

Chemical analysis of the yellow (benzene insoluble) solid gave S, 63.8; N, 19.2; Cl, 15.4 (98.4%). S_4N_3Cl required S, 62.3; N, 20.4; Cl, 17.3 (100.0%).

6.2.2 Reaction of CH_3CN with $(NSCl)_3$



(i) Thin layer chromatography

R_f values (in CS_2) for solutions A and B (labelled in scheme above) were as follows:

A	0.00 (white)	0.23 (f)	0.64 (s, brown)
B	0.00 (white)		0.66 (f)

(ii) Infra-red spectroscopy

Absorptions recorded for various solids (labelled in scheme above) were as follows (Nujol mulls).

IR(1) = 3130(vs,br), 1750(m,vbr), 1400(vs,br) cm^{-1} (hydrolysis product).

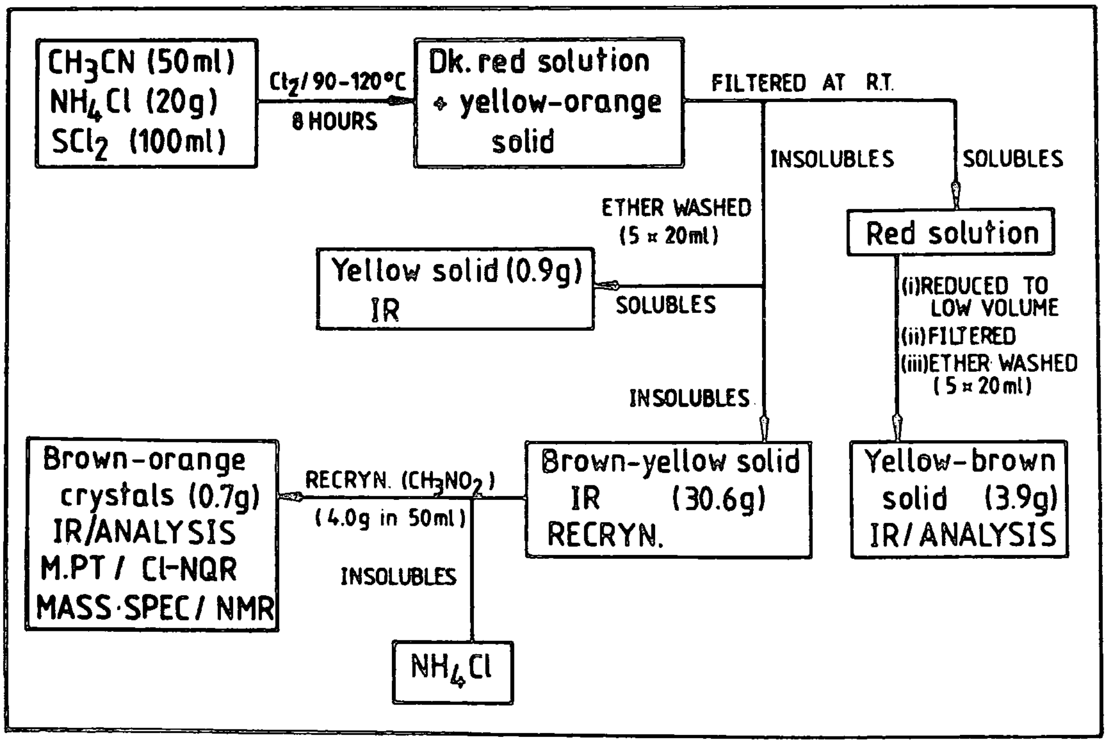
IR(2) = 3150(vw,br), 1400(w,br), 1163(m,br), 1000(s), 682(m), 565(m), 470(ms), 452(m) cm^{-1} (cf, S_4N_3Cl, Chapter 1).

IR(3) = 3140(w,br), 1675(w,br), 1570(m,br), 1405(w), 1355(m), 1320(mw), 1308(mw), 1178(m), 1122(s), 1019(w), 900(m,br), 858(m), 840(m,br), 779(m), 582(m), 532(ms), 522(ms), 473(ms), 440(m) cm^{-1}. (cf. underlined peaks with $CH_3CN_2S_2Cl$, section 6.2.3).

IR(4) = 1015(vs,br), 702(ms), 620(w,br), 519(s,sh,br), 390(vs) cm^{-1} (cf. $(NSCl)_3$[7]).

IR(5) = 1010(vs,br), 955(ms,br), 885(m,br), 690(m,br), 570(w), 540(m), 508(s), 455(m), 382(s) cm^{-1} (cf. underlined peaks with IR(4) above).

6.2.3 Reaction of CH_3CN with NH_4Cl/SCl_2 and chlorine



The main product (brown-yellow solid) had weak i.r. absorptions due to NH_4Cl (its presence was confirmed by recrystallisation from nitromethane) and major peaks at 1342(ms), 1025(ms), 989(m), 858(vs), 842(vs), 630(m), 624(ms) and 530(s) cm^{-1}. These bands were also present in the spectrum of the yellow solid (0.9 g). The brown-orange crystals (obtained by nitromethane recrystallisation) had i.r. absorptions at 1680(w,br), 1390(sh), 1348(m), 1130 (mw,br), 1029(s), 982(mw), 882(mw), 861(vs), 848(vs), 740(w), 637(w), 630(w), 535(s) cm^{-1}. Analysis found S, 41.10; Cl, 22.74; C, 15.74; H, 2.20; N, 18.42(100.20%). $CH_3CN_2S_2Cl$ required S, 41.47; Cl, 22.96; C, 15.52; H, 1.94; N, 18.12 (100.01%). Melting point (dark red liquid) = 182°C, some decomposition (yellow-white sublimate and darkening of crystals) occurred at 150°C - 170°C. The ^{35}Cl-n.q.r. spectrum (RT and 77K) showed no peaks in the range 5 - 35 MHz.

A sample of pure $CH_3CN_2S_2Cl$ in deuterated nitromethane gave the following p.m.r. spectrum (shifts measured relative to T.M.S.,downfield direction positive). δ = 1.05 ($\underset{\sim}{CH_3}CN_2S_2Cl$), 4.33 (residual protons from CD_3NO_2). Mass spectral peaks were at m/e (relative intensity):- 32(100)-S^+; 35(10)-Cl^+; 36(45)-HCl^+; 37(4)-iCl^+; 38(25)-CCN^+; 39(33)-$CHCN^+$; 40(86)-CH_2CN^+; 41(97);CH_3CN^+; 46(100)-SN^+; 58(4)-CNS^+; 64(27)-$S_2{}^+$; 70(4)-$CCNS^+$; 71(5)-$CHCNS^+$; 72(10)-CH_2CNS^+; 73(71)-CH_3CNS^+; 78(80)-S_2N^+; 87(2)-$CH_3CN_2S^+$; 119(81)-$CH_3CN_2S_2{}^+$ and 154(2)-$CH_3CN_2S_2Cl$ (parent peak).

A separate recrystallisation of crude material (8.6 g) from nitromethane (100 ml) gave a dark orange-brown powder which analysed as follows: S, 41.30; Cl, 22.86; C, 16.28; H, 1.94; N, 17.85 (100.23%).

Recrystallisation was also attempted of the crude solid (5.0 g) from acetonitrile (40 ml). The solution rapidly became turbid however, and the brown-green crystalline solid isolated had the following i.r. absorptions <u>in addition to</u> peaks due to $CH_3CN_2S_2Cl$: 2042(w), 1680(s,br), 1105(w,br), 445 (m) cm^{-1}. Chemical analysis found S, 31.20; Cl, 23.40; C, 18.41; H, 3.35; N, 21.11 (97.47%).

The yellow-brown solid (3.9 g) isolated from the mother liquor had i.r. absorptions (Nujol mull) at 3150(w,br), 1400(w,br), 1325(w), 1282(vs,br), 1220(s,br), 1150(w,vbr), 1080(m,br), 1020(vs,br), 868(m), 848(w), 837(m), 818 (ms), 740(m), 640(w), 598(w), 540(mw), 510(ms) cm^{-1}. Chemical analysis found S, 39.83; Cl, 25.50; C, 14.46; H, 1.05; N, 15.98 (96.82%) which gave an approximate empirical formula, $C_3S_3N_3H_3Cl_2$.

6.2.4 Synthesis of 4-methyl-1,2,3,5-dithiadiazolium hexachlorostannate (VI)

Tin (IV) chloride (0.15 ml, 1.3 mmol) was added with stirring (RT/½h) to $CH_3CN_2S_2Cl$ (0.4 g, 2.59 mmol) in thionyl chloride (30 ml). The solution was filtered to give a buff-coloured solid which was washed with pentane (2 x 10 ml), ether (2 x 10 ml) and dried *in vacuo*. Yield = 0.6 g. Analysis found C, 9.14; H, 1.37; N, 10.20; S, 21.46; Sn, 20.70; Cl, 37.13 $(CH_3CN_2S_2)_2SnCl_6$ required C, 8.42; H, 1.05; N, 9.83; S, 22.50; Sn, 20.83; Cl, 37.37. I.r. absorptions (Nujol mull) were at 1680(mw), 1392(s), 1353(s), 1043(s), 1029(m), 995(m), 876(vs), 843(vs), 624(m), 544(ms) and 315(br) cm^{-1}. The ^{35}Cl-n.q.r. spectrum (RT and 77K) showed no peaks in the range 12-20 MHz.

6.2.5 Reaction between Bu^t-CN and SCl_2/NH_4Cl

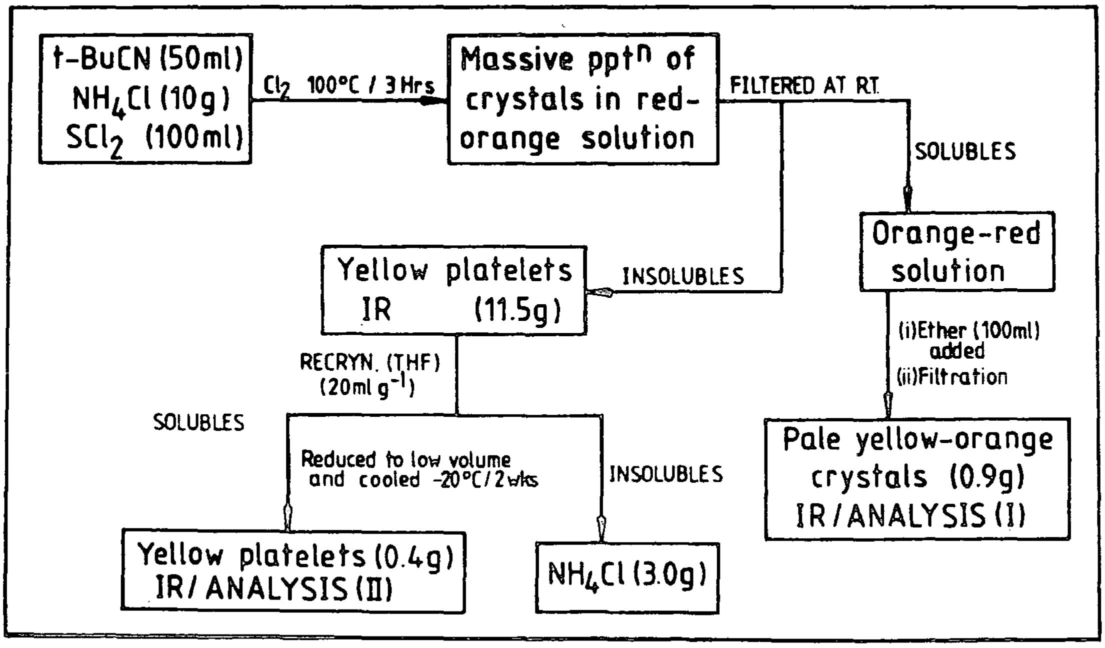


Table 6.2 contains analytical data for the yellow-orange crystals (I) and the yellow platelet crystals (II).

TABLE 6.2

	I	II	Calculated for $Bu^{t}CN_2S_2Cl$
S	32.36	32.40	32.61
Cl	18.05	17.70	17.75
C	30.98	30.87	30.51
H	4.13	4.28	4.58
N	13.78	14.12	14.25
	99.30	99.37	99.70

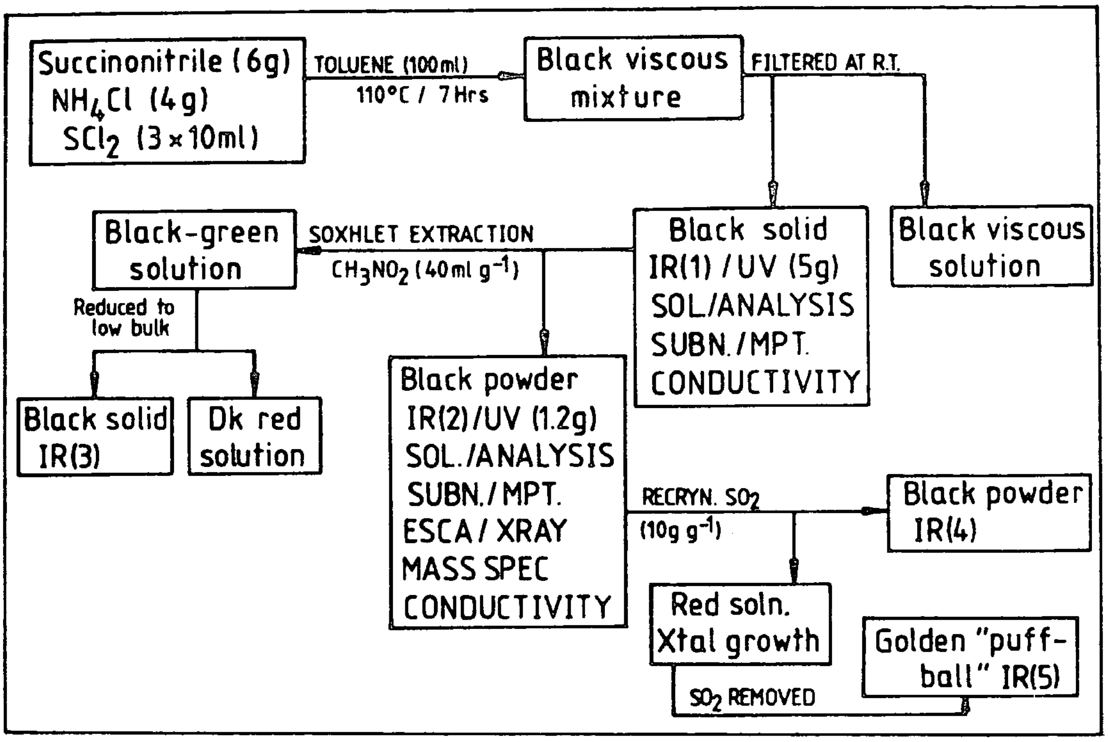
The pure crystals (II) had i.r. absorptions (Nujol mull) at 1402(m), 1364(vs), 1222(s), 1205(mw), 981(w), 942(mw,sh), 886(vs), 857(s), 732(ms) and 557(m) cm^{-1}. (<u>cf</u>. Reference 5). The infra-red spectrum of the crude yellow solid (11.5 g) showed it to be a mixture of $Bu^{t}CN_2S_2Cl$ and unreacted NH_4Cl.

Major mass spectral peaks were at m/e (relative intensity): 15(17)-CH_3^+; 26(14)-CN^+; 32(15)-S^+; 35(>100)-Cl^+; 36(>100)-HCl^+; 37(>100)-iCl^+; 38(>100)-$iHCl^+$; 41(>100)-CH_3CN^+; 42(>100)-$(CH_3)_2C^+$; 46(>100)-SN^+; 57(>100) - $(CH_3)_3C^+$; 64(76)-S_2^+; 67(48)-$CH_3C_2N_2^+$; 68(>100)-$(CH_3)_2C_2N^+$; 82(100)-$(CH_3)_2C_2N_2^+$; 83(10)-$(CH_3)_2C_2N^+$; 100(56)-$(CH_3)_2C_2NS^+$; 115(25)-$(CH_3)_3C_2NS^+$; 131(8)-$CH_3C_2N_2S_2^+$; 146(>100)-$(CH_3)_2C_2N_2S_2^+$; 161(>100)-$(CH_3)_3C_2N_2S_2^+$; 196(1)-$(CH_3)_3C_2N_2S_2Cl$. A sample of pure $Bu^{t}CN_2S_2Cl$ in deuterated nitromethane gave the following p.m.r. spectrum (shifts measured relative to T.M.S., downfield direction positive). δ = 1.66 $(CH_3)_3CN_2S_2Cl$; 4.33 (residual protons from CD_3NO_2).

6.2.6 Attempted synthesis of t-butyl-1,2,3,5 dithiadiazolium hexachlorostannate (VI)

$Bu^{t}CN_2S_2Cl$ (0.5 g, 2.54 mmol) was stirred with tin (IV) chloride (0.3 ml, 2.54 mmol) in thionyl chloride (30 ml) for 20 mins. during which time the yellow solution became colourless. The mixture was filtered to give a fine white solid, however, on washing with ether an instantaneous reaction occurred to produce a yellow oil. Further decomposition to give a milky-white suspension was observed on exposure to moisture. The reaction was not investigated further.

6.2.7 Reaction between $(CH_2CN)_2$ and SCl_2/NH_4Cl



Sulphur dichloride (10 ml) was added to start the reaction and again after 2½ h. and 5 h. of refluxing. Positive tests were obtained for the evolution of Cl_2 and HCl gases, though only HCl was detected after about ¾ h.

(i) Infra-red spectroscopy on the black solid products was largely uninformative with spectra showing few weak, broad absorptions (Nujol mulls): IR(1): 3150(m,vbr), 1675(m,vbr), 1400(m), 1300(w,br), 1150(w,br), 1090(w,br), 1030(w,br), 1000(w), 960(w,br), 840(br), 520(w,br) cm^{-1}. IR(2) when compared with this showed the absorption at 1675 and slightly better resolution of those at 1300 and 1150 (including a very weak absorption at 1168 cm^{-1}. There were absorptions at 965(w,br), 890(w), 840(br) cm^{-1}. When IR(2) was repeated as a KBr disc, strong, very broad absorption between 3500 and 2500 cm^{-1} was observed. IR(3) was virtually identical to IR(2). The black solid remaining after attempts to recrystallise a product from liquid SO_2 gave IR(4) which was similar to IR(2). Some material was extremely soluble in the SO_2, dissolving to give an intense red-black solution. Attempts to grow crystals from this solution were unsuccessful. When the solution was evaporated to dryness a honey-coloured, resinous "puff ball" formed in the flask which had an i.r. spectrum, IR(5) similar to IR(4).

(ii) Chemical analysis on two black powders, before (I) and after (II) Soxhlet extraction with acetonitrile are contained in Table 6.3.

TABLE 6.3

	I	II	Calculated for $C_4H_5N_2SCl$
C	29.09	26.58	32.32
H	3.16	2.58	3.36
N	18.10	18.50	18.85
S	20.30	17.94	21.54
Cl	24.80	19.90	23.91
	95.45	85.50	99.98

(iii) Solubility tests on the two black powders produced similar results. The materials were insoluble in most low polarity solvents (e.g. ether and toluene); slightly soluble in hot polar solvents (e.g. CH_3CN and benzonitrile) and very soluble (giving intense red-brown solutions) in formic acid and concentrated sulphuric and nitric acids. There was some decomposition in nitric acid. Attempts to precipitate a solid from sulphuric acid solution (by addition of glacial acetic acid according to Jolly[8])were unsuccessful.

(iv) Melting point determination The black solid decomposed above 300°C to give yellow-white oily droplets and white crystals.

(v) Mass spectroscopy The following data was obtained on the acetonitrile washed solid $[m/e\ (I/I_o)]$: 69(13.5), 76(12.6), 77(60.5), 91(11.5), 105(85.9), 178(80.4), 179(12.3), 180(10.4), 182(37.8), 202(3.1), 289(32.7), 290(28.8).

(vi) Sublimation attempts Sublimation (120°C, 10^{-1} mm Hg) of the black solid resulted in a sticky black-brown film on the coldfinger (10°C). A smear (between KBr plates) showed absorptions at 3150(w,br), 1312(w), 1296(w), 1150(w), 1004(w), 960(w,br), 810(w), 782(w), 610(w,br), 480(w) cm^{-1}.

Sublimation (140°C, 10^{-2} mm Hg) of the Soxhlet extracted black solid however produced only a thin white layer on the coldfinger. The i.r. spectrum of the black residue was similar to IR(2).

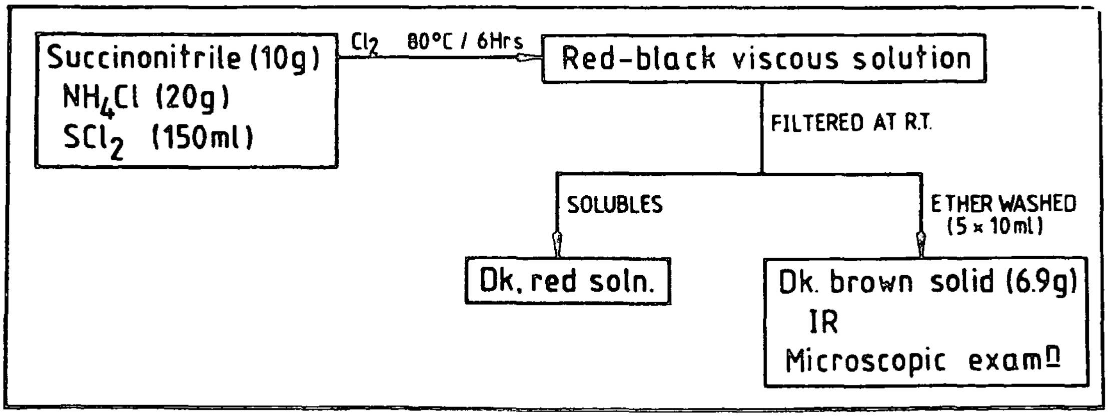
(vii) Ultra-violet spectroscopy U.V. spectra (450-200 nm) of the black solids dissolved in conc. sulphuric acid (0.11 mg ml^{-1}) showed similar results. A weak, broad absorption at 400 nm (Absorbance, $\varepsilon = 0.6$) and a stronger one at 237 nm ($\varepsilon = 1.8$) with a shoulder at 265 nm. After 72 hours, some decomposition had occurred. The absorption at 237 nm had become broader with a new peak forming at 305 nm ($\varepsilon = 1.2$). The absorption at 400 nm was unchanged.

(viii) X-ray diffraction An X-ray powder diagram of the acetonitrile washed solid (8 h exposure to FeK$_{\alpha 1}$ radiation) showed no strong diffraction lines.

(ix) Conductivity The room temperature D.C. resistance (measured with an Avometer) of pressed pellets (5 mm diam. x 5 mm) of the black solids was found to be greater than 10^{8} ohms.

(x) ESCA Binding energies measured for the acetonitrile washed solid were as follows: 164.1 - S(2p); 197.6 (50%), 201.1 (50%) - Cl(2p); 400.1 - N(1s) and 532.4 - O(1s)eV. Measurement of peak intensities gave the empirical formula $C_4N_2S_2Cl_2O$ (see discussion, section 6.3.3).

6.2.8 Reaction between $(CH_2CN)_2$, NH_4Cl and SCl_2/Cl_2

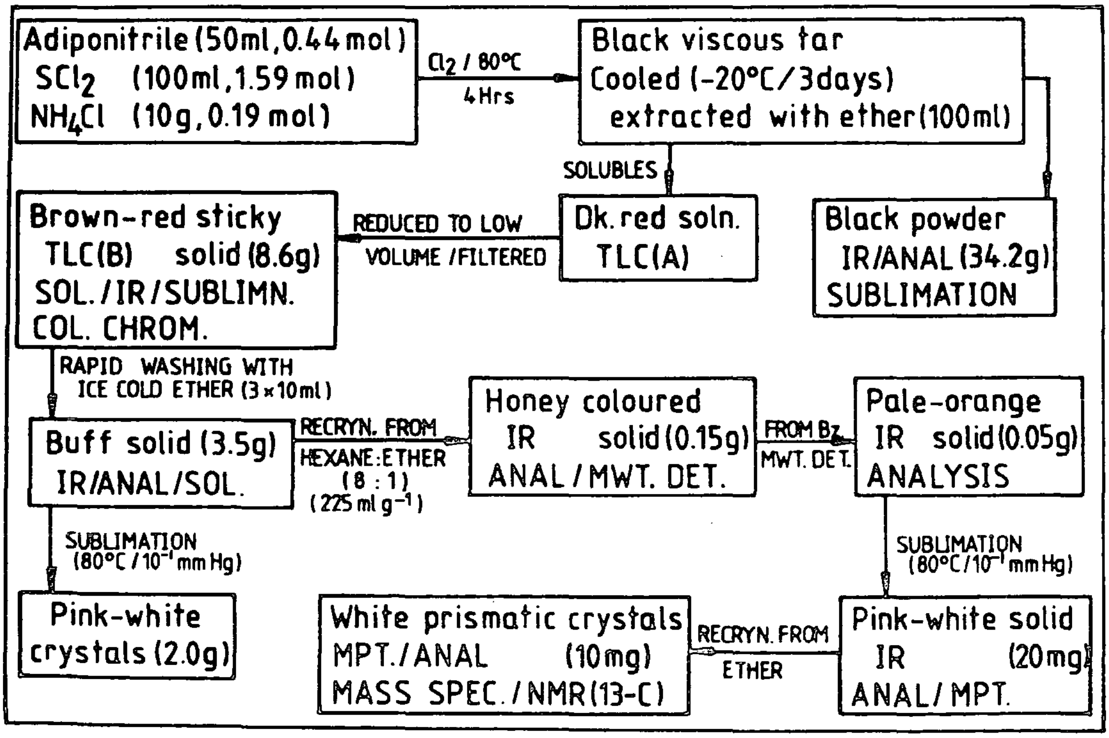


The dark brown solid appeared under the microscope to be a mixture of massive, transparent block crystals (unreacted NH_4Cl) and a dark orange-brown powdery solid. I.r. spectroscopy confirmed the presence of NH_4Cl, but there were a few extra peaks at 1690(vs), 1050(ms), 850(m,br), 680(m,vbr) and 580(m) cm^{-1}. Recrystallisation was attempted from nitromethane but no solid could be precipitated from the filtrate and evaporation to low volume produced a sticky brown resin.

6.2.9 Reaction of $(CH_2CN)_2$ with $(NSCl)_3$

$(CH_2CN)_2$ (0.1 g, 1.25 mmol) was stirred with $(NSCl)_3$ (0.2 g, 0.82 mmol) in toluene (30 ml) for 21 days at room temperature. The orange-brown solution was filtered to produce a pale yellow solid (0.1 g) which was identified as mainly S_4N_3Cl. The filtrate was evaporated to low volume, cooled to -20°C (10 days) and filtered to give a few large dark brown-orange crystals. These were characterised as unreacted $(NSCl)_3$.

6.2.10 Reaction of $(CH_2CH_2CN)_2$ with NH_4Cl and SCl_2/Cl_2



(A) Ether insolubles

The black powder gave only weak, broad i.r. absorptions at 1680, 1300, 1150 and 890 cm^{-1}. In an attempt to extract a product by sublimation

(80°C/0.1 mm Hg) the powder melted and liquid droplets condensed at the top of the flask. A thin white film condensed on the coldfinger (-197K) which was not characterised because of its low concentration. The black solid residue smelled of SO_2 and dissolved readily (with some oxidation) in conc. nitric acid. Analysis found S, 82.4; Cl, 5.5; N, 4.3; C, 7.1.

(B) Ether solubles

(i) Thin layer chromatography

Both the dark red ether solution and a solution of the brown-red solid in $CHCl_3$ were investigated by t.l.c. (in $CHCl_3$). R_f values were measured as follows:

TLC(A):	0.24(f)	0.68(f)	0.75(f)	0.91(s, dk. red)	0.95(s)	0.98(s)
TLC(B):				0.90(s, dk. red)	0.94(s)	0.96(s)

(ii) Solubility tests

In qualitative solubility tests the brown red solid was found to be very soluble in polar organics like CH_3NO_2 and CH_3CN, also in less polar solvents ($CHCl_3$, Et-O-Et, C_6H_6 and CS_2) but not in hexane or diisopropyl ether. A second set of tests on the buff solid confirmed these results and showed that it was slightly less soluble in ether than in chloroform.

(iii) Column chromatography

A sample of the brown-red solid was chromatographed on a silica gel column (30 cm x 1 cm) eluting with $CHCl_3$ (2 ml min^{-1}). The results are shown in Table 6.4. The strongest infra-red absorptions (Table 6.4) were recorded as follows:

Fraction 1: 2225(s), 1491(m), 1421(m), 1348(vs), 1311(ms), 1182(ms), 1122(m,br), 929(m), 892(m), 885(m), 850(s), 843(sh), 577(ms), 520(m), 438(ms), 397(m) cm^{-1} (cf. section (iv) below).

Fraction 6: 3600(br), 2940(s), 2875(m), 2242(s), 1455(s), 1422(m), 1350(m), 1330(m), 920(mw), 898(m), 888(m) cm^{-1}.

TABLE 6.4

Fraction (colour)	Volume (cc)	Reduced volume (colour)	Tests on reduced volume	
			Tlc(CH_3NO_2)	Evaporation to dryness
1 (orange)	15	2.0 (orange-red)	0.83(s)	Orange solid
2 (pale yellow)	16	-		
3 (yellow)	18	1.5 (orange)	0.83(f)	Some orange solid (sticky)
4 (yellow)	12	-		
5 (yellow-orange)	14	-		
6 (orange)	11	1.5 (dk. red)	0.70(f) 0.77(s) 0.83(f)	Red-oil
7 (yellow)	14	-		
8 (pale yellow)	16	1.0 (yellow)		Yellow oil
9 (colourless)	7	-		

[*cf.* pure adiponitrile: 3000(w,br), 2940(s), 2875(ms) (ν_{CH}), 2245(s) (ν_{CN}), 1458(s), 1422(s) (δ_{CH_2}), 1350(w), 1330(m), 1314(w) (w, τ_{CH_2}), 920(w), 898(m), 888(w), 733(m) (ρ_{CH_2}) cm^{-1}].

Fraction 6 also contained weaker absorptions corresponding to those recorded for fraction 1.

Ultra-violet absorptions were also measured on these two fractions (700-200 nm):

Fraction	Concentration ($CHCl_3$)	Absorption (ε)
1	4×10^{-4} mol dm^{-3}	280(1.92) 303(1.00) shoulder
6	0.02% V/V solution	274(1.22)

(iv) Infra-red spectroscopy

The crude red-brown, sticky solid (in Nujol) showed two nitrile absorptions at 2245(ms) and 2224(s). Other very strong absorptions (at 1350, 1183, 852, 578, *etc*.) corresponded to the strong peaks in fraction 1 (section iii) above . There were other peaks assignable to adiponitrile (*viz*. ν_{CH} and δ_{CH}) as well as weaker impurity peaks at 1460, 1415, 1205, 1075, 1008, 1000, 818, 741, 732, 482 and 470 cm^{-1}. After rapid ether washing, the pale buff solid had predominantly the absorptions as for fraction 1 (section iii) and none of the impurity peaks listed above. I.r. absorptions recorded after subsequent stages of purification (see reaction scheme) were identical in frequency and relative intensity. In general excellent spectra were obtained using KBr discs. The pure product (characterised below as 3,4-dichloro-2,5-dicyanothiophene) had absorptions at 2225(vs), 1496(mw), 1426(m), 1350(vs), 1314(ms), 1188(s), 1125(m), 932(ms), 895(mw), 887(mw), 853(s), 848(sh), 742(w), 579(m), 522(mw), 439(m), 415(w), 399(m) cm^{-1}.

Example of errors treatment (Benzene method) ‡

		PROBABLE ERROR	
ΔT	(deg)	$\delta\Delta T$	0.03
w	(mg)	δw	0.50
W	(g)	δW	0.01

w = weight of solute
W = weight of solvent
M = molecular weight.
K = cryoscopic constant

$$M = \frac{K.1000.w}{\Delta T.W}$$

Superposition of errors

$$\delta M^2 = \left(\frac{\partial M}{\partial \Delta T} \times \delta\Delta T\right)^2 + \left(\frac{\partial M}{\partial W} \times \delta W\right)^2 + \left(\frac{\partial M}{d w} \times \delta w\right)^2$$

$$\sqrt{\delta M^2} = \sqrt{\left(-\frac{K.1000.w}{W(\Delta T)^2}\right)^2 \times 9\times10^{-4} + \left(-\frac{K.1000.w}{\Delta T.W^2}\right)^2 \times 10^{-4} + \left(\frac{K.1000}{\Delta T.W}\right)^2 \times 25\times10^{-2}}$$

$$= \frac{K.1000.w}{\Delta T.W}\sqrt{\frac{9\times10^{-4}}{(0.184)^2} + \frac{1\times10^{-4}}{(17.75)^2} + \frac{25\times10^{-2}}{(95)^2}}$$

$$= 148.95\sqrt{0.026 + 32\times10^{-8} + \cancel{28\times}10^{-6}}$$

$$\therefore \underline{\delta M = \pm 24}$$

‡ I acknowledge help from Dr. Z. V Hauptman.

The largest error comes from measurement of temperature.

(v) Sublimation

On sublimation (80°C/0.1 mm Hg) the brown-red solid melted to a viscous dark-red liquid. A white semi-liquid deposit on the cold finger (-197K) was shown to be a mixture of adiponitrile and the substituted thiophene product. Some colourless prismatic crystals of the latter were also isolated from the walls of the sublimation apparatus.

Pure 3,4-dichloro-2,5-dicyanothiophene was isolated by sublimation of the pale buff and orange solids under similar conditions.

(vi) Molecular weight determination

Two independent cryoscopic techniques were used (i) freezing point depression of benzene and (ii) the Rast method (in camphor):

	Wt. Solute (g)	Wt. Solvent (g)	ΔT (°C)	MWt. Solute
Benzene	0.0950	17.7470	0.1840	149 ± 24
Rast	0.0045	0.0630	12.5000	227 ± 9

The latter method is recommended because of the large cryoscopic constant of camphor (39.7 $\text{mol}^{-1}\ \text{kg}^{-1}$). It is also a quicker procedure.

(vii) Analysis

Chemical analysis (Table 6.5) was the main criterion used to assess the purification steps outlined in the reaction scheme.

TABLE 6.5

Element	Solid					Calculated for $C_6Cl_2N_2S$
	Buff	Honey	Pale-orange	Pink-white	Transparent crystals	
C	31.92	33.88	35.28	35.48	35.94	35.46
H	0.61	-	-	-	-	-
N	12.00	12.56	12.84	12.95	13.78	13.79
S	27.40	19.36	17.38	18.40	15.75	15.79
Cl	29.30	32.36	31.10	34.50	34.63	34.96
Total	101.23	98.16	97.02	101.33	100.10	99.99

(viii) Melting point determination

The product (after sublimation) had a melting point of 125-126°C. The transparent prismatic crystals melted at 128.5°C (cf. 129°C).[9]

(ix) Mass spectrum

Mass spectral data (Table 6.6) was obtained on the transparent crystals.

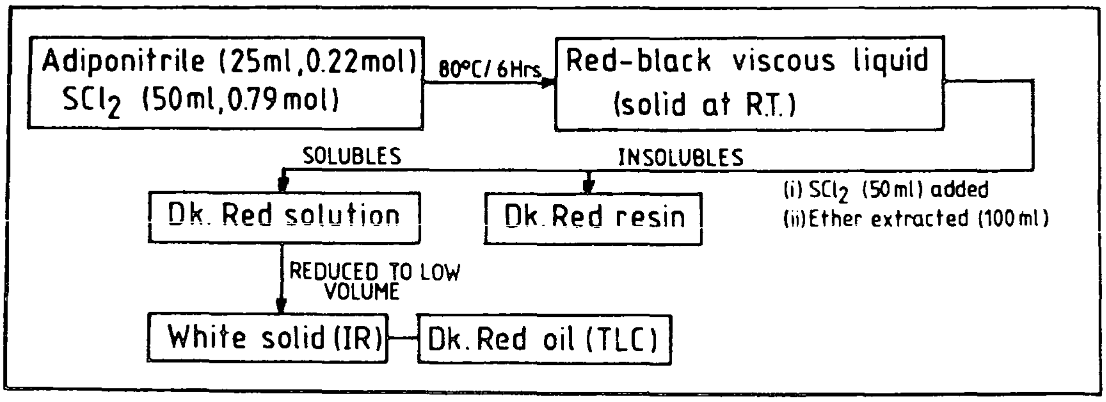
TABLE 6.6

$^m/_e$	I/I_o(%)	Fragment	$^m/_e$	I/I_o(%)	Fragment	$^m/_e$	I/I_o(%)	Fragment
38	(2)	C_2N^+	80	(5)	C_4S^+	117	(3)	C_3ClNS^+
44	(4)	CS^+	82	(5)	C_3NS^+	132	(9)	$C_4Cl_2N^+$/ $C_6N_2S^+$
56	(6)	C_2S^+	85	(2)	C_3ClN^+			
62	(9)	C_4N^+	94	(10)	C_4NS^+	167	(5)	$C_6ClN_2S^+$
68	(6)	C_3S^+	97	(6)	C_4ClN^+	202	(100) (P)	$C_6Cl_2N_2S^+$
70	(12)	C_2NS^+	106	(5)	C_5NS^+	204	(67)	isotope
						206	(14)	isotope

(x) ^{13}C-n.m.r. spectrum

A sample of pure 3,4-dichloro-2,5 dicyanothiophene in deuterated chloroform gave three resonances at 109.6, 111.3 and 135.5 ppm (chemical shift values were measured relative to T.M.S.).

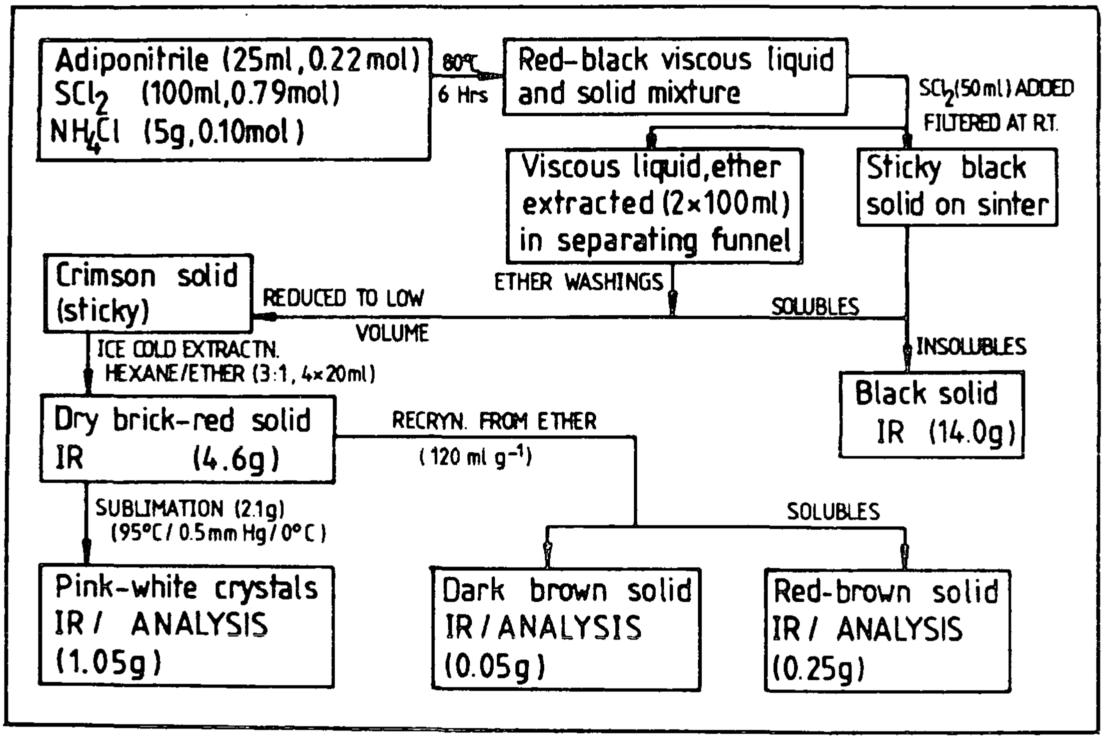
6.2.11 Reaction of $(CH_2CH_2CN)_2$ with SCl_2



The white solid (ca. 5 mg) showed only weak absorptions at 2915, 2840, 460 and 390 cm^{-1}. The red oil was chromatographed (in $CHCl_3$) and gave several brightly coloured components.

R_f	Component
0.00	grey-black/red-orange spots
0.91	purple band
0.95	broad orange band

6.2.12 Reaction between $(CH_2CH_2CN)_2$ and NH_4Cl/SCl_2



(i) Infra-red spectroscopy

The dry brick-red solid had absorptions at 3400(w,br), 2225(vs), 1675(w,br), 1497(m), 1425(ms), 1348(vs), 1314(s), 1265(ms), 1186(vs), 1124(ms), 1004(ms), 932(vs), 895(m), 888(m), 852(vs), 847(sh), 809(m,br), 742(w), 579(ms), 522(m), 472(w), 440(ms), 416(mw), 399(m) cm^{-1} (KBr disc) (cf. underlined absorptions with 3,4-dichloro-2,5-dicyanothiophene, section 6.2.10(iv). The remaining absorptions were also the strongest observed in the spectrum of the dark brown solid (ether insolubles) after recrystallisation: 1690(vbr), 1429(s), 1268(s), 1003(s), 809(ms), 705(mw), 678(w), 465(mw) cm^{-1}).

The pink-white crystals, obtained by sublimation were shown, by i.r. spectroscopy and chemical analysis (Table 6.7) to be largely 3,4-dichloro-2,5-dicyanothiophene.

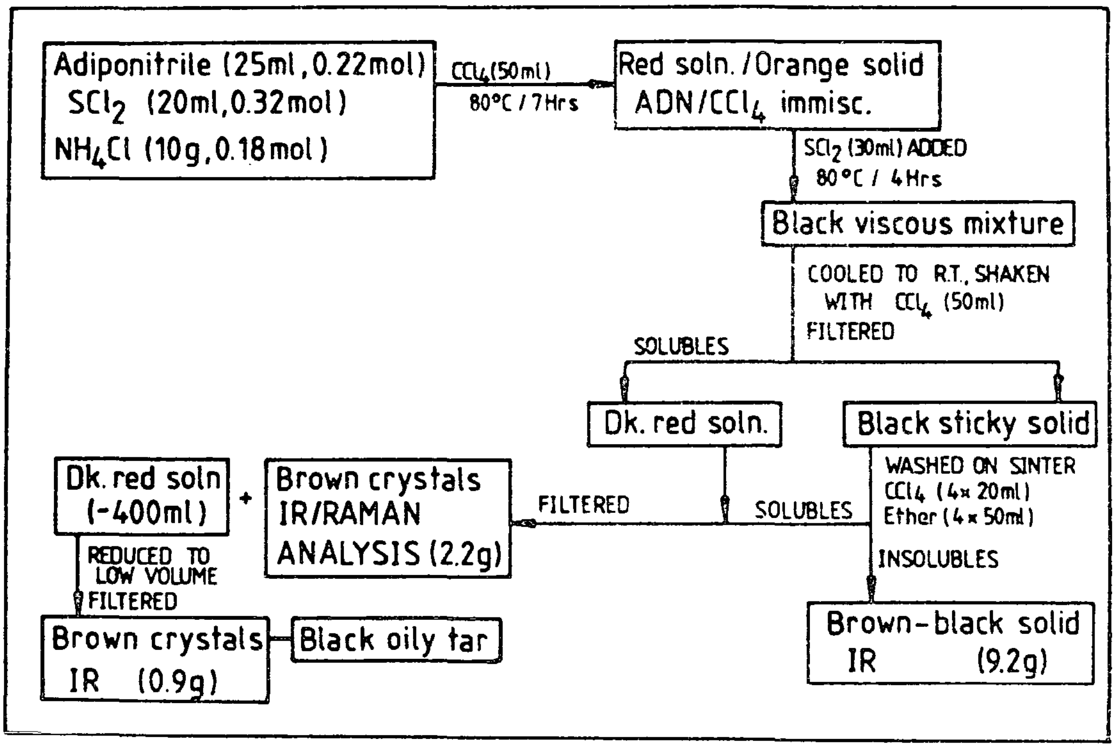
(ii) Analysis

Chemical analysis of the isolated products (named as shown in the reaction scheme) is contained in Table 6.7.

TABLE 6.7

Element	Solid			Calculated for $C_6Cl_2N_2S$
	Pink-white	Dk. brown	Red-brown	
C	34.77	21.08	33.48	35.46
N	13.59	8.53	12.94	13.79
S	17.55	39.80	20.30	15.79
Cl	34.20	22.80	31.80	34.96
	100.11	92.21	98.52	100.00

6.2.13 Reaction between $(CH_2CH_2CN)_2$ and SCl_2 (low conc) in CCl_4



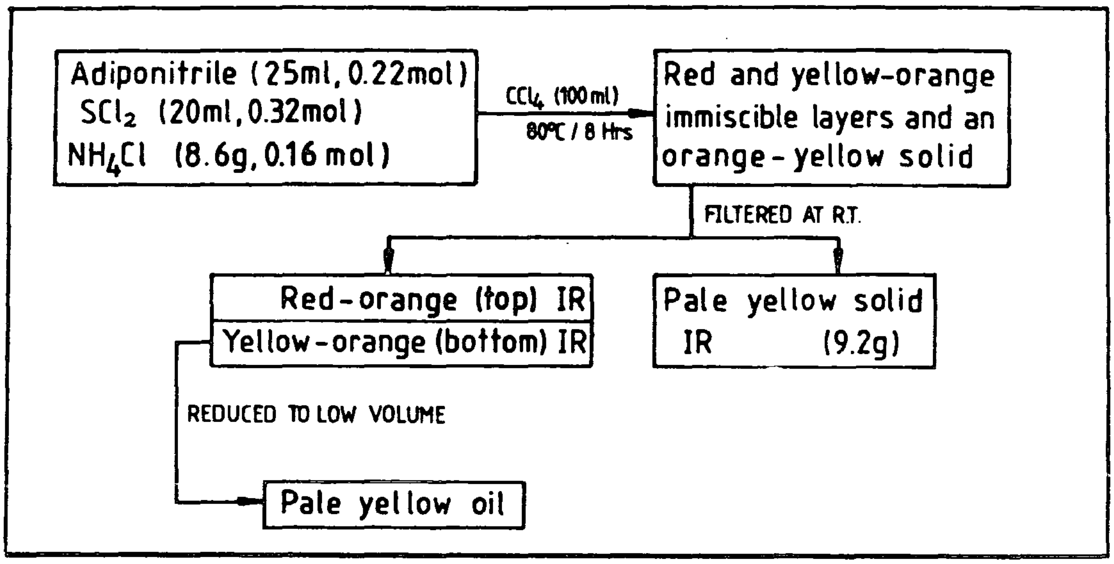
The brown crystals had no strong i.r. absorptions in the range 4000-400 cm^{-1}, had a sulphur analysis of 89.3% and gave Raman bands at 475(vs), 440(s), 244(s), 221(vs), 189(m) and 157(vs) cm^{-1}. (cf. sulphur standard; 477, 442, 250, 220, 190 and 157 cm^{-1}).

The brown-black solid had i.r. absorptions at 2150(s,vbr), 2242(mw), 1680(s), 1490(m,br), 1455(w,br), 1420(w), 1389(mw), 1308(mw), 1240(w,br), 1210(w,br), 1020(ms), 852(m,sh), 848(m), 700(m,vbr), 620(w) and 530(ms,br) cm^{-1}.

There was no spectral evidence for the presence of 3,4-dichloro-2,5-dicyanothiophene.

6.2.14 Reaction between $(CH_2CH_2CN)_2$, NH_4Cl and SCl_2 (low conc) in CCl_4

This reaction was a repeat of 6.2.13, performed in order to isolate the orange solid which was observed before the addition of extra SCl_2 (see reaction scheme 6.2.13).



The pale yellow solid had i.r. absorptions at 3150(w,br), 1395(m,br), 1158(m,sh), 997(s), 672(m,br), 560(m), 462(s), 448(m), 322(s) cm^{-1}. (Underlined peaks were due to S_4N_3Cl, cf. Chapter 1). I.r. solution spectra of the immiscible layers contained the following absorptions:

(i) Red-orange layer 2940(s), 2870(s), 2240(s), 1458(vs), 1422(vs), 1350(m), 1330(s), 1313(m), 1275(w), 1205(w), 1060(w), 1000(w), 920(w), 898(ms), 887(m) and 844(s) cm^{-1} (cf. adiponitrile, section 6.2.10(iii)).

(ii) Yellow-orange layer 1540(w,br), 1240(w), 1205(w), 1020(w), 1000(w), 970(w), 775(vs,br) cm^{-1} (due to CCl_4) and 2970(m), 2860(m), 1438(w), 1377(m), 1345(m), 1145(m), 1115(s) and 1070(m) cm^{-1} (unassigned).

6.3 Discussion

6.3.1 The 4-methyl-1,2,3,5-dithiadiazolium salts

Two synthetic routes to $CH_3CN_2S_2Cl$ were investigated, the reactions of CH_3CN with (i) $(NSCl)_3$ and (ii) SCl_2/NH_4Cl. Route (i) was previously studied by Alange[2b] who obtained an uncharacterised black oily product. To date, only Cl_3C- and $Ph-CN_2S_2Cl$ have been prepared by route (ii).

It was therefore decided to see whether other dithiadiazolium compounds could be prepared using this method.

$S_3N_2Cl_2$ and S_4N_3Cl were the major products of the reaction between CH_3CN and $(NSCl)_3$ in the presence of sulphur. No unreacted $(NSCl)_3$ was detected in the reaction mixture. Since S_2Cl_2 was observed in the mixture, it seemed likely that the sulphur caused dechlorination of $(NSCl)_3$ with subsequent ring expansion to S_4N_3Cl:

$$(NSCl)_3 + \tfrac{3}{8}S_8 \longrightarrow S_2Cl_2 + S_4N_3Cl$$

The $S_3N_2Cl_2$ was probably produced (as in the preparation of $S_3N_2Cl_2$)[10] by further reaction of S_2Cl_2 with $(NSCl)_3$:

$$\tfrac{2}{3}(NSCl)_3 + S_2Cl_2 \longrightarrow S_3N_2Cl_2 + SCl_2$$

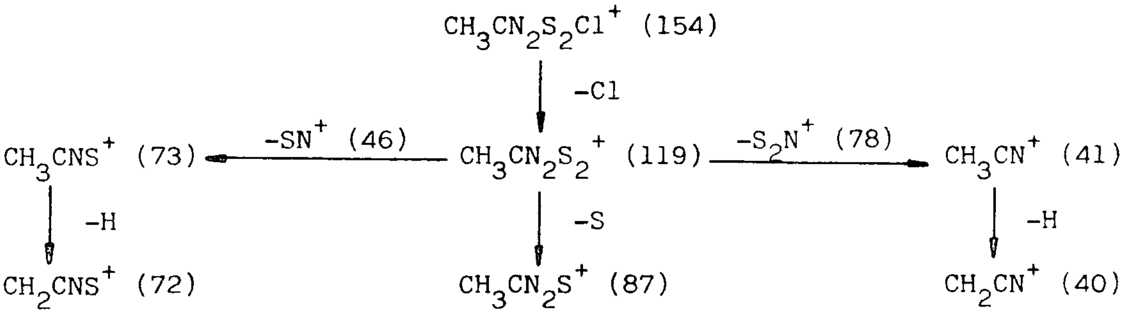
When $(NSCl)_3$ was stirred in excess CH_3CN for 15 hours, a very slow reaction occurred and some S_4N_3Cl was isolated. The product also contained a few mgs of dark red-orange crystals which were separated by hand under the microscope. The i.r. spectrum was very complex and contained several sharp absorptions in the region associated with S-N ring vibrations (1000-650 cm^{-1}). There was some similarity to the spectrum of $CH_3CN_2S_2Cl$ (section 6.2.3) but since the product was unlikely to have been a mixture it was probably a quite different C-S-N heterocycle. Subsequent filtrations however produced only unreacted $(NSCl)_3$.

The reaction of CH_3CN with NH_4Cl/SCl_2 in the presence of chlorine gas produced $CH_3CN_2S_2Cl$ in good yield (5.5 g of pure material as estimated from the recrystallisation data, section 6.2.3). The yield (based on excess CH_3CN) was only 2%, however it is unlikely that the reaction went to completion.

The i.r. absorption at 1348 cm^{-1} was assigned to a symmetrical bending vibration of the methyl group, $\delta_s CH_3$ (cf. 1375 cm^{-1} in aliphatic hydrocarbons)[11] and the other major absorptions (1029, 861, 848 and 535 cm^{-1} to complex C-S-N ring vibrations. C-S-N frequencies for the $RCN_2S_2^+$ cation are discussed in more detail in Chapter 7, page 239).

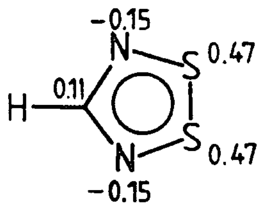
All the major peaks in the mass spectrum were assigned, and the following fragmentation pattern is suggested (Figure 6.1).

FIGURE 6.1



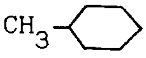
The ^1H chemical shift obtained for $CH_3CN_2S_2Cl$ was compared with several standards (Table 6.8). As expected the methyl protons in $CH_3CN_2S_2Cl$ are more strongly deshielded than those in methyl cyclohexane. The substituted groups -CN, -COOH and $-NO_2$ however are very much more strongly deshielding than $-CN_2S_2^+$.

An M.N.D.O. calculation of the net atomic charges in $HCN_2S_2^+$ [12] (III) indicated that most of the positive ring charge resides on the sulphur atoms. This was consistent with the small chemical shift observed for the protons in $CH_3CN_2S_2Cl$.



(III) TOTAL RING CHARGE = +0.98

TABLE 6.8

Compound	δCH_3 (ppm) [13]
$CH_3-(CH_2)_5-CHO$	0.89
	0.92
$CH_3CN_2S_2Cl$	1.05
$(CH_3CH_2)_2O$	1.16
CH_3-CN	1.95
CH_3-COOH	2.05
CH_3-NO_2	4.33

If an n.q.r. signal were to be detected at all in $CH_3CN_2S_2Cl$ it would be at a low frequency because the Cl^- anion is fairly symmetrical. However no signal was detected down to 5 MHz (the instrumental limit). This may have been because of the large size of the RCN_2S_2 cation. In n.q.r. spectroscopy weaker signals are generally observed for large cations (signal to noise ratio is typically only 2:1)[14]. This result might therefore suggest that there is very little covalent interaction between cation and anion in $CH_3CN_2S_2Cl$. Other evidence for the ionic nature of the compound came from its low solubility in low-medium polarity solvents.

Hexachlorostannates have been found to give ^{35}Cl n.q.r. frequencies in the range 15-18 MHz[15]. Salts with large cations give signals at the high frequency end of the range (e.g. $(Et_4N)_2SbCl_6$ 16.3-17.6 MHz) however, no signals were detected for $(CH_3CN_2S_2)_2SnCl_6$. This was probably due to the amorphous nature of the sample (strongest signals are obtained from highly crystalline solids) or because less than half of the required amount of sample was available (n.q.r. technique needs ideally 1-2 g).

The i.r. spectrum of $(CH_3CN_2S_2)_2SnCl_6$ was similar to that of $CH_3CN_2S_2Cl$ except that there was some shifting of the bands associated with the cation (Table 6.9) as would be expected for the altered cation symmetry caused by differing cation-anion interaction.

TABLE 6.9

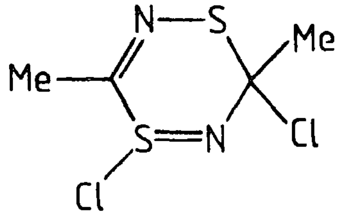
$CH_3CN_2S_2Cl$	$(CH_3CN_2S_2)_2SnCl_6$
1390	1392
1348	1353
1029	1043
992	995
861	876
848	843
630	624
535	544

The broad band centred at 315 cm^{-1} was due to Sn-Cl stretch (cf. 311,303 cm^{-1} for $SnCl_6^{2-}$)[16].

Evidence was obtained for the presence of a second (nonionic) C-S-N heterocycle in the reaction of CH_3CN with NH_4Cl/SCl_2 (section 6.2.3). The yellow-brown (SCl_2 soluble) solid (3.9 g) showed i.r. absorptions (at 1325, 1020, 868, 848 and 540) which were similar in position (though not in intensity) to absorptions in the spectrum of $CH_3CN_2S_2Cl$ (1348, 1029, 861, 848 and 535 cm^{-1}). The strongest bands however (at 1282 and 1220 cm^{-1}) were unique. It is difficult to construct a heterocycle from the empirical formula ($C_3S_3N_3H_3Cl_2$) bearing in mind that it should be covalent in nature and have a ring structure very similar to dithiadiazoles.

One possibility, a nonaromatic species (IV) could be formed by the reaction of CH_3CN, S (present as S_xCl_2 in reactions involving NH_4Cl/SCl_2) and the species $CH_3C(Cl){=}NSCl$ (postulated as an intermediate in the formation of $RCN_2S_2^+$, see Chapter 7, page 235).

(IV)



	CALC.	FOUND
S	29.53	39.83
N	12.90	15.98
C	22.10	14.46
Cl	32.69	25.50
H	2.76	1.05

Comparison with the experimental analysis was not very good however. Further study is required to determine the nature of this heterocycle.

6.3.2 The 4-t-butyl-1,2,3,5-dithiadiazolium salts

Bu^t-CN_2S_2Cl of a high purity was isolated from the reaction of Bu^t-CN with SCl_2/NH_4Cl. Previously it has only been prepared on a small scale from $(NSCl)_3$ (Table 6.1). The yield of pure material (estimated from the T.H.F. recrystallisation data) was 2.1 g (2% based on Bu^t-CN). The i.r. absorptions were similar to those reported by Bell[5]. The absorptions at 1402 and 1364 cm^{-1} were assigned to C-H bending vibrations (cf. 1395 and 1370 cm^{-1} in Me_3CH)[11]. Close correlation of absorptions at

981, 886, 857, 732 and 557 cm^{-1} with those in $CH_3CN_2S_2Cl$ (Table 6.10) confirmed their general assignment to C-S-N ring stretching vibrations.

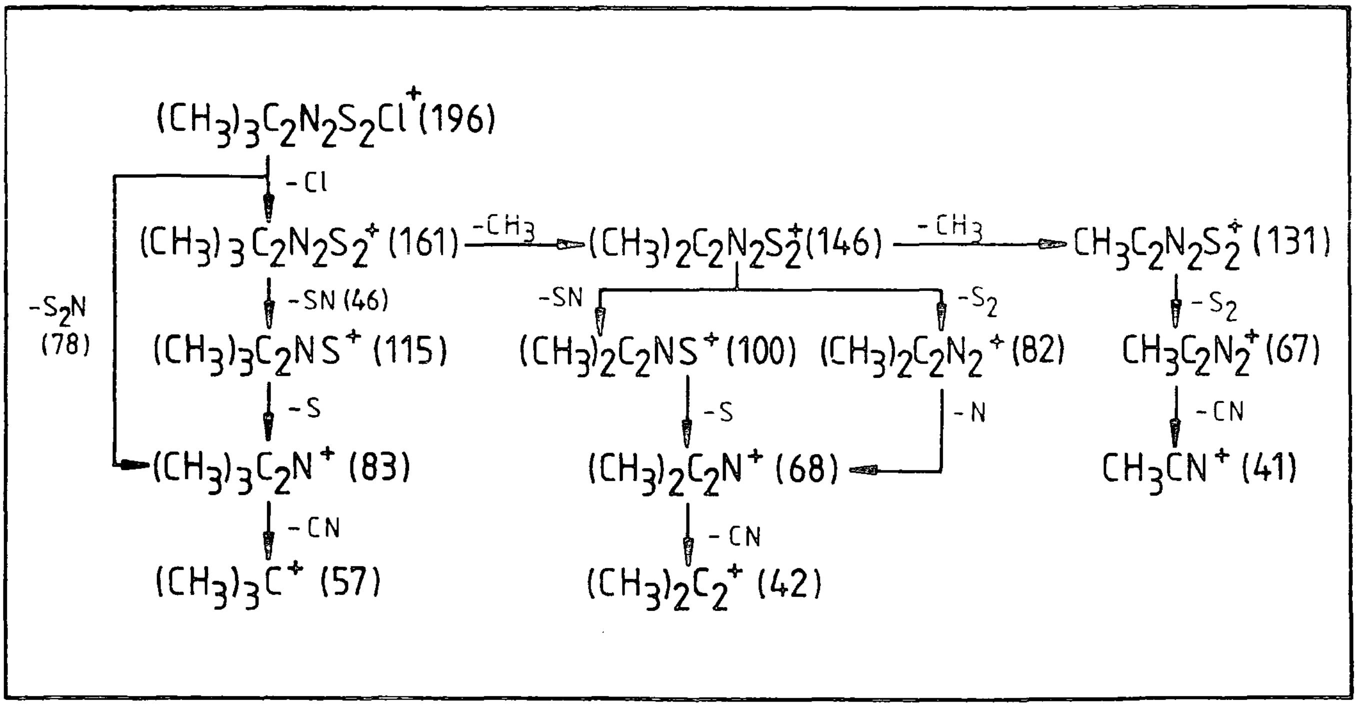
TABLE 6.10

$CH_3CN_2S_2Cl$	Bu^t-CN_2S_2Cl
1390	1364
1348	1222
1029	
992	981
861	886
848	857
630	732
535	557

The methyl protons of the t-butyl group were deshielded slightly (δ = 1.66) compared with those in $CH_3CN_2S_2Cl$ (page 202). The methyl protons in a similar compound, $(CH_3)_3CH$ absorbed at δ = 1.50.[17] As with $CH_3CN_2S_2Cl$, therefore, the dithiadiazolium ring in $Bu^tCN_2S_2Cl$ was only weakly deshielding.

All the major fragments in the mass spectrum of $Bu^tCN_2S_2Cl$ were assigned, and a breakdown pattern similar to $CH_3CN_2S_2Cl$ was constructed (Figure 6.2).

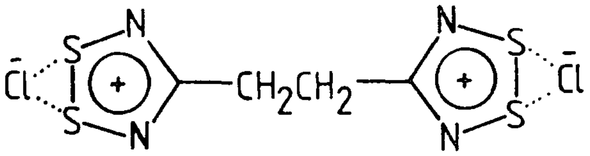
FIGURE 6.2



$(Bu^{t}-CN_2S_2)_2$ $SnCl_6$ was prepared in an analogous manner to $(CH_3CN_2S_2)_2SnCl_6$, however it was highly moisture sensitive and was not successfully isolated.

6.3.3 Reactions of succinonitrile and adiponitrile

The synthesis of double dithiadiazolium salts (e.g. V) was attempted from the aliphatic dinitriles, succinonitrile $(CH_2CN)_2$ and adiponitrile $(CH_2CH_2CN)_2$. There was, however, no evidence for the formation of the dithiadiazolium system in any of the reactions investigated (sections 6.2.7 - 6.2.14).

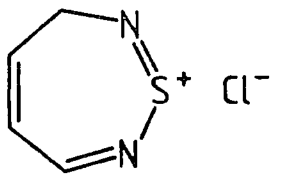

(V)

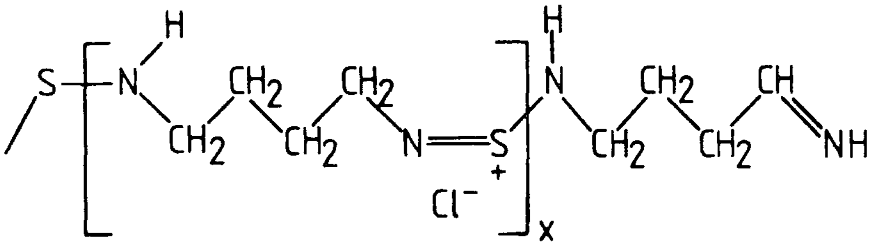
A slow reaction occurred at room temperature between succinonitrile and $(NSCl)_3$ to give S_4N_3Cl. This result was similar to that obtained in the reaction of CH_3CN and $(NSCl)_3$ (section 6.2.2). Only unreacted $(NSCl)_3$ was isolated from solution.

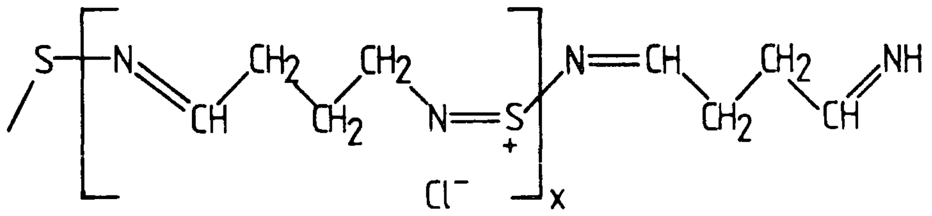
When $(CH_2CN)_2$ was reacted with $NH_4Cl/SCl_2(Cl_2)$ at low temperatures (section 6.2.8) a product was detected which had i.r. absorptions suggestive of a C-S-N heterocycle. The band at 1690 cm^{-1} was assigned to a C=N stretching vibration (cf. 1675 cm^{-1} in benzamidine hydrochloride)[18]. The compound decomposed when recrystallisation from hot nitromethane was attempted.

A different product was obtained when $(CH_2CN)_2$ was reacted with SCl_2/NH_4Cl at a higher temperature (in refluxing toluene). There was evidence from a variety of physical techniques (in particular the i.r. spectrum which contained only weak, broad absorptions) to suggest that the black powder (section 6.2.7) was polymeric in nature. Absorptions at 3150 and 1400 cm^{-1} were due to N-H stretching and bending vibrations respectively, whilst the one at 1675 cm^{-1} was probably due to C=N stretch.

The empirical formula, $C_4H_5N_2SCl$ (from elemental analysis) was consistent with a thiadiazepine ring (VI) or a C-S-N polymer (such as VII or VIII). The latter were more likely in view of the spectral data, and the observations of (i) high solubility in formic and concentrated sulphuric acids (ii) high melting point and (iii) lack of conductivity.


(VI)


(VII)


(VIII)

The presence of a strong UV absorption at 237 nm was also indicative of an isolated chromaphoric group, such as C=N or S=N. The presence of S=N (as in species VII) is more likely in view of the fact that the azomethine group ($>C{=}N-$) absorbs at 190 nm whereas S-N compounds have one or more absorptions in the region 235-262 nm (Table 6.11).

TABLE 6.11

Compound (solvent)	λ(nm) (19)
S_4N_4 (pentane)	260
$S_3N_2Cl_2$(c.H_2SO_4)	235/416
S_4N_3Cl	262/335
S_3N_2Cl (c. H_2SO_4)	248/356

After Soxhlet extraction with acetonitrile, chemical analysis indicated the presence of oxygen (total analysis was only 85% for five elements) and an empirical formula $C_4H_5N_2SOCl$. ESCA analysis confirmed that the material contained oxygen but suggested a different empirical formula ($C_4N_2S_2Cl_2O$).

The N(1s) B.E. suggested (Chapter 5, page 149) a secondary amine-like environment ($>$N — H) as in structure VII above. However the S(2p) B.E. was characteristic of nonoxidised sulphur, such as present in thiophene or diphenyl disulphide (Chapter 5, page 152). The value was too low for sulphur bonded to oxygen and neither structure VII nor VIII were consistent with this data.

There were two types of chlorine present in the polymer, the peak at 197.6 eV correlated well with anionic chlorine whilst that at 201.1 (of equal intensity) suggested oxidised chlorine (e.g. chlorine bonded to oxygen, Cl–O).

In summary, $(CH_2CN)_2$ was converted into a C-S-N polymer when reacted with NH_4Cl/SCl_2 under conditions which would normally produce a dithiadiazolium salt with a nitrile. It was readily oxidized, probably to an oxychloride, however the nature of these polymers was not determined and further investigation is necessary to characterise them.

Reactions of adiponitrile

Adiponitrile, $(CH_2CH_2CN)_2$ is an aliphatic dinitrile in which the chain length, compared to succinonitrile, is greater by two $-CH_2$ groups. When refluxed with SCl_2/NH_4Cl and chlorine under the usual conditions to form a dithiadiazolium cation (section 6.2.3), the chlorine was almost completely absorbed by the reaction, to produce a viscous black tar. (Usually in dithiadiazolium salt preparations the chlorine, involved only in the equilibrium between SCl_2 and S_2Cl_2 (see Chapter 7, page 233), left the reaction vessel in copious amounts).

The insoluble black powder (presumably polymer) was the major solid product, and appeared (from its i.r. spectrum) to be similar to the product obtained in the succinonitrile reaction. The i.r. absorption at 1680 cm^{-1} was probably due to C=N stretch. Chemical analysis showed that the polymer contained a high proportion of sulphur.

The dark red ether solution contained six covalent species of varying solubility and the sticky brown-red solid isolated from it contained the three least soluble components. These were very soluble in chloroform (R_f values from 0.9 - 1.0). On the basis of column chromatographic separation (using $CHCl_3$), and i.r. spectroscopy, two of these species were characterised (Table 6.12).

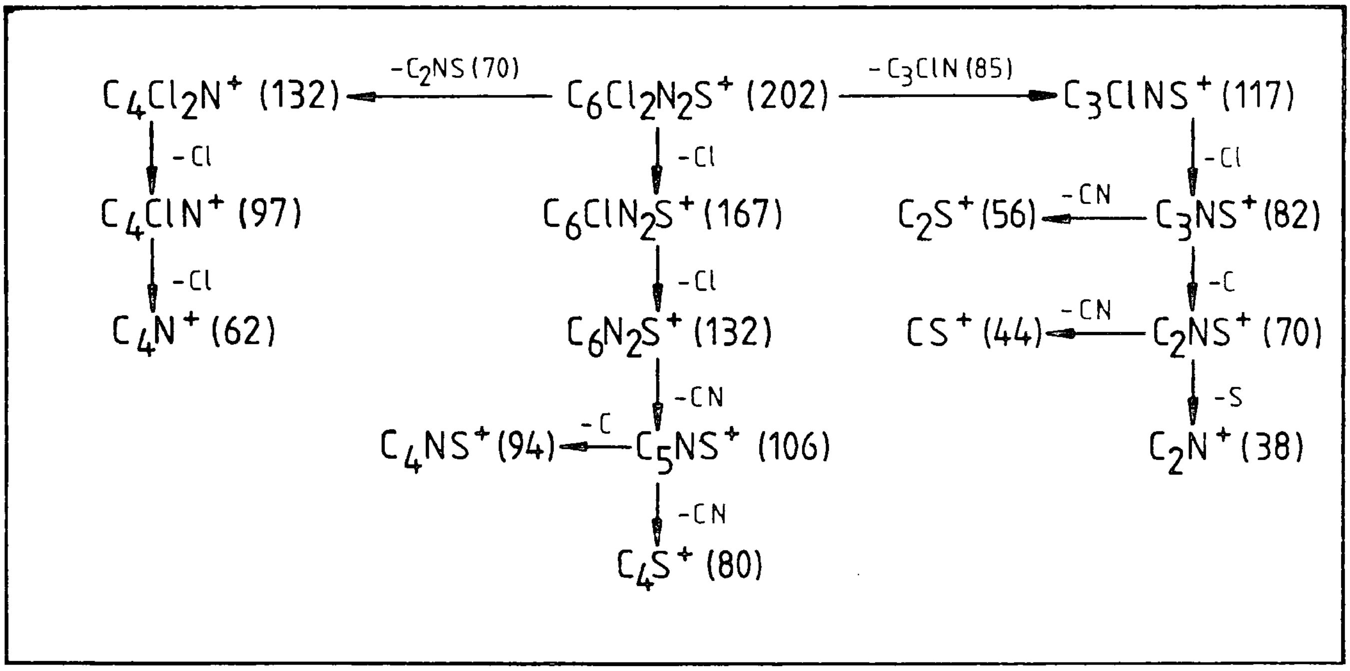
TABLE 6.12

R_f		Product
$CHCl_3$	CH_3NO_2	
0.96	0.83	3,4-dichloro-2,5-dicyanothiophene
0.94	0.77	adiponitrile
0.90	0.70	dark red oil

The dark red oil and the viscous adiponitrile adhered to the brown-red solid precipitated from ether solution, and because they had low volatilities, they could not be removed by pumping on the solid in vacuo. Furthermore their presence confounded attempts to obtain pure substituted thiophene by sublimation of the brown-red solid. A solvent was therefore required which was miscible with adiponitrile and the red oil and in which the thiophene product was insoluble. In practice only rapid washing with ice-cold ether was successful, although in terms of solid product lost (ca. 55-60%) this procedure was far from satisfactory.

The buff solid was largely 3,4 dichloro-2,5-dicyanothiophene with a sulphur impurity (13.6% by weight, based on chemical analysis). Sublimation at this stage of purification produced a pink-white crystalline solid. This was further recrystallised from ether to give transparent white prismatic crystals which were characterised by chemical analysis and melting point. The melting point was within 0.5°C of that reported by Goralski[9]. Analytical data (section 6.2.10B(vii)) showed that the C, N and Cl analyses were low (but increased) and S was high (but decreased) as the purity of the sample increased. This was consistent with a sulphur impurity. There are no recorded i.r. data on 3,4-dichloro-2,5-dicyanothiophene, however the spectrum obtained for the pure sample had strong, sharp absorptions with very little background noise. The mass spectrum showed a clear parent peak at $^{m}/e$ = 202 (100% intensity) and a detailed fragmentation pattern was constructed (Figure 6.3).

Figure 6.3



As expected, all the chlorine containing fragments had isotope peaks at m+2, m+4 (e.g. Table 6.13).

TABLE 6.13

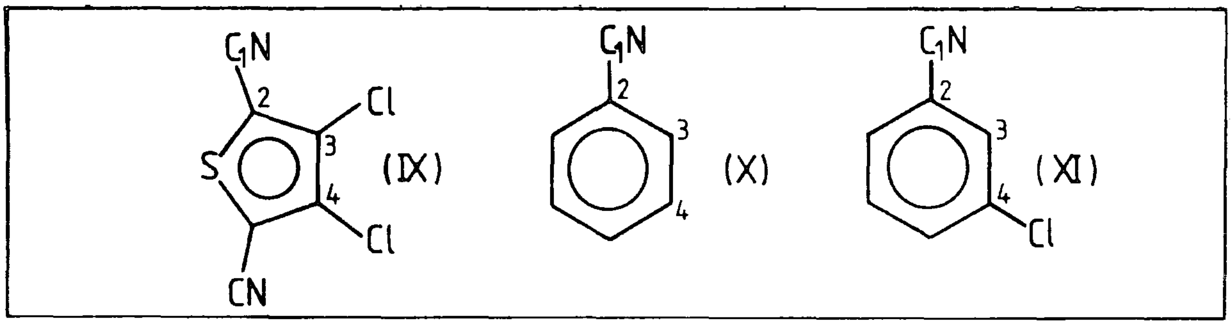
$^{m}/e$	Intensity	Theoretical for 2 chlorine-37 isotopes
(P) 202	100%	100%
204	67%	65.3%
206	14%	10.6%

Assignment of the 13-carbon chemical shifts measured for 3,4-dichloro-2, 5-dicyanothiophene, was made on the basis of comparison of these results with literature values for similar compounds (Table 6.14). No results were available for 2-chlorobenzonitrile.

TABLE 6.14

Compound (Ref)	Chemical shift (ppm)*			
	C (1)	C (2)	C (3)	C (4)
IX	111.3	109.6	135.5	135.5
X (20)	115.9	109.4	129.8	126.9
XI (20)	113.4	109.9	-	131.4

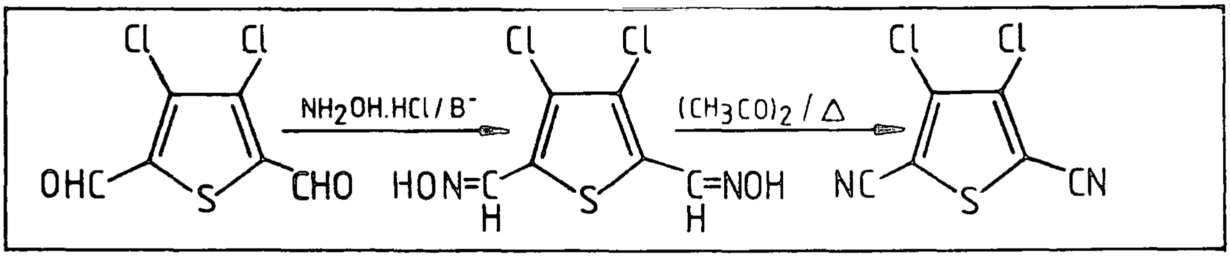
* All values measured wrt to T.M.S.



The deshielding effect of substituent chlorine can be seen by comparing the C(4) chemical shifts in compounds (IX) and (XI) with that in (X) (there is a downfield shift of 4-9 ppm). Resonances for C(1) and C(2) appear further upfield than might be expected, due to the shielding effect of circulating π-electrons in the nitrile group (magnetic anisotropy). The C(2) resonance is further shielded by the ring current present in these aromatic species.

3,4-Dichloro-2,5-dicyanothiophene

This compound was previously synthesised by Goralski[9] by the following route:



Since the carboxyaldehyde starting material also has to be prepared, the route is at least a 3-stage synthesis whereas the reaction described in this section is a simple one-stage preparation. The recommended purification procedure is as follows:

(1) Room temperature ether extraction of reaction mixture.

(2) Evaporation of ether to isolate crude solid (100).

(3) Rapid washing of sticky solid to remove viscous adherents (40).

(4) Sublimation of crude solid at 80°C/0.1 mm Hg (23).

(5) Recrystallisation of sublimate from ether (10).

The values in brackets compare the weight of product at each stage (based on details in section 6.2.10). The values show that the greatest loss of product occurred in stages (3) and (5) because of the high solubility of the thiophene in ether.

3,4-Dichloro-2,5-dicyanothiophene has been tested as a pesticide and used, in particular against bean mildew. Since the new route to this compound would be of significant interest to the chemical industry, it was felt desirable to assess the commercial viability of the synthesis. The estimated cost of raw materials to industry for the preparation is shown in Table 6.15 (prices as at 7.8.81)[21].

TABLE 6.15

Material	Unit cost	Cost per g. of thiophene
ADN	90c/lb	£0.05
SCl_2	£400/ton	£0.06
NH_4Cl	£210/10 ton	£0.0002

The total cost per gram of product is approximately £0.12 but inclusion of process costs (energy, labour, purification, etc.) would substantially increase this amount. Discussion with Mr. Young (Croda Chemicals, U.K.) has revealed that a 5-10-fold increase in yield (to 35% - 70%) would substantially increase the financial viability of the process.

Role of ammonium chloride and chlorine

The reactions described in sections 6.2.11 and 6.2.12 were done in order to determine whether NH_4Cl and chlorine were necessary for the formation of thiophene, since NH_4Cl appeared to take no part in the reaction.

No thiophene product was produced in the reaction between adiponitrile and SCl_2. However, it was formed when NH_4Cl was added (in the absence of chlorine). The results are summarised in Table 6.16.

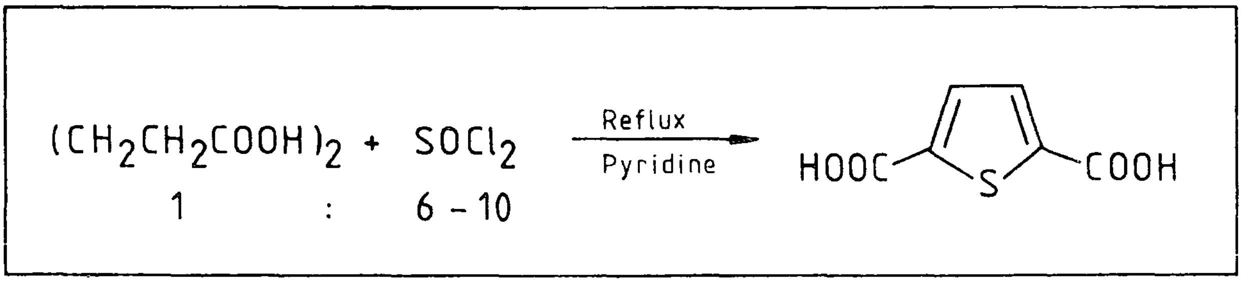
TABLE 6.16

Reagent	Reaction		
	6.2.10	6.2.11	6.2.12
ADN	✓	✓	✓
SCl_2	✓	✓	✓
NH_4Cl	✓		✓
Cl_2	✓		
Thiophene	✓	X	✓

Clearly NH_4Cl was essential for the formation of thiophene, whereas apparently chlorine was not. The mechanism (postulated below) requires the presence of a base, thus it may be that NH_4Cl fulfils this role, either as ammonia or as NSCl (by reaction with SCl_2):

$$NH_4Cl + 2SCl_2 \rightleftharpoons NSCl + 4HCl + \tfrac{1}{8} S_8$$

A thiophene synthesis, similar to the one described in this work was reported, in 1978, by Rauner[22] from adipic acid and thionyl chloride:



In this case pyridine (present in a catalytic amount) is probably also acting as a base in activating the 2,5-carbon atoms.

Table 6.17 compares the yield of thiophene obtained from reactions described in sections 6.2.10 and 6.2.12.

TABLE 6.17

Reaction	ADN (moles)	Wt. crude thiophene/gram (% of total wt)	Wt. Black solid/gram (% of total wt)	% yield crude thiophene (based on ADN)
6.2.10 (with Cl_2)	0.44	8.6 (20.1%)	34.2 (79.9%)	9.5
6.2.12 (without Cl_2)	0.22	4.6 (24.7%)	14.0 (25.3%)	10.3

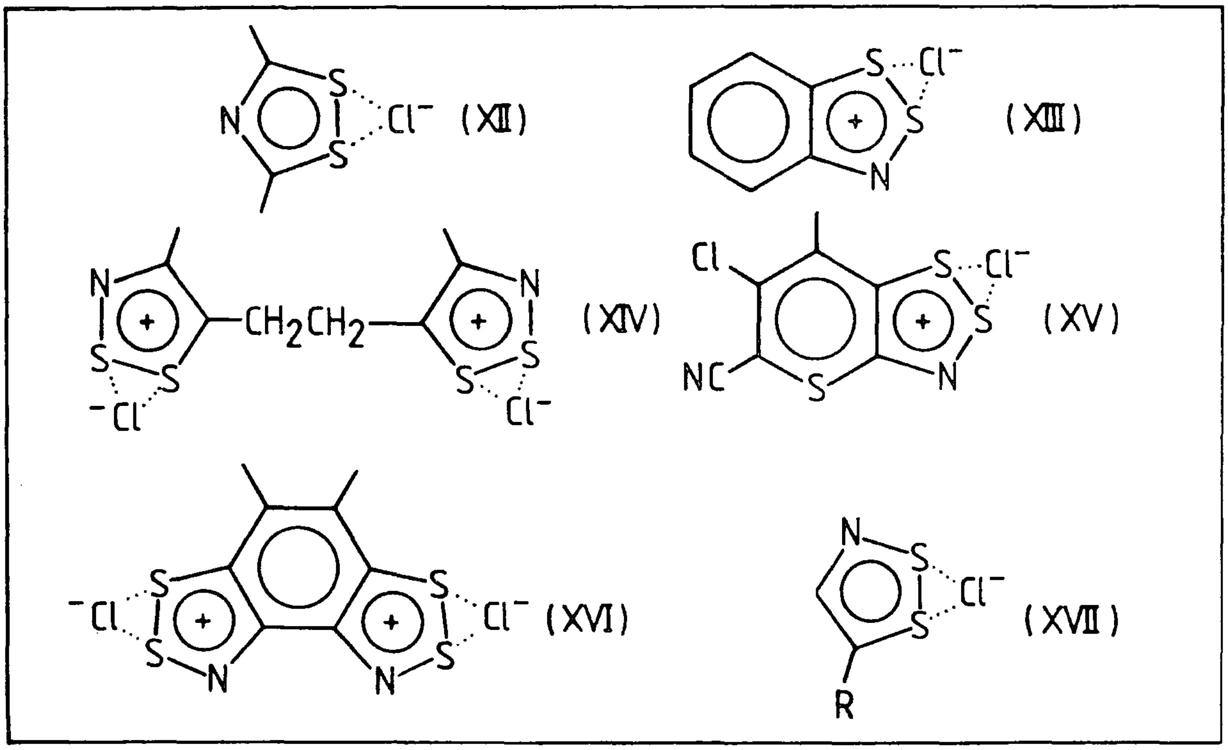
The results in Table 6.17 suggest, if anything, that the presence of chlorine had an adverse effect on the yield of thiophene possibly by increasing the amount of polymerisation of adiponitrile.

Reaction 6.2.11 showed that SCl_2 also caused polymerisation of ADN (when the molar ratio was approximately $4SCl_2$: 1 ADN). T.l.c. on the ether extract showed that there were several covalent species, very soluble in chloroform and intensely coloured. They were not studied further since they were not of central importance to the thiophene investigation.

The brick-red solid in reaction 6.2.12 was shown to contain 3,4-dichloro-2,5-dicyanothiophene, and also an ether insoluble impurity (14% by weight based on the ether recrystallisation data). Analysis gave the empirical formula C_3S_2NCl. Although this impurity contained no nitrile group and, in view of its solubility in other organic solvents, was probably ionic with organic groups, it was certainly not a dithiadiazolium compound since the stoichiometry of S : N was incorrect. The compound may therefore be a dithiazolium compound. The 1,2,4 dithiazolium chlorides (XII) and the benzo-1,2,3-dithiazolium chlorides (Herz compounds) (XIII) are a commonly known group of compounds. Some possible structures for the unknown impurity are shown in Figure 6.4.

Structures (XIV) and (XVI) are less favoured in view of evidence (sections 6.3.3 and 7.3.2) which suggested that it is not possible to isolate a double dithiadiazolium salt from reactions of dinitriles. Structure XV in which the adiponitrile skeleton has cyclised to form a fused ring is also

FIGURE 6.4



unlikely since it has a high sulphur content. Also any structure in which one nitrile group remains intact should show a nitrile absorption in the infra-red, which this impurity does not. Further work (e.g. proton, n.m.r. and mass spectroscopy) on a pure sample might be worthwhile since it is believed that, to date, no monosubstituted 1,2,3-dithiazolium salts (e.g. structure XVII) have been reported.

Reactions in carbon tetrachloride solution

The reaction of adiponitrile, SCl_2 and NH_4Cl was investigated (sections 6.2.13 and 6.2.14) in a moderating solvent, in order to try and reduce the quantity of black viscous resin present when neat SCl_2 was used. Carbon tetrachloride was chosen since it had a boiling point close to that of SCl_2.

The first stage, in which the ratio of $SCl_2 : NH_4Cl$ was approximately 2 : 1 produced only a yellow-orange solid which was subsequently identified (section 6.2.14) as S_4N_3Cl. There was no formation of a black viscous mixture until excess SCl_2 was added in the second stage. However, extraction of this mixture failed to produce any substituted thiophene. The only solid isolated from the ether/chloroform solution was identified as sulphur. This experiment showed that the ratio of SCl_2 : NH_4Cl was critical for the formation of 3,4-dichloro-2,5-dicyanothiophene. It should be greater than 2 : 1 and can be as high as 8 : 1. It is probable that there are two major requirements for the synthesis of the thiophene product:

(i) that SCl_2 can react with NH_4Cl to give NSCl and

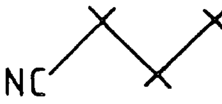
(ii) that NSCl performs the function of a base and in the presence of excess SCl_2 causes cyclisation of adiponitrile.

In the absence of excess SCl_2 (as in the first stage of reaction 6.2.13) adiponitrile remains unreacted and the NSCl is converted to S_4N_3Cl.

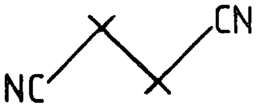
Reaction mechanism

When adiponitrile is refluxed with excess SCl_2 and NH_4Cl (with or without chlorine gas), the predominant reaction which occurs is cyclisation of the adiponitrile carbon skeleton with inclusion of sulphur, to form a very stable thiophene derivative; rather than reaction at the nitrile function which is the more usual occurrence (see reactions 6.2.3, 6.2.5, 7.1.1 and 7.2.3). Reaction at the nitrile group does occur, but to a lesser extent, although the product may be a dithiazolium, or a Herz, compound rather than a dithiadiazolium salt.

The factor which influences this change of mechanism may be the susceptibility of the α-CH_2 group to base attack (XVIII). This factor would also be significant in succinonitrile (XIX), and explains why the succinonitrile reaction (section 6.2.7) is closely analogous to the adiponitrile reaction. In acetonitrile (XX) and t-butyl cyanide (XXI) the mono nitrile groups are activated (by the positive inductive effect of the methyl groups) towards nucleophilic attack on sulphur dichloride (see mechanism (ii), Chapter 7, page 234). In these cases therefore the usual reaction occurs to give 4-methyl dithiadiazolium and 4-t-butyl dithiadiazolium salts.



(XVIII)



(XIX)

Me-CN

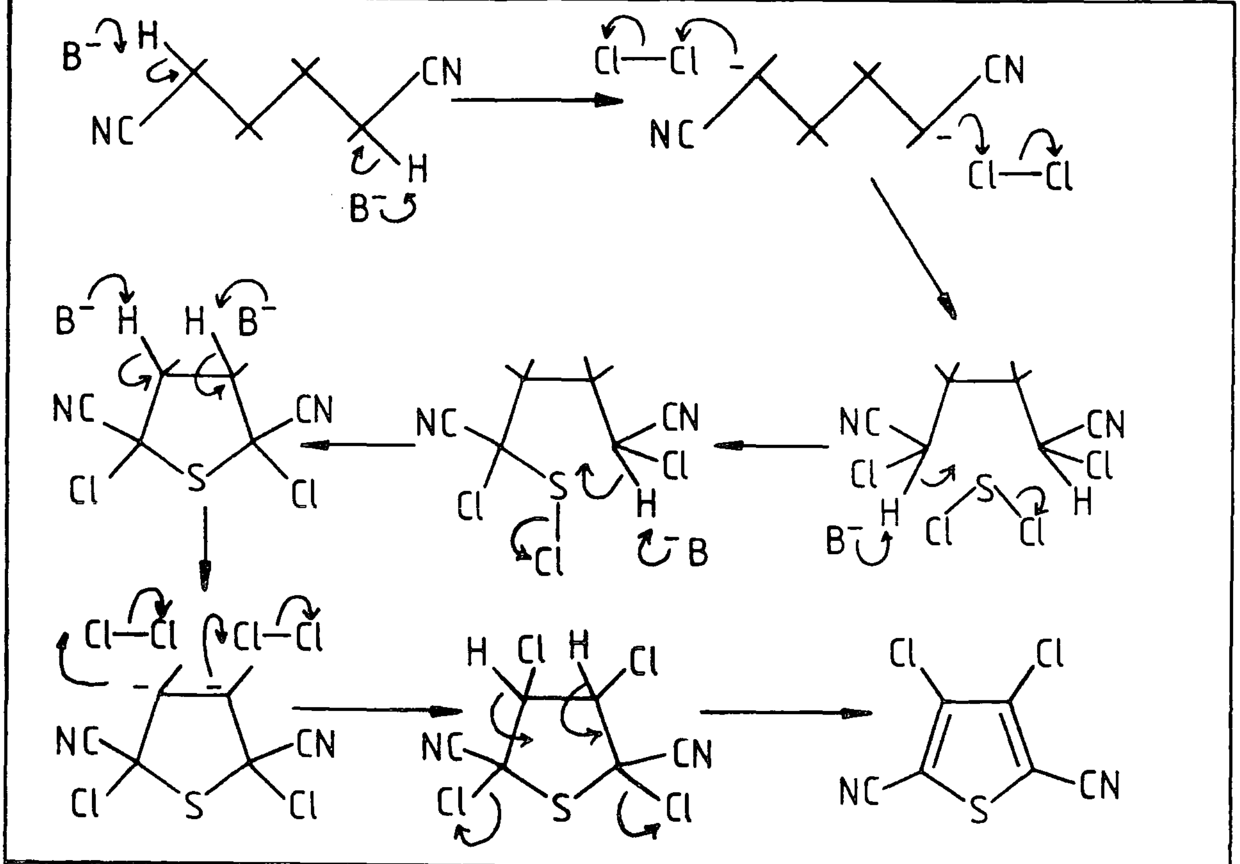
(XX)

$(Me)_3$-C-CN

(XXI)

A possible reaction mechanism for the formation of 3,4-dichloro-2,5-dicyanothiophene is shown in Figure 6.5.

FIGURE 6.5



It is likely that SCl_2 acts not only as a source of sulphur for ring closure, but also, by slow decomposition at reflux temperatures, it provides the chlorine required for substitution at carbon atoms 2,5 and 3,4 as follows:

$$2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2$$

This would explain why SCl_2 is required to be present in excess, and also why, when chlorine gas in passed through the reaction mixture there is no effect on the course of the reaction or on the yield of thiophene produced. The elimination of hydrogen chloride in the last stage of the mechanism is preferred to the loss of hydrogen cyanide or chlorine and the driving force for the elimination is the extra stability gained by delocalisation (thiophene has a delocalisation energy of $\sim$130 $KJmol^{-1}$ compared with $\sim$150 $KJmol^{-1}$ for benzene).[23]

6.3.4 Conclusions

Although the $RCN_2S_2^+$ ring system can be synthesised from the reactions of NH_4Cl/SCl_2 with nitriles, double dithiadiazolium salts cannot be prepared from dinitrile starting materials. Instead, with long chain aliphatic dinitriles, reaction occurs either at the nitrile groups to form C-S-N polymers, and/or at the α-methylene group (as the first stage towards cyclisation) to form sulphur heterocycles. It is likely that other sulphur and S-N heterocycles can be synthesised using this method.

6.4 References

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CHAPTER 7

PREPARATION OF SOME DITHIADIAZOLIUM SALTS WITH AROMATIC SUBSTITUENTS

7.1 Introduction

Preparations of $CH_3CN_2S_2Cl$ and $Bu^t-CN_2S_2Cl$ from the appropriate aliphatic nitrile, SCl_2 and NH_4Cl, were described in Chapter 6. This chapter describes attempts to prepare dithiadiazolium chlorides with aromatic substituents:

RCN_2S_2Cl R = Ph-, $NC{\cdot}C_6H_4$-, $O_2N{\cdot}C_6H_4$-, $Cl{\cdot}C_6H_4$-

A modification of the published synthesis of $PhCN_2S_2Cl$[1] and a new preparation from toluene are described (section 7.1.2). Several preparative routes to the 4(4-cyanophenyl) (section 7.2.1); 4(4-nitrophenyl) (section 7.2.2 and 4(4-chlorophenyl) (section 7.2.3) substituted salts were investigated: (i) nitrile/NH_4Cl/SCl_2 and (ii) nitrile/$(NSCl)_3$ (as described in the literature)[1] (iii) nitrile/NH_4Cl/SCl_2/toluene[2] and (iv) nitrile/NH_4Cl/SCl_2/Cl_2 (a modification of (i) described in section 7.1.1).

7.1.1 Preparation of $PhCN_2S_2Cl$ from PhCN, NH_4Cl, SCl_2 and Cl_2

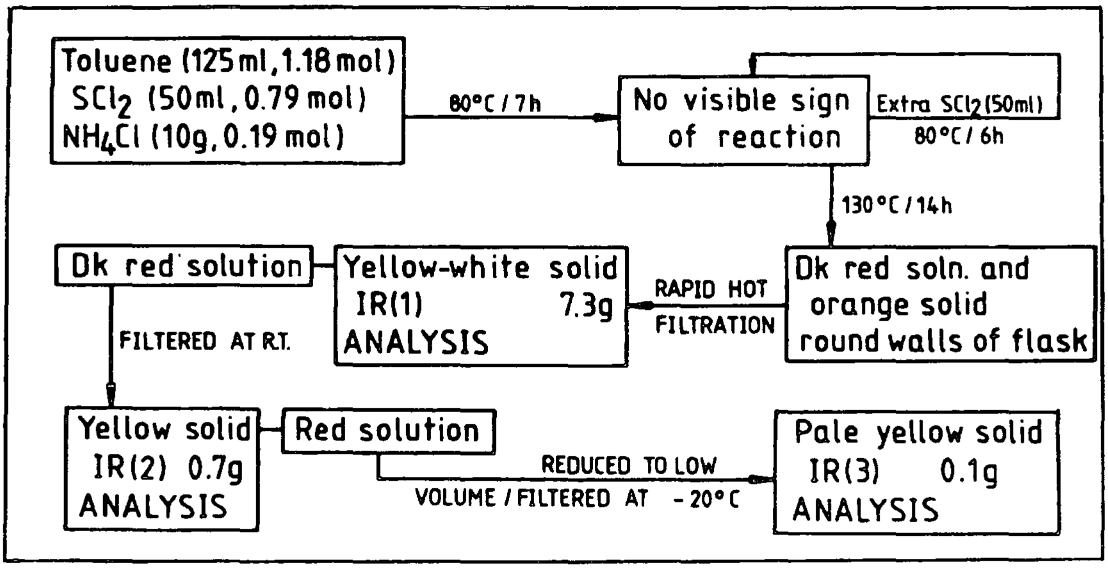
This procedure is a modification of the published method[1]. Benzonitrile (38 ml, 0.37 mol), SCl_2 (100 ml, 1.58 mol) and NH_4Cl (20 g, 0.37 mol) were refluxed for 5 hours with a stream of dry chlorine passing at a rate of 3-4 bubbles per sec. After 2-3 hours the chlorine was stopped for ½ hour during which time a build-up of red-brown crystals of $S_3N_2Cl_2$ was observed in the neck of the condenser. These had "melted" back into the flask within 30 minutes of restarting the chlorine flow. [$S_3N_2Cl_2$ reacts with Cl_2 to give $(NSCl)_3$ which is soluble in the refluxing S_2Cl_2/SCl_2 mixture.] After 5 hours the reaction was stopped and the contents of the flask were allowed to cool to room temperature. The mixture was filtered to give an orange-white solid (33.2 g) which was washed with ether (4 x 20 ml) and dried in vacuo. Microscope examination showed this solid to be a mixture of transparent crystal conglomerates (NH_4Cl) and orange prismatic crystals ($PhCN_2S_2Cl$).

I.r. absorptions (Nujol mull) were at 3150(w,br), 1594(w), 1579(vw), 1393(m), 1363(m,sh), 1348(m,sh), 1292(w), 1207(w), 1168(w), 1148(m), 1065(w), 1035(vw), 1030(w), 1000(w), 930(vw), 920(m), 890(vs), 842(s), 792(m), 780(m), 709(m), 697(vs), 543(ms), 520(w) cm^{-1}. (cf. underlined peaks with those for PhCN$_2$S$_2$Cl)[3] Analysis found S, 26.60; Cl, 14.70; C, 41.27; H, 2.75; N, 12.14 (97.46%) PhCN$_2$S$_2$Cl required S, 29.56; Cl, 16.39; C, 38.79; H, 2.31; N, 12.93 (99.98%). Purification of the crude PhCN$_2$S$_2$Cl is described in section 7.1.3. Estimated yield of pure PhCN$_2$S$_2$Cl recrystallised once from liquid sulphur dioxide, 15 g g^{-1} (section 7.1.3) was 23.3 g (30% based on benzonitrile).

The ^{35}Cl n.q.r. spectrum (R.T. and 77K) of a sample of pure PhCN$_2$S$_2$Cl showed no peaks in the range 5-35 MHz.

7.1.2 Preparation of PhCN$_2$S$_2$Cl from toluene

FIGURE 7.1



IR(1) showed mainly absorptions (Nujol mull) at 3300-3000(m,vbr), 2000(m,vbr), 1750(m,vbr) and 1400(m) (due to NH$_4$Cl) with weak absorptions at 1150, 920 885, 840, 790, 779, 693 and 545 cm^{-1} (due to PhCN$_2$S$_2$Cl). Analysis found S, 5.60; Cl, 54.60; C, 6.40; H, 8.56; N, 23.71 (98.90%) required for NH$_4$Cl : N, 26.17; H, 7.47; Cl, 66.35 (99.99%).

The pale yellow solid (0.1 g) had no strong absorptions in the infra-red, IR(3) and gave a sulphur analysis of 67.6%. The yellow solid (0.7 g) had i.r. absorptions, IR(2) (Nujol mull) at 3150(w,br), 1594(w), 1577(w), 1397(m), 1350(m,sh), 1290(w,br), 1207(w,br), 1167(w), 1148(m,br), 1065(w), 1025(w), 1000(w), 932(vw), 920(mw), 890(vs), 842(ms), 792(m), 780(m), 708(mw), 694(vs) and 542(ms) cm^{-1}. (cf. $PhCN_2S_2Cl$, section 7.1.1). Analysis found S, 32.60; Cl, 18.60; C, 34.30; H, 2.37; N, 12.25 (100.12%) required for $PhCN_2S_2Cl$: S, 29.56; Cl, 16.39; C, 38.79; H, 2.31; N, 12.93 (99.98%).

No reaction was observed when 4-methyl toluene was reacted, under similar conditions, with SCl_2/NH_4Cl.

7.1.3 Purification of $PhCN_2S_2Cl$

Crude $PhCN_2S_2Cl$ from several sources was recrystallised from a variety of organic solvents including toluene, nitromethane, nitrobenzene and liquid SO_2 and analytical results are compared (Table 7.1) with data for pure $PhCN_2S_2Cl$.

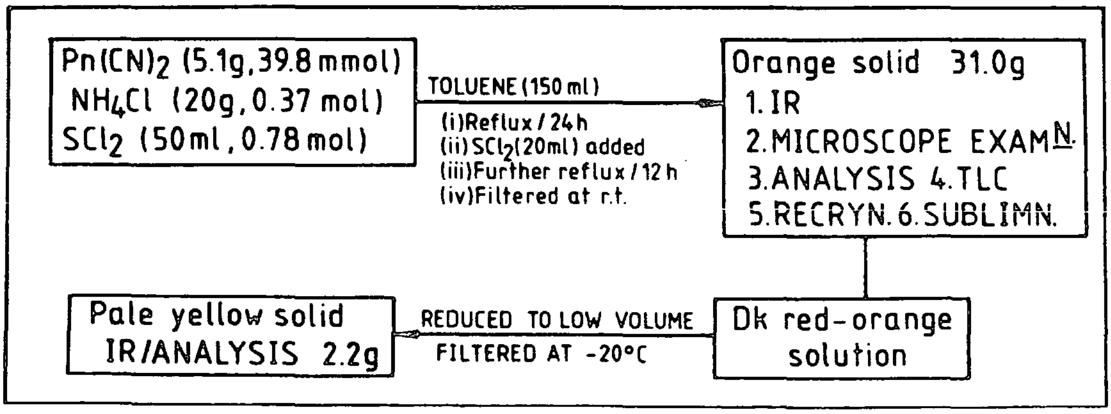
7.2 Modifications of the phenyl ring

7.2.1 Attempted preparation of 4(4-cyanophenyl)-1,2,3,5-dithiadiazolium chloride

Whilst trying to synthesise the double dithiadiazolium salt from dicyanobenzene, Hey claimed to have isolated $NC\cdot C_6H_4\cdot CN_2S_2Cl$.[2] This section describes attempts made to repeat this synthesis.

FIGURE 7.2

$Pn = C_6H_4$



(A) Pale yellow solid I.r. and elemental analysis showed this to be largely sulphur. I.r. absorptions at 2235(w), 843(m) and 562(m) cm^{-1} (Nujol mull) were due to unreacted dicyanobenzene (cf. Table 7.2). Analysis found

TABLE 7.1

Sample	Recry^{n}.	Solvent	Yield	Analyses					
				C	H	N	S	Cl	Total
Pure $PhCN_2S_2Cl$				38.79	2.31	12.93	29.56	16.39	98.98
Section 7.1.1	1st	Toluene (35 ml g^{-1})	50%	43.04	3.16	12.21	25.96	14.10	98.47
	1st	$PhNO_2$ (25 ml g^{-1})	35%	39.49	2.80	11.83	27.90	14.04	96.06
	2nd	$PhNO_2$	80%	38.45	2.68	12.24	29.93	15.89	99.19
	1st	Liq.SO_2 (15 g g^{-1})	70%	34.48	2.34	11.68	32.90	16.20	97.60
	2nd	Liq.SO_2	90%	34.94	2.20	11.53	32.30	15.30	96.27
		Repeat	–	34.69	2.18	11.59	32.12	15.64	96.22
Section 7.1.2				34.30	2.37	12.25	32.60	18.60	100.12
	1st	$PhNO_2$	34%	39.00	3.15	11.95	27.30	13.30	94.70
	2nd	Liq.SO_2	80%	34.80	2.06	10.68	28.34	14.82	90.70
Expt. 3, Table 7.4	1st	CS_2 wash $MeNO_2$ (35 ml g^{-1})		35.53	2.80	12.35	27.42	16.10	94.20

C, 11.25; H, 0.57; N, 2.80: S, 78.60; Cl, 1.20 (94.42%). A mixture of sulphur (82%, 1.8 g), NH_4Cl (2%, 0.04 g) and $C_6H_4(CN)_2$ (16%, 0.35 g) required C, 11.97; H, 0.64; N, 3.99; S, 82.3; Cl, 1.26 (100.16%).

(B) Characterisation of orange solid

(1) I.r. spectroscopy

Table 7.2 compares absorptions recorded for product, $C_6H_4(CN)_2$ and $PhCN_2S_2Cl$.

TABLE 7.2

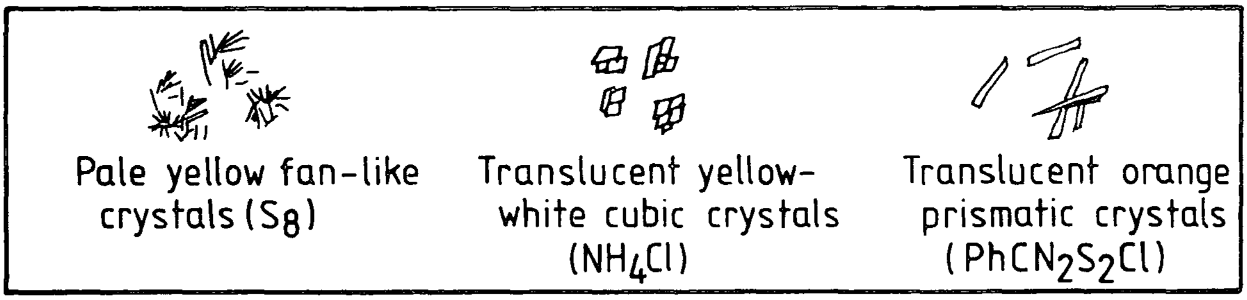
ORANGE SOLID	$C_6H_4(CN)_2$	$PhCN_2S_2Cl$	ORANGE SOLID	$C_6H_4(CN)_2$	$PhCN_2S_2Cl$
3120 m,br			1168 w		1168 w
	3094 m		1148 m		1148 m
	3050 m		1068 w		1065 w
2235 mw	2235 s		1027 mw	1027 u	
2030 w,br			1000 w		1000 w
	1940 w,br		972 w,br	978 w	
	1810 w,br		920 m		920 m
1750 w,vbr			891 s		890 vs
	1690 w,br		842 vs	843 vs	842 s
1595 w		1594 w	792 mw		792 m
1502 w,sh	1503 s		780 mw		780 m
1395 s	1400 m	1393 m	708 mw		709 m
		1348 m,sh	696 s		697 vs
1304 m,br	1294 w	1292 w	558 s	561 vs	
1274 m	1278 m		548 ms		543 ms
					520 w
1200 w,br	1200 m	1207 w			

Underlined peaks were due to NH_4Cl.

(2) Microscope examination

A sample of the orange product, dissolved in hot nitromethane, was cooled on a watchglass and observed under a microscope (objective x 10). Three types of crystal were identified (Figure 7.3).

FIGURE 7.3



(3) Elemental analysis

Analysis of the orange product found C, 14.85; H, 5.28; N, 16.44; S, 27.80; Cl, 32.90 (97.27%). A mixture of $C_6H_4(CN)_2$ (12%, 3.7 g), $PhCN_2S_2Cl$ (20%, 6.2 g), NH_4Cl (44%, 13.6 g) and sulphur (24%, 7.4 g) required C, 16.63; H, 4.16; N, 16.82; S, 29.57; Cl, 32.80 (99.98%).

(4) Thin layer chromatography

R_f values (Table 7.3) were measured for the orange product (dissolved in hot CH_3NO_2) (I); and for $C_6H_4(CN)_2$ (in $PhNO_2$) (II) and sulphur (in CS_2) (III) standards.

TABLE 7.3

Sample	R_f values (CH_3NO_2)			
I	0.00(f)	0.75(m)	0.83(f)	0.93(m)
II			0.86(s)	
III				0.92(s)

(5) Recrystallisations

Attempts were made to obtain a pure product by recrystallisation of the orange solid. In experiment 3 (Table 7.4) the product from sequence (a) was further purified in sequence (b).

(6) Sublimation

Sublimation (140°C/10^{-2} mm Hg) of the orange solid produced a brown-red

TABLE 7.4

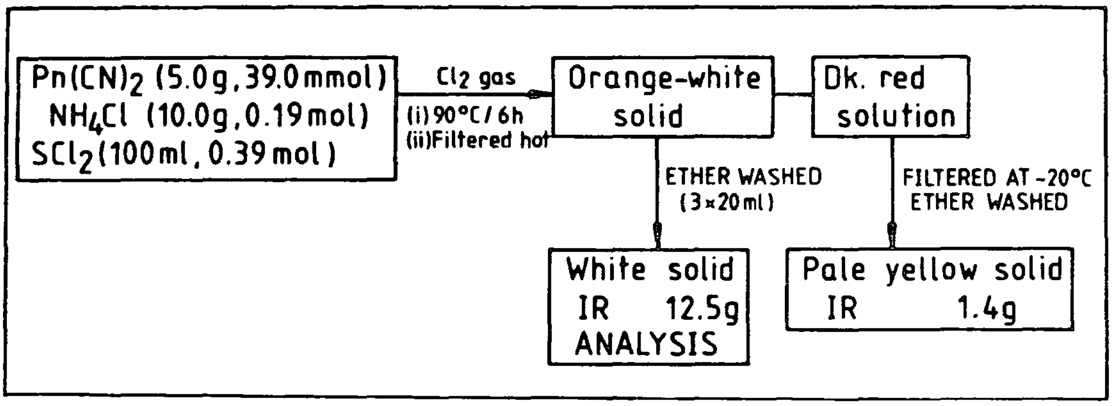
Expt.	Solvent	Insolubles			Solubles		
		% Total Weight	IR	Analysis - Conclusion	% weight recovered	IR	Analysis - Conclusion
1	Benzene (10 ml g^{-1})	43	$PhCN_2S_2Cl$ NH_4Cl	C,13.18; H,7.77; N,20.04; S,13.24; Cl,46.63— $PhCN_2S_2Cl$ (39%) NH_4Cl (60%) sulphur (1%)	3	virtually blank	S,86.3
2	CH_3NO_2 (15 ml g^{-1})	50	NH_4Cl	—	20	$PhCN_2S_2Cl$	C,23.16; H,1.62; N,9.24; S,57.00; Cl,8.02 - $PhCN_2S_2Cl$ (63%) sulphur (37%)
3a	CS_2 washing (3 x 5 ml)	79	$PhCN_2S_2Cl$ $C_6H_4(CN)_2$	—	6	virtually blank	C,2.26; H,0.17; N,0.80; S,63.30.
b	CH_3 NO_2 (35 ml g^{-1})	50	NH_4Cl	N,25.03; H,7.44; Cl,64.60; -NH_4Cl (98%)	16	$PhCN_2S_2Cl$	C,35.53; H,2.80; N,12.35; S,27.42; Cl,16.10 (section 7.1.3)
4	SO_2 extract$^{n.}$ (14 g g^{-1})	72	NH_4Cl	C,2.24; H,5.87; N,17.46; S,32.90; Cl,39.70 - NH_4Cl (61%) $C_6H_4(CN)_2$ (3%) and sulphur (36%)	24	$PhCN_2S_2Cl$ $C_6H_4(CN)_2$	C,49.63; H,2.82; N,10.97; S,22.78; Cl,10.28 - $PhCN_2S_2Cl$ (77%) $C_6H_4(CN)_2$ (23%)
5	SO_2 (11 g g^{-1})	60	NH_4Cl	—	35	$PhCN_2S_2Cl$ $C_6H_4(CN)_2$	C,45.74; H,2.42; N,13.55; S,26.50; Cl,9.30 - $PhCN_2S_2Cl$ (60%), $C_6H_4(CN)_2$ (30%), sulphur (10%)

coating on the coldfinger ($0^{o}C$) and pale yellow crystals on the sublimator walls, which had major i.r. absorptions (Nujol mull) at 2235(s), 1502(ms), 1399(ms), 1275(m), 1199(m), 841(vs), 562(vs) and 360(m) cm^{-1} (cf. $C_6H_4(CN)_2$, Table 7.2). The brown-red solid also had absorptions due to $C_6H_4(CN)_2$ with extra peaks at 1300(br), 1150(w,br) and 1680(br) cm^{-1}. The residue after sublimation, had absorptions due to $PhCN_2S_2Cl$ and $C_6H_4(CN)_2$, however, the intensity of bands due to $C_6H_4(CN)_2$ were greatly reduced compared with those in the spectrum of the product prior to sublimation.

A second attempt to prepare $NC{\cdot}C_6H_4{\cdot}CN_2S_2Cl$ was made using conditions similar to those described in section 7.1.1.

FIGURE 7.4

Pn = C_6H_4



Infra-red spectroscopy showed that the white solid was largely NH_4Cl (strong, broad absorptions at 3300, 2000 and 1750 cm^{-1}) with some unreacted $C_6H_4(CN)_2$ (2230, 841 and 562 cm^{-1}). Analysis found N, 22.25; H, 7.57; C, 17.12; Cl, 41.80 (88.74%) required for NH_4Cl N, 26.17; H, 7.47; Cl, 66.35 (99.99%).

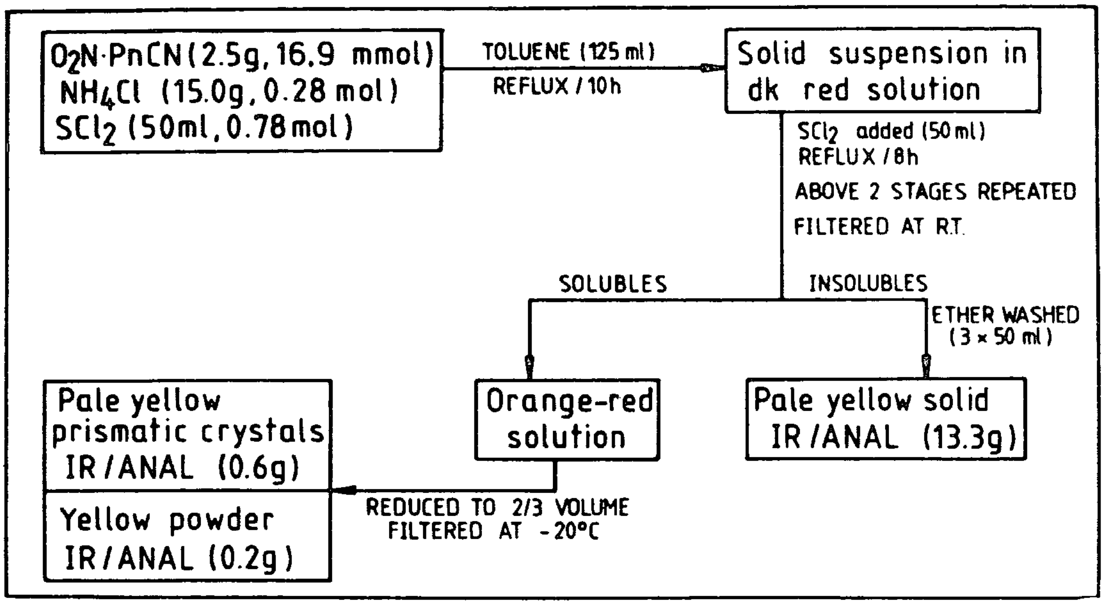
The pale yellow solid was unreacted $C_6H_4(CN)_2$ which had i.r. absorptions (KBr disc) at 3100(s), 3055(s), 3000(w), 2235(vs), 1940(w), 1805(w), 1685(w), 1499(s), 1397(s), 1365(sh), 1272(s), 1198(s), 1119(w), 1022(w), 972(w), 878(w), 842(vs), 639(m), 565(vs) and 362(m) cm^{-1} (cf. Table 7.2).

7.2.2 Attempted preparation of 4(4-nitrophenyl)-1,2,3,5-dithiadiazolium chloride

The synthesis of $O_2N{\cdot}C_6H_4{\cdot}CN_2S_2Cl$ was attempted using three separate methods.

FIGURE 7.5

Pn = C_6H_4



(A) Pale yellow solid (toluene insolubles)

This was found to be mainly NH_4Cl (i.r. spectrum). Elemental analysis found N, 25.70; H, 8.83; Cl, 64.00 (98.53%) required for NH_4Cl N, 26.17; H, 7.47; Cl, 66.35 (99.99%).

(B) Mixture of solids (toluene solubles)

The pale yellow prismatic crystals had i.r. absorptions (KBr disc) at 3105(m), 3075(m), 3052(m), 2240(s), 1940(w), 1805(w), 1690(w), 1600(s,br), 1522(s,br), 1488(s), 1404(m), 1348(s,br), 1315(ms), 1292(s), 1188(mw), 1150(br), 1117(m), 1107(m), 1015(m), 860(vs), 762(w), 750(vs), 682(s), 639(m), 569(m), 559(w) and 539 cm^{-1} (cf. standard $O_2N\cdot C_6H_4\cdot CN$, 3105, 3079, 3055 (C-H aromatic stretch); 2240 ($C\equiv N$ stretch); 1940, 1806, 1691 (benzene substitution bands); 1602 (C=C stretch); 1524 (NO_2 asymmetric stretch); 1488, 1404; 1348 (NO_2 symmetric stretch); 1315, 1294, 1188, 1150, 1117, 1107, 1016, 860, 764, 750, 682 640, 569, 559 and 539 cm^{-1}). Analysis found C, 56.95; H, 2.57; N, 17.87 (77.39%) required for $O_2N\cdot C_6H_4\cdot CN$ C, 56,76; H, 2.70; N, 18.92 (78.38%).

Analysis of the yellow powder found S, 22.62; Cl, 15.60; C, 39.54; H, 1.39; N, 13.54 (93.69%) required for $O_2N\cdot C_6H_4\cdot CN_2S_2Cl$ S, 25.68; Cl, 14.22; C, 28.84; H, 1.60; N, 16.83 (87.17%). A mixture of $PhCN_2S_2Cl$ (75%, 0.15 g) and $O_2N\cdot C_6H_4\cdot CN$ (25%, 0.05 g) would require S, 22.29; Cl, 12.34;

C, 43.21; H, 2.40; N, 14.41 (94.65%). The infra-red spectrum also strongly suggested a mixture of these species (Table 7.5, which lists major peaks only).

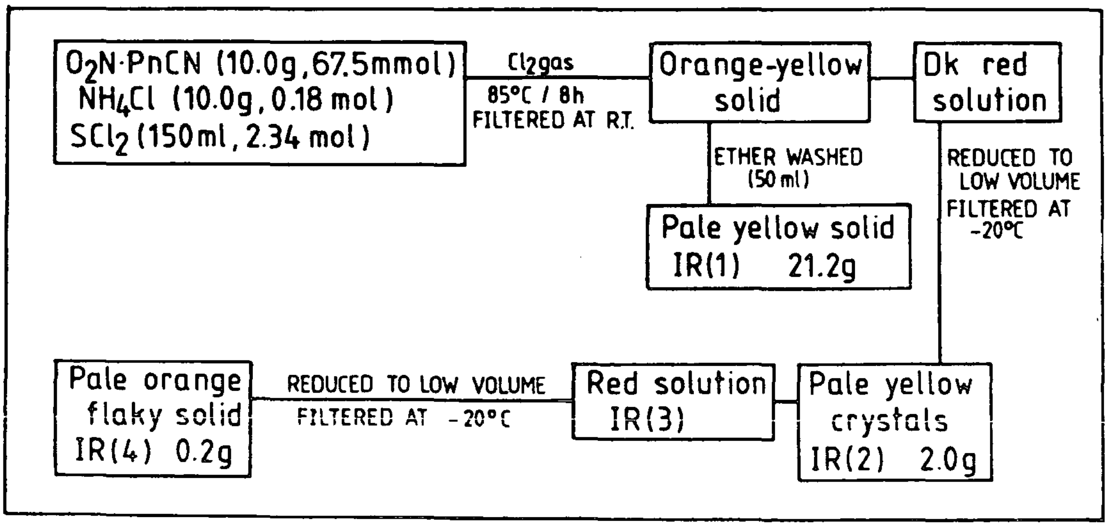
TABLE 7.5

Yellow powder	$PhCN_2S_2Cl$	$O_2N\cdot C_6H_4\cdot CN$	Yellow powder	$PhCN_2S_2Cl$	$O_2N\cdot C_6H_4\cdot CN$
2240		2240	891	890	
1600		1602	860		860
1523		1524	842	842	
1488		1488	794	792	
1400		1404	781	780	
1348		1348	750		750
1315		1315	697	697	
1295		1294	681		682
1150		1150	545	543	539
922	920		541		

The second attempt to prepare $O_2N\cdot C_6H_4\cdot CN_2S_2Cl$ used a similar method to that described in section 7.1.1.

FIGURE 7.6

$Pn = C_6H_4$



Infra-red spectra of products

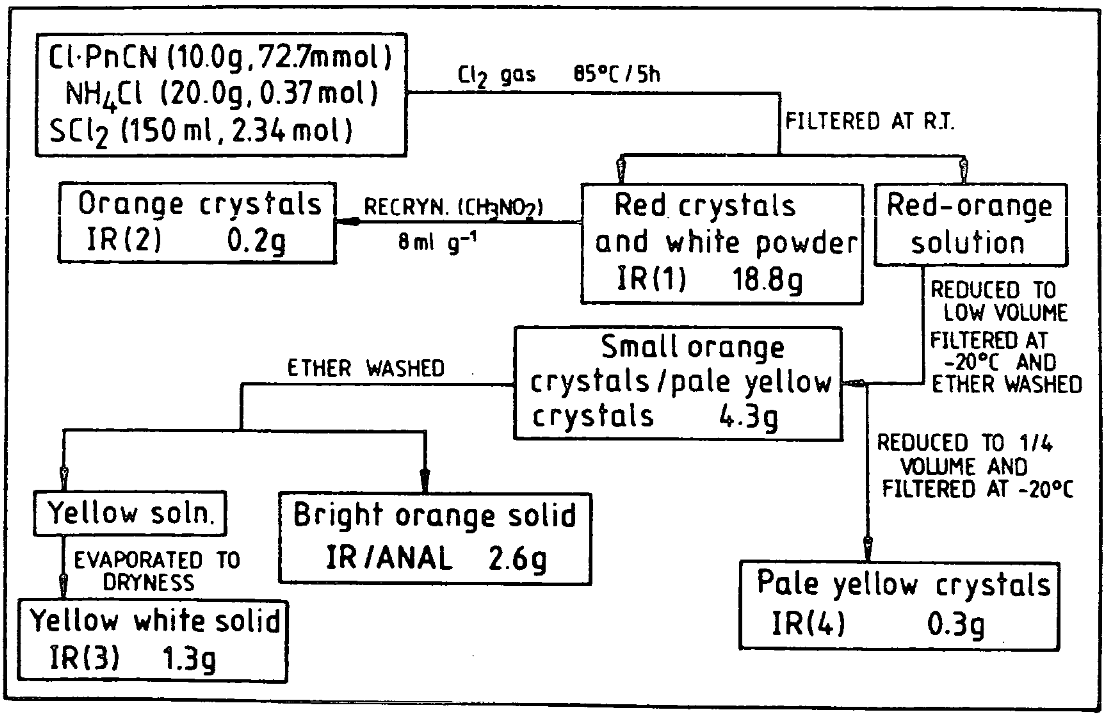
Spectrum IR(1) contained absorptions at 3300, 2000 and 1750 cm^{-1} (due to NH_4Cl) and weak ones at 2238, 1520, 1345, 858 and 535 cm^{-1} (due to $O_2N\cdot C_6H_4\cdot CN$). The pale yellow crystals were unreacted $O_2N\cdot C_6H_4\cdot CN$ and had absorptions, IR(2), at 3120, 3078, 3059, 2239, 1600, 1522, 1488, 1404, 1348, 1314, 1293, 1187, 1116, 1106, 1014, 862, 858, 750, 681, 640, 570, 558 and 538 cm^{-1} (cf. Table 7.5). Analysis found C, 56.43; H, 2.38; N, 17.93 required for $O_2N{\cdot}C_6H_4{\cdot}CN$ C, 56.76; H, 2.70; N, 18.92. The solution spectrum, IR(3) indicated the presence of $O_2N{\cdot}C_6H_4{\cdot}CN$ (strong absorptions at 2235, 1529, 1342 and 758 cm^{-1}) and S_2Cl_2 (S-Cl stretch at 450 cm^{-1}) (cf. Reference 4). IR(4) contained mainly absorptions due to unreacted $O_2N{\cdot}C_6H_4{\cdot}CN$ with extra bands (unassigned) at 1230, 1085, 895 and 843 cm^{-1}.

In a final attempt at preparation, 4-nitrobenzonitrile (0.6 g, 4.09 mmol) was stirred with $(NSCl)_3$ (1.0 g, 4.09 mmol) in toluene (30 ml) for 3 weeks at room temperature. The mixture was filtered to give a brown-yellow solid (10 mg) and an orange-brown solution. The solid had i.r. absorptions at 3140(s,br), 3040(s,br), 1405(s,br), 1290(m,br), 1150(w,br), 1050(m), 1015(m), 855(mw), 745(mw) and 460(mw) cm^{-1} which corresponded to a mixture of unreacted $O_2N{\cdot}C_6H_4{\cdot}CN$ (underlined) and hydrolysis product.

The solution was evaporated to low volume, cooled (-20°C) and filtered to give pale brown, prismatic crystals which were also shown to be unreacted $O_2N{\cdot}C_6H_4{\cdot}CN$ (i.r. spectrum).

7.2.3 Preparation of 4(4-chlorophenyl)-1,2,3,5-dithiadiazolium chloride

FIGURE 7.7 (Pn = C_6H_4)



Spectrum IR(2), of the orange crystals produced from nitromethane showed the following absorptions (KBr disc): 1597(mw), 1413(mw), 1404(m), 1390(m), 1368(m), 1282(mw), 1174(mw), 1153(ms), 1091(vs), 1012(ms), 970(w), 959(w), 919(mw), 890(ms), 846(vs), 734(vs), 727(vs), 682(ms), 626(w), 543(ms), 498(mw) and 489(w) cm^{-1}. Elemental analysis found S, 24.84; Cl, 28.00; C, 34.27; H, 1.46; N, 11.58 (100.15%) required for $Cl{\cdot}C_6H_4{\cdot}CN_2S_2Cl$ S, 25.53; Cl, 28.26; C, 33.44; H, 1.59; N, 11.15 (99.97%). Spectrum IR(1) contained absorptions due to $Cl{\cdot}C_6H_4{\cdot}CN_2S_2Cl$ (above) and NH_4Cl (at 3300 - 3000(s,br), 2000(br), 1750(vbr) and 1400(br) cm^{-1}).

First filtration of the SCl_2 solution produced a mixture of crystals (4.3 g) containing an ether soluble product (1.3 g) and a bright orange ether insoluble product (2.6 g). The former had i.r. absorptions (KBr disc, IR(3)) at 3090(w), 2230(w), 1920(w), 1775(w), 1650(w), 1595(m), 1490(m), 1482(ms), 1398(mw), 1300(w), 1275(w), 1260(w), 1195(w), 1175(w), 1092(vs), 1017(m), 900(mw), 829(vs), 780(mw), 583(m), 539(s) and 440(w) cm^{-1}. (<u>cf</u>. standard 4-chlorobenzonitrile 3090(m), 3070(w), 3040(m); 2230(s) ($C{\equiv}N$ stretch); 1915(m), 1780(mw), 1655(m) (benzene substitution bands); 1592(m) ($C = C$ stretch); 1490(m), 1482(s), 1398(s), 1303(m), 1278(m), 1260(m), 1198(m), 1176(m), 1116(m); 1092(vs) ($C-Cl$ stretch); 1017(s), 962(w), 952(w), 829(vs), 780(s), 704(mw), 585(s), 540(vs) and 440(m) cm^{-1}.

The orange crystals had major peaks at 1598(m), 1392(ms), 1172(m), 1155(m), 1092(s), 1012(s), 919(mw), 890(s), 847(vs), 737(vs), 729(s), 681(ms), 542(s) and 498(m,sh) cm^{-1} (<u>cf</u>. IR(2) above). Elemental analysis found S, 26.70; Cl, 27.00; C, 34.30; H, 1.36; N, 12.36 (101.72%) $Cl{\cdot}C_6H_4{\cdot}CN_2S_2Cl$ required S, 25.53; Cl, 28.26; C, 33.44; H, 1.59; N, 11.15 (99.97%).

The pale yellow crystals giving IR(4), were characterised as unreacted $Cl{\cdot}C_6H_4{\cdot}CN$.

<u>Further characterisation of $Cl{\cdot}C_6H_4{\cdot}CN_2S_2Cl$</u>

A sample of 4(4-chlorophenyl)-1,2,3,5-dithiadiazolium chloride, recrystallised from nitromethane, gave the following mass spectral data, $^{m}/e$ (relative intensity, %): 35(14)-Cl^+; 37(17)-iCl^+; 46(44)-SN^+; 58(43)-CSN^+; 64(17)-S_2^+; 75(79)-$C_6H_3^+$; 76(35)-$C_6H_4^+$(Pn); 78(73)-S_2N^+; 102(100)-$C_6H_4CN^+$; 111(29)-$C_6H_4Cl^+$; 113(12)-i$C_6H_4Cl^+$; 137(98)-$ClPnCN^+$; 139(88)-i$ClPnCN^+$; 151(23)-$ClPnCN_2^+$; 153(11)-i$ClPnCN_2^+$; 169(79)-$ClPnCNS^+$; 171(48)-i$ClPnCNS^+$; 215(98)-$ClPnCN_2S_2^+$; 217(63)-i$ClPnCN_2S_2^+$. The ^{35} n.q.r. spectrum of a sample of $Cl\cdot C_6H_4\cdot CN_2S_2Cl$ showed no peaks in the range 5-35 MHz.

Controlled hydrolysis of $Cl\cdot C_6H_4\cdot CN_2S_2Cl$

$Cl\cdot C_6H_4\cdot CN_2S_2Cl$ (0.3 g, 1.19 mmol) was stirred with H_2O (65 μL, 3.38 mmol) in T.H.F. (20 ml) for 2 hours at room temperature and the solution filtered to give a white solid (0.12 g). This had i.r. absorptions (Nujol mull) at 3050(ms,br), 1675(ms,br), 1615(w), 1550(m,br), 1525(m), 1408(ms), 1115(m), 1080(s), 1050(s,br), 810(ms), 770(s), 690(s) and 510(s) cm^{-1}. (cf. benzamidine. HCl, Chapter 8, section 8.2.1). Chemical analysis gave C, 36.29; H, 4.40; N, 12.19; Cl, 30.34; S, 15.68 (98.79%). A mixture of $Cl\cdot C_6H_4\cdot CN_2H_4Cl$ and sulphur in the molar ratio 8:1 would require C, 37.66; H, 3.58; N, 12.56; Cl, 31.83; S, 14.37 (100.00%).

7.3 Discussion

7.3.1 Preparations of $PhCN_2S_2Cl$

In the usual preparation of $PhCN_2S_2Cl$, a major problem (blockage of the condenser by crystals of by-product $S_3N_2Cl_2$)^2 was avoided by passing chlorine gas through the reaction mixture (section 7.1.1). This regenerated active NSCl (equation 5 below) and increased the yield of $PhCN_2S_2Cl$ (from 25%^{1} to 30% in the modified preparation). Reaction time and consumption of SCl_2 were also reduced thereby increasing the efficiency of the process.

It is likely that the main reaction steps are as follows:

(1) $NH_4Cl + 2SCl_2 \rightleftharpoons 4HCl + (NSCl) + \frac{1}{8}S_8$ (Initiation)

(2) $RCN + SCl_2 + (NSCl) \xrightarrow{NH_4Cl} RCN_2S_2Cl + 2HCl$ (Ring synthesis)

$$\left.\begin{array}{ll} (3) & 2SCl_2 \longrightarrow S_2Cl_2 + Cl_2 \\ (4) & 2NSCl + S_2Cl_2 \longrightarrow S_3N_2Cl_2 + SCl_2 \end{array}\right\} \text{Removal of active reagent}$$

(5) $S_3N_2Cl_2 + Cl_2 \longrightarrow \tfrac{2}{3}(NSCl)_3 + SCl_2$

(6) $S_2Cl_2 + Cl_2 \longrightarrow 2SCl_2$

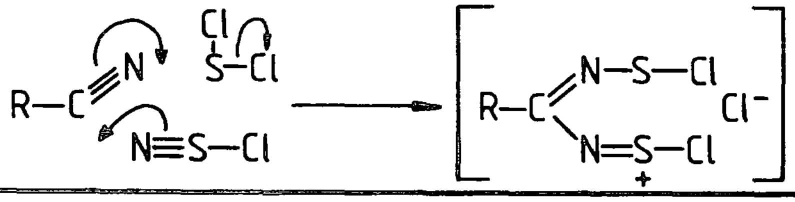
} Regeneration of active reagents

Gas evolved during the course of the reaction was shown to contain hydrogen chloride (as required by equations 1 and 2) by testing with ammonia and potassium iodide solution.

Equation 3 is known to occur for SCl_2 at temperatures below its boiling point (59°C) and the reverse reaction (equation 6) is the first stage in the preparation of S_4N_4.[5] In the reaction mixture, therefore, there will be an equilibrium between the two processes which can be made to favour SCl_2 in the presence of excess chlorine (Le Chatelier). Equations 4 and 5 represent known preparations of $S_3N_2Cl_2$ and $(NSCl)_3$ respectively.[6,7]

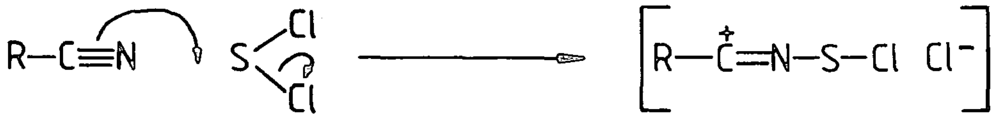
The following mechanisms are postulated for the ring synthesis stage (equation 2).

(i) Concerted This involves simultaneous transfer of charge among three molecules in close proximity:



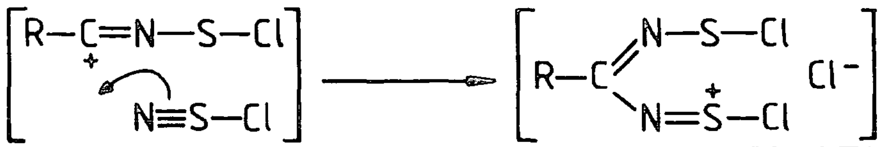
(I)

(ii) Nucleophilic attack by the nitrile The first stage of this mechanism involves attack by the nitrile on the electrophilic sulphur of SCl_2. Heal and Kane[8] have shown that strong Lewis bases readily displace chloride ion from sulphur chorides, and suggested that the weak conductivity detected in the CH_3CN/SCl_2 system was due to the presence of $[CH_3\overset{+}{C}=N\text{-}SCl]$ (II).



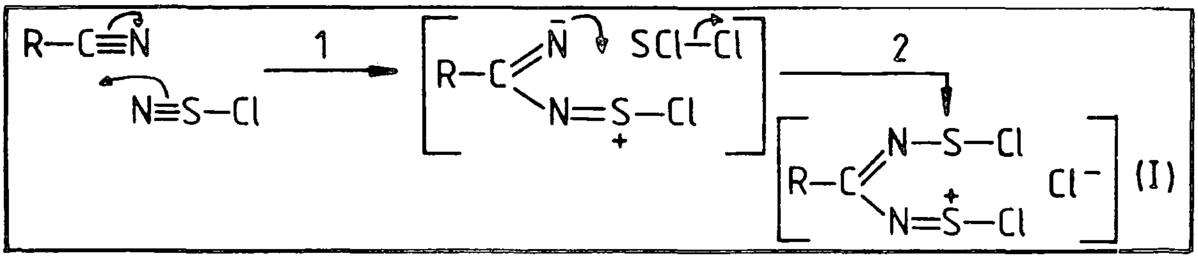
(II)

The intermediate (II) would be readily stabilised by conjugation with a benzene ring (i.e. R = Ph). The second stage would then be reaction of (II) with NSCl to give (I) as with the concerted mechanism.

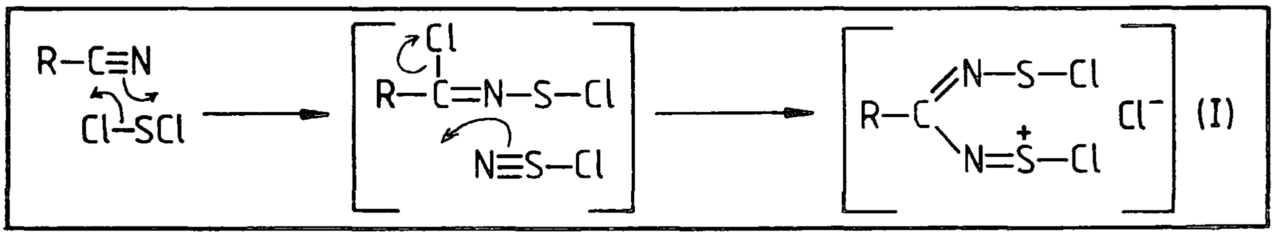


(I)

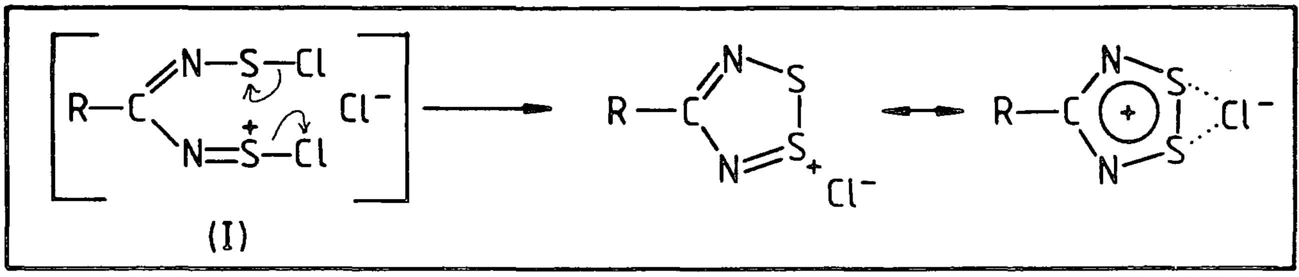
(iii) A third variation is similar to mechanism (ii) - again the reaction occurs in two stages, but it is initiated by nucleophilic attack on the carbon of the nitrile group.



(iv) Finally there could be concerted addition of sulphur dichloride across the C≡N bond, followed by base attack on the chlorine activated carbon atom.



The intermediate (I), formed in mechanisms (i) - (iv) above, could then undergo ring closure with elimination of chlorine and rearrangement to gain extra resonance stability.



Some insight into the preferred mechanism was gained by varying the substituent R-group in the reactant nitrile (section 7.3.3).

Preparation from toluene

The reaction of toluene with SCl_2/NH_4Cl was originally performed as a control experiment for the reactions described in sections 7.2.1 (Figure 7.2) and 7.2.2 (Figure 7.5) (see discussion, section 7.3.2). However it stands on its own as a preparation of $PhCN_2S_2Cl$. Elemental analyses recorded for the crude yellow-white solid (Figure 7.1) were consistent with a mixture of

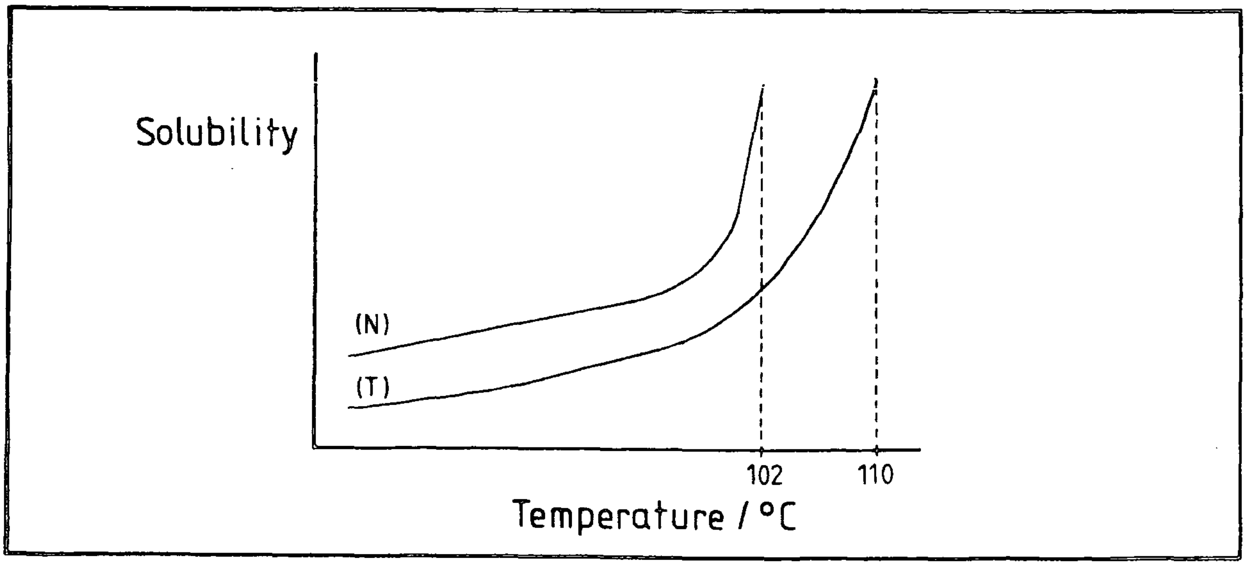
NH_4Cl (95%) and $PhCN_2S_2Cl$ (5%). The total yield of crude $PhCN_2S_2Cl$ from the reaction was therefore 1.1 g (0.4% based on toluene). Comparison of this value with that obtained for the benzonitrile preparation is invalid since toluene was used in excess (conditions were chosen to be similar to those for the reactions in Figures 7.2 and 7.5, not to maximise the yield of $PhCN_2S_2Cl$).

Purification of $PhCN_2S_2Cl$

It is generally difficult to obtain highly pure $PhCN_2S_2Cl$. Elemental analyses invariably totalled less than 100% (Table 7.1) indicating the presence of some impurity. In the case of recrystallisation from toluene, high C and H analysis, coupled with low N, S and Cl suggested some toluene of recrystallisation (0.29 mole per mole of $PhCN_2S_2Cl$ required C, 44.53; H, 3.00; N, 11.51; S, 26.35; Cl, 14.59, cf. Table 7.1). Hey[2] also prepared crystals from toluene which were shown by X-ray crystallography[9] to contain 0.16 mole toluene per mole of $PhCN_2S_2Cl$.[‡] The compound $PhCN_2S_2Cl$ has a very low solubility gradient in toluene which increases greatly within 5 - 10°C of the boiling point. Consequently, in order to avoid blockage of the sinter, it was necessary to filter rapidly using hot apparatus. A similar problem was encountered with nitromethane though in this case the solubility of $PhCN_2S_2Cl$ was higher (Figure 7.8).

FIGURE 7.8

Qualitative representation of solubility of $PhCN_2S_2Cl$ in toluene (T) and nitromethane (N)



Traditionally, samples of high purity have only been obtained after several recrystallisations from pure, dry nitrobenzene and best results were obtained in this solvent (Table 7.1).

Hey recommended liquid SO_2 as a "facile single-stage purification solvent", however, poor results (especially from double recrystallisation) were generally obtained using it. Since the SO_2 recrystallised sample was heated in vacuo (50^{o}/4h) to remove any adsorbed SO_2, and repeat analysis showed little change; it is probable that some hydrolysis of the $PhCN_2S_2Cl$ had occurred as a result of the finely divided nature of the recrystallised solid.

7.3.2 Modifications of the phenyl ring

In chapter 6 it was shown that double dithiadiazolium salts cannot be prepared from aliphatic dinitrile starting materials. This was apparently also true for aromatic dinitriles since Hey[2] reported the isolation of $NC{\cdot}C_6H_4{\cdot}CN_2S_2Cl$ from $C_6H_4(CN)_2$. Synthesis of new dithiadiazolium salts by modification of the phenyl group of $PhCN_2S_2Cl$ was therefore attempted.

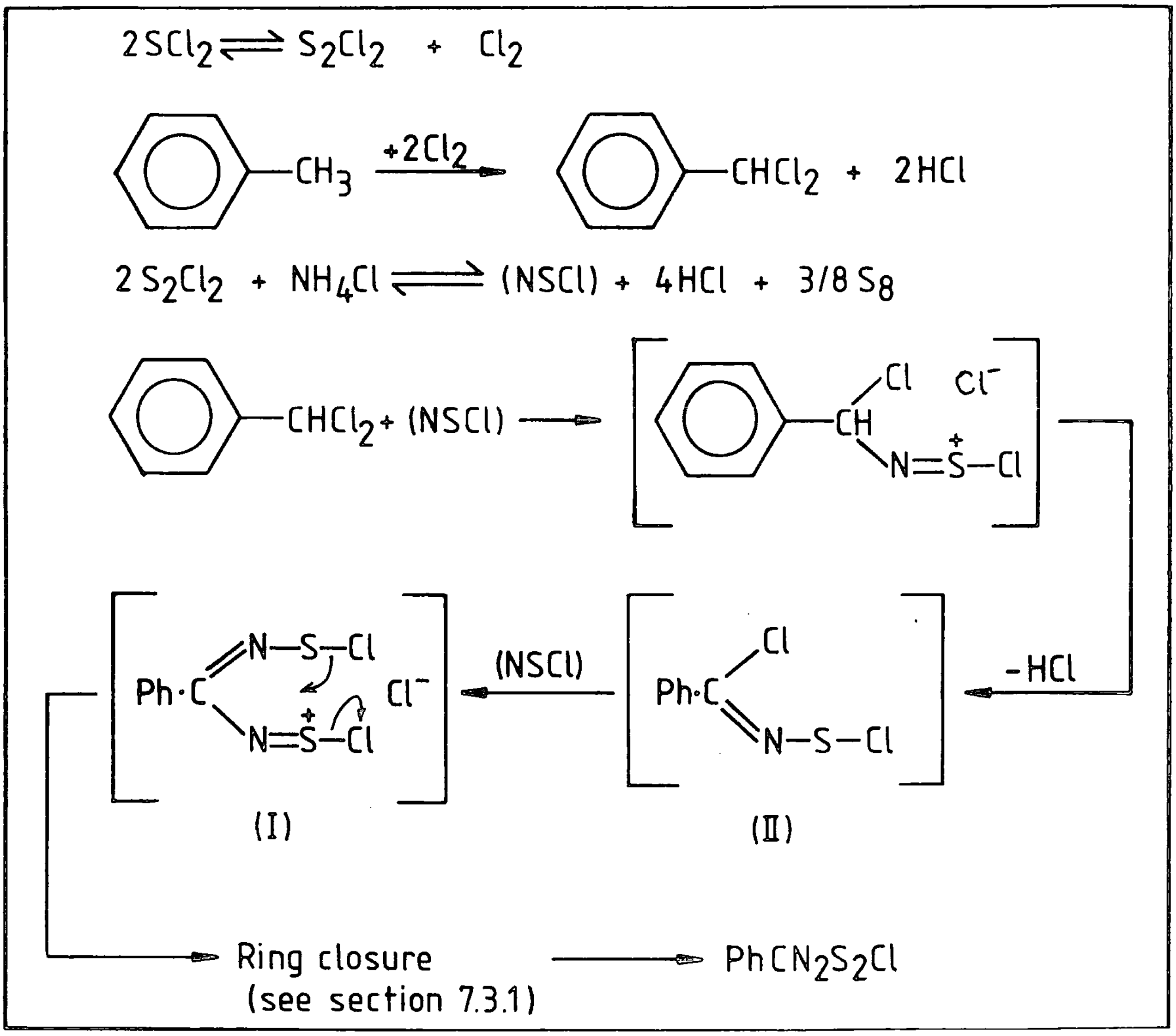
Experimental work (section 7.2.1(B)) however showed conclusively that the reaction of dicyanobenzene with NH_4Cl and SCl_2 in toluene did not produce $NC{\cdot}C_6H_4{\cdot}CN_2S_2Cl$. $NC{\cdot}C_6H_6{\cdot}CN_2S_2Cl$ would give a spectrum containing absorptions due to $C{\equiv}N$ stretching, and C-S-N ring vibrations; however the frequencies, in particular the C-S-N ring vibrations, would be expected to be shifted (relative to $PhCN_2S_2Cl$) because of the electron withdrawing effect of the -CN group. This effect was not observed and the i.r. spectrum (Table 7.2 had strong absorptions at 2235 ($C{\equiv}N$ stretch) and 1503, 843 and 561 cm^{-1} (due to $C_6H_4(CN)_2$) and at 890, 842, 697 and 543 cm^{-1} (due to $PhCN_2S_2Cl$). Microscope examination, elemental analysis and t.l.c. evidence also strongly suggested that the major product (section 7.2.1(B)) was a mixture of $PhCN_2S_2Cl$, sulphur, $C_6H_4(CN)_2$, and NH_4Cl (equation 7) with R_f values (Table 7.3) of 0.75, 0.93, 0.83 and 0.00 respectively.

$$(7)\quad C_6H_4(CN)_2 + NH_4Cl + SCl_2 \xrightarrow{\text{toluene}} PhCN_2S_2Cl + C_6H_4(CN)_2 + S_8 + NH_4Cl$$

This was confirmed by recrystallisation, and reasonably pure $PhCN_2S_2Cl$ was isolated (experiment 3, Table 7.4).

It was thought unlikely that the $PhCN_2S_2Cl$ was produced as a result of nucleophilic aromatic substitution (by H^-) at the para position in $NC\cdot C_6H_4-CN_2S_2Cl$ and in fact evidence obtained from a control experiment (section 7.1.2) showed clearly that it was formed from toluene. A possible reaction mechanism is suggested in Figure 7.8.

FIGURE 7.8



In a final attempt to prepare $NC\cdot C_6H_4\cdot CN_2S_2Cl$, dicyanobenzene was reacted with NH_4Cl and SCl_2/Cl_2 (Figure 7.4). As expected, in the absence of toluene, no $PhCN_2S_2Cl$ was formed, and only unreacted starting materials were isolated.

Similar results were obtained when the synthesis of $O_2N\cdot C_6H_4\cdot CN_2S_2Cl$ in toluene was attempted (Figure 7.5). Unreacted 4-nitrobenzonitrile was recovered from the reaction mixture and $PhCN_2S_2Cl$ was the only product isolated (in less than 0.1% yield based on toluene). 4-Nitrobenzonitrile did not react with either NH_4Cl and SCl_2/Cl_2 (Figure 7.6) or $(NSCl)_3$ (section 7.2.2).

The 4-chloro derivative, $Cl\cdot C_6H_4\cdot CN_2S_2Cl$, was however the major product of the reaction between 4-chlorobenzonitrile and $NH_4Cl/SCl_2/Cl_2$ (section 7.2.3). There were some similarities between i.r. absorptions in $PhCN_2S_2Cl$ and $Cl\cdot C_6H_4-CN_2S_2Cl$ (Table 7.6), and, as expected some absorptions (associated with C-S-N ring vibrations) were shifted (cf. absorptions at 682, 727, 734 and 1368 with those at 697, 780, 792 and 1348 respectively in $PhCN_2S_2Cl$).

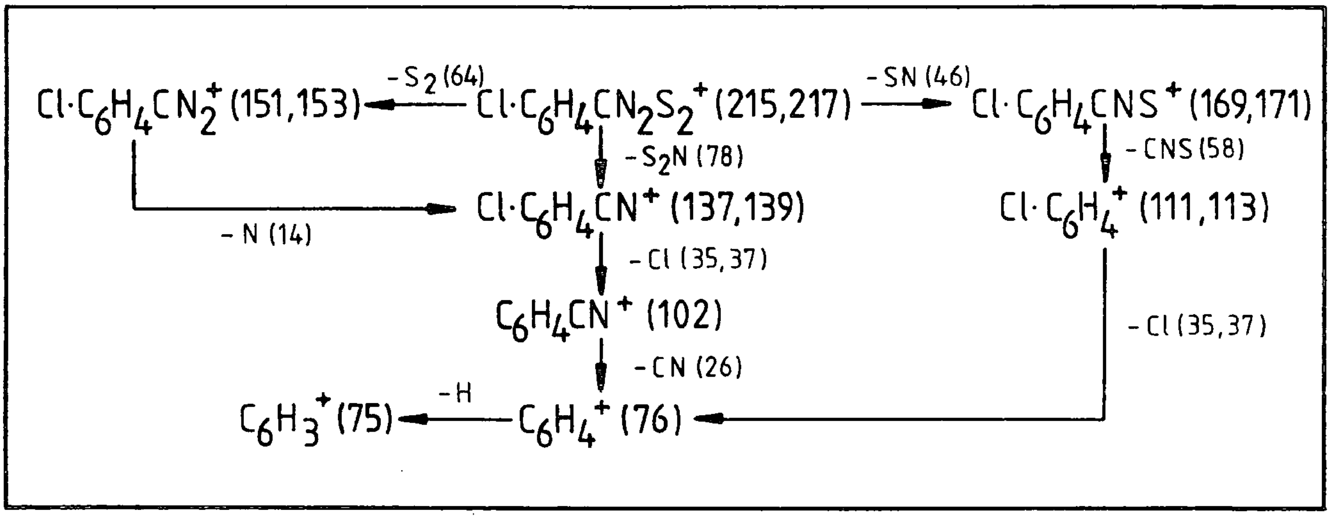
TABLE 7.6

$PhCN_2S_2Cl$	$Cl\cdot C_6H_4\cdot CN_2S_2Cl$	$Cl\cdot C_6H_4\cdot CN$
		2230 s
	1404 m	1482 s
1393 m	1390 m	1398 s
1348 m	1368 m	1303 m
		1198 m
1148 m	1153 ms	1176 m
		1116 m
	1091 vs	1092 vs
	1012 ms	1017 s
890 vs	890 ms	
842 s	846 vs	829 vs
792 m		
780 m	734 vs	780 s
	727 vs	
697 vs	682 ms	
		585 s
543 ms	543 ms	540 vs

The strong absorption at 1091 cm^{-1} was due to C-Cl stretch (cf. 1092 cm^{-1} in 4-chlorobenzonitrile).[10] Comparison of the spectra of $Cl\cdot C_6H_4\cdot CN$ and $Cl\cdot C_6H_4\cdot CN_2S_2Cl$ suggested that absorptions at 890, 846, 734 and 727 cm^{-1} in the latter were associated with dithiadiazolium ring vibrations (cf. $CH_3CN_2S_2Cl$ and $Bu^t-CN_2S_2Cl$, Chapter 6, page 205).

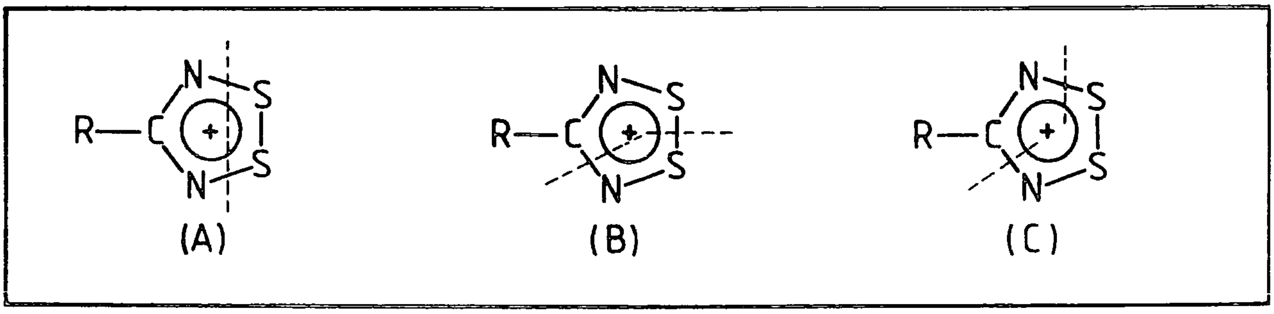
All the major peaks in the mass spectrum of $Cl{\cdot}C_6H_4{\cdot}CN_2S_2Cl$ were assigned (page 233) and the fragmentation pattern is shown in Figure 7.9. In the mass spectra of $CH_3CN_2S_2Cl$ and $Bu^tCN_2S_2Cl$ (Chapter 6, sections 6.3.1 and 6.3.2 respectively) and $Cl{\cdot}C_6H_4{\cdot}CN_2S_2Cl$, the highest mass peak detected was due to the stable parent cation, $RCN_2S_2^+$. This peak is generally strong and easily detected.

FIGURE 7.9



Three modes of fragmentation were observed for the $RCN_2S_2^+$ ring (Figure 7.10), however the major route to breakdown (based on spectral intensities) was via loss of S_2N^+(C).

FIGURE 7.10



No peaks were observed for the chloride ion in the n.q.r. spectra of $PhCN_2S_2Cl$ or $Cl{\cdot}C_6H_4{\cdot}CN_2S_2Cl$. N.q.r. spectroscopy is not a very sensitive technique and it may be that these materials, like $CH_3CN_2S_2Cl$ and $(CH_3CN_2S_2)_2SnCl_6$ (Chapter 6, sections 6.2.3 and 6.2.4) were not sufficiently covalent to give a detectable signal. No absorption was observed for the

4-phenyl substituted chlorine in $Cl\cdot C_6H_4\cdot CN_2S_2Cl$. Frequencies in the range 35-38 MHz (outside the region examined) would be expected for chlorine in this environment, e.g. penta-chlorobenzene, C_6HCl_5 which has nine frequencies (at 77K) ranging from 37.46 to 38.30 MHz.[11,12]

7.3.3 Organic derivatives of $PhCN_2S_2Cl$

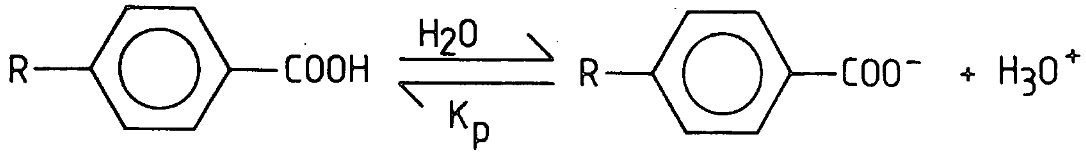
There are several possible consequences of the electron withdrawing effect of the para-chlorine in $Cl\cdot C_6H_4\cdot CN_2S_2Cl$. Compared with $PhCN_2S_2Cl$ there is likely to be a stronger 3-centre interaction between the sulphurs and chlorine. The increased ionic nature of $Cl\ C_6H_4\ CN_2S_2Cl$ was suggested by its increased solubility in organic solvents such as nitromethane (from ca. 0.03 g ml^{-1} for $PhCN_2S_2Cl$ to ca. 0.13 g ml^{-1} for $Cl\cdot C_6H_4\cdot CN_2S_2Cl$). A similar trend was observed in toluene for the series $PhCN_2S_2X$ changing X from chloride to bromide to iodide.[13]

The dark red colour of $Cl\cdot C_6H_4\cdot CN_2S_2Cl$ (compared with yellow-orange for $PhCN_2S_2Cl$) is a consequence of an electronic absorption being shifted into the visible region from the UV. Similar colour changes (orange to red to black-purple) were reported [14] for the compounds $PhCN_2S_2X$ (for X = Cl^-, Br^- and I^-).

Increased S····Cl interaction in $Cl\cdot C_6H_4CN_2S_2Cl$ (and greater susceptibility of the ring towards nucleophilic attack) would also explain the ease of hydrolysis observed for this compound (section 7.2.3, page 233).

Rates of dissociation for various para-substituted benzoic acids (K_p) can be compared with K_o (the value for benzoic acid at 25°C) to give a quantitative measure of the substituent effect (Figure 7.11).

FIGURE 7.11



Para substituent constant, $\sigma_p = \log (K_p/K_o)$
where $K_o = 6.46 \times 10^{-5}$ (25°C)
for benzoic acid (ref. 15)

Comparison of σ_p values for the substituents -H, -Cl, -CN and $-NO_2$ (Table 7.7) showed clearly that p-cyano and p-nitro are more strongly electron withdrawing than p-chloro.

TABLE 7.7

Substituent	σ_p (Ref)
-OMe	-0.27 (15)
-Me	-0.17 (15)
-H	0.00 (15)
$-CH_2CN$	0.01 (15)
$-SO_3^-$	0.09 (16)
$-CH_2Cl$	0.18 (15)
-CHO	0.22 (15)
-Cl	0.23 (15)
$-PO_3H^-$	0.26 (16)
-CN	0.66 (16)
$-NO_2$	0.78 (15)

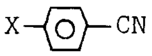
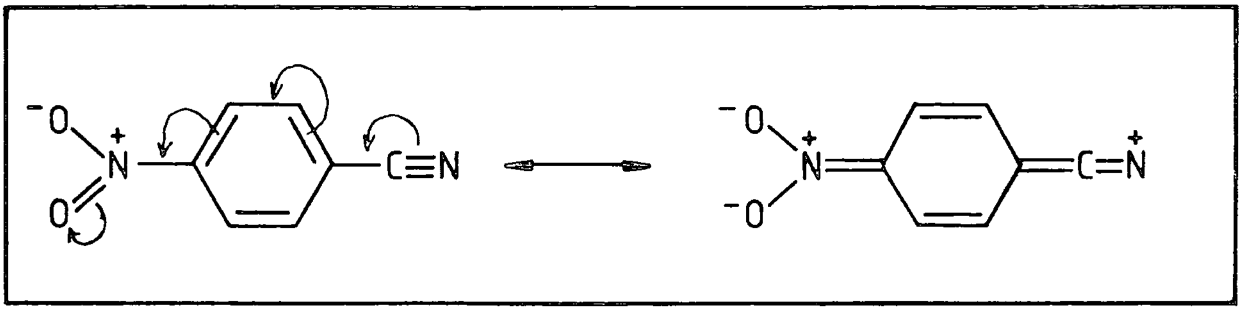
Because of conjugation with the benzene ring, electron density at the nitrile group will be influenced by the nature of the para-substituent. Thus in systems such as  where X is strongly electron withdrawing (e.g. NO_2, CN) electron density would be reduced compared with that on the nitrile group in benzonitrile (X = H). This can be represented, for example, in 4-nitro-benzonitrile, by the valence canonicals shown in Figure 7.12. Thus it is likely that $O_2N \cdot C_6H_4 \cdot CN_2S_2Cl$ and $NC \cdot C_6H_4 \cdot CN_2S_2Cl$ were not formed because the nitrile groups in the respective starting materials ($O_2N \cdot C_6H_4 \cdot CN$ and $NC \cdot C_6H_4 \cdot CN$) were deactivated with respect to dithiadiazolium ring formation. This implied that the most likely mechanism for the reaction of nitriles with SCl_2 and NH_4Cl is the nucleophilic attack on SCl_2 by the nitrile group (mechanism (ii), page 234).

FIGURE 7.12



Clearly substituent -Cl with a lower σ_p value, does not reduce the electron density at the nitrile group sufficiently to avoid reaction with SCl_2 in the first stage of the sequence leading to $Cl{\cdot}C_6H_4CN_2S_2Cl$. Consequently it should be possible, if desired, to prepare dithiadiazolium salts from para substituted benzonitriles, $X\text{-}C_6H_4{\cdot}CN$, where the X group has a value of σ_p similar to, or lower than that for Cl (for example CHO, PO_3H^- and CH_2Cl, Table 7.7), or indeed where X is an electron donating group (e.g. MeO). Successful preparation of $R{\cdot}C_6H_4CN_2S_2Cl$, where R is an electron donating group would strengthen the belief that it is the electron density at the nitrile group which determines whether or not reaction with SCl_2 will occur.

7.4 Summary (Chapters 6 and 7)

The reaction of RCN with SCl_2/NH_4Cl is a general synthetic route to dithiadiazolium compounds, which involves relatively inexpensive starting materials. It was shown that R can be aliphatic (e.g. CH_3- or Bu^t-) or aromatic (e.g. Ph- or Cl C_6H_4-) and the method is probably limited only by the nucleophilicity of the nitrile group towards SCl_2.

Under the same experimental conditions, aliphatic and aromatic dinitriles do not give dithiadiazolium products, probably because of the symmetrical environment or reduced nucleophilicity of the nitrile groups. Similar results were obtained when the toluene route to dithiadiazolium compounds was investigated using p-methyl toluene. In the presence of a base, however, adiponitrile, $(CH_2CH_2CN)_2$ cyclised to form a five-membered sulphur heterocycle.

Some insight into the nature of the mechanism of reaction of mononitriles with SCl_2/NH_4Cl was gained by varying the para substituent at benzene in the series $R{\cdot}C_6H_4{\cdot}CN_2S_2Cl$ (R = H, Cl, CN and NO_2).

7.5 References

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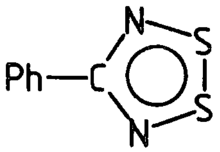
CHAPTER 8

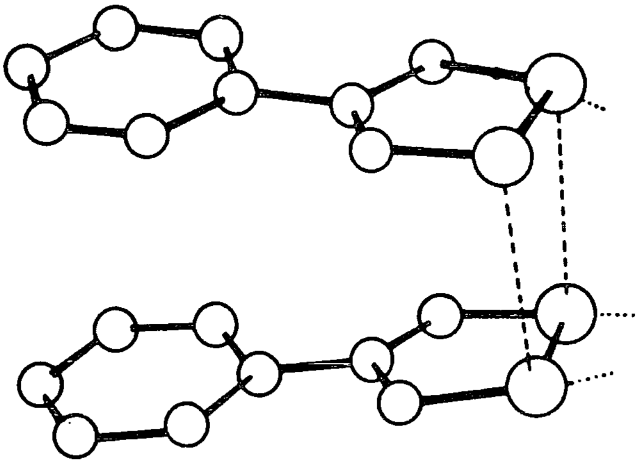
SOME ASPECTS OF THE CHEMISTRY OF THE DITHIADIAZOLE AND DITHIADIAZOLIUM RING SYSTEMS

8.1 Introduction

4-phenyl-1,2,3,5-dithiadiazole, $PhCN_2S_2$ (I) was first isolated by Hey[1] from reductions of phenyl dithiadiazolium salts using the following reductants: anhydrous NaNCS, LiN_3, KCN, PhMgBr, butyl and methyl lithium, $SnCl_2$ and various metals (Zn/Cu, K, Hg).



(I)



(II) Dimer structure (2)

Species (I) (formally a 7π-radical) exists as a dimer, $(PhCN_2S_2)_2$ in the solid state. The crystal structure was determined by Vegas[2] who showed that the dimer unit contained an eclipsed conformation of 6π rings held together by a 2 electron, 4 centre sulphur bridge (II).

$(PhCN_2S_2)_2$ was readily oxidised by chlorinating reagents (such as $SOCl_2$, SO_2Cl_2, $(NSCl)_3$) and the halogens (Br_2, I_2) to give the corresponding dithiadiazolium salt. It also formed $PhCN_2S_2^+$ salts with oxidising Lewis acids such as $SnCl_4$ (III) and group VI polycations (IV), but did not react with unsaturated systems such as phenyl acetylene or S_4N_4.

$$(PhCN_2S_2)_2 + 2SnCl_4 \longrightarrow (PhCN_2S_2)_2SnCl_6 + SnCl_2 \qquad (III)$$

$$(PhCN_2S_2)_2 + Se_4(AsF_6)_2 \longrightarrow 2PhCN_2S_2^+\ AsF_6^- + 4Se \qquad (IV)$$

In this chapter, further investigations of $(PhCN_2S_2)_2$ and attempts to prepare analogous dimers are described.

8.2 Experimental

8.2.1 Preparation and purification of $(PhCN_2S_2)_2$

The following procedure is a modification of the method described by Hey[3]. $PhCN_2S_2Cl$ (7.3 g, 33.7 mmol) and zinc-copper couple (6.6 g, 101.1 mmol) were stirred in dry T.H.F. (40 ml) at room temperature for 2 hours. The purple-black solution was then evaporated to dryness. A small quantity (0.1 g) of green-purple (dichroic) crystals were sublimed from the crude product (10 hours, 80°C/10^{-1} mmHg, coldfinger 10-15°C). I.r. absorptions (Nujol mull) were at 1597(w), 1495(sh), 1448(sh), 1448(sh), 1320(w), 1238(w), 1222(w), 1182(w), 1175(m), 1168(m), 1154(m), 1145(m), 1136(m), 1073(m), 1025(m,br), 970(br), 919(w), 898(w), 855(vw), 832(s), 830(s,br), 800(s), 776(vs), 768(vs), 688(s), 682(s), 668(mw), 660(w), 652(vs) and 508(s) cm^{-1}. (*cf.* $(PhCN_2S_2)_2$)[1]. Analysis found C, 47.08; S, 34.47; N, 15.24; H, 2.25 (99.04%). $(PhCN_2S_2)_2$ required C, 46.40; S, 35.42; N, **15.47**; H, 2.76 (100.05%).

The remaining crude material (*ca.* 12 g) was Soxhlet extracted for 4 hours with pentane (Na-dried, 140 ml). The solution was cooled to -20°C and filtered to give purple crystals of $(PhCN_2S_2)_2$ (2.5 g, 41% based on $PhCN_2S_2Cl$). Analysis found C, 48.16; S, 33.90; N, 15.23; H, 2.19 (99.48%). I.r. absorptions (for a strong Nujol mull) were 1597(mw), 1490(sh), 1452(sh), 1320(m), 1239(m), 1229(m), 1185(mw), 1178(mw), 1159(mw), 1145(ms,sh), 1139(s), 1078(m), 1025(m), 1003(mw), 982(w,br), 970(br), 922(mw), 901(mw), 838(ms), 832(sh), 805(s), 780(vs), 772(s), 690(s), 687(s), 655(s) and 511(s) cm^{-1}.

Attempted recrystallisation from pentane

A sample of the Soxhlet extracted dimer (2 g) was recrystallised from hot pentane (120 ml). The green-brown solution was cooled (-20°C) to induce crystallisation. After 3 weeks the solution had turned red-orange and deposited a yellow-orange solid and several colourless prismatic crystals (0.5 - 1 mm in length).

The yellow-orange solid had i.r. absorptions (Nujol mull) at 3150(w,br), 1580(w,br), 1550(ms), 1485(mw), 1445(sh), 1310(w), 1269(s), 1227(s), 1178(mw), 1157(w), 1128(m,br), 960(w,br), 780(sh), 771(mw), 688(mw), 670(mw), 528(mw,br) cm^{-1}. (cf. $PhCN_2S_2OH$, 1550(vs), 1486(m), 1310(m), 1180(m), 1130(ms), 782(m), 770(ms), 728(ms), 690(ms), 530(m) cm^{-1})[4]. Analysis found C, 36.33; S, 39.74; N, 12.63; H, 2.63 (91.33%). A mixture of $PhCN_2S_2OH$ and sulphur (12% by weight) required C, 37.29; S, 40.51; N, 12.44; H, 2.66 (92.90%).

The residual pentane solution was evaporated to low volume and cooled (-20°C) for a further 6 weeks when a cream-white solid was isolated which had i.r. absorptions (Nujol mull) at 3330(m,br), 3170(m,br), 1680(m,br), 1625(mw,br), 1545(sh,br), 1515(m,br), 1295(w), 1225(m,vbr), 1080(w,br), 1047(w), 1012(s), 930(w,br), 782(mw), 695(s), 620(mw,br), 525(w,br) cm^{-1} (cf. benzamidine.HCl 3300-3100(m,br), 1672(vs,br), 1605(m), 1585(mw), 1520(ms,br), 1295(mw), 1105(m), 1080(m,br), 1029(w), 1000(w), 920(mw), 845(mw), 792(s), 785(s), 690(vs), 660(ms), 620(mw), 522(m) and 409(ms) cm^{-1}).

Purification by sublimation

The purple-brown (pentane insoluble) material from the recrystallisation (1.5 g) was heated at 100°C/10^{-2}mm Hg for ½ hour during which time metallic-green crystals formed in the crude residue. These were separated (with the aid of a microscope) under dry nitrogen. Yield was 0.8 gram. Analysis found C, 45.07; S, 35.10; N, 15.50; H, 3.00 (98.67%). $(PhCN_2S_2)_2$ required C, 46.40; S, 35.42; N, 15.47; H, 2.76 (100.05%).

8.2.2 Effect of heat on $(PhCN_2S_2)_2$

A sample of dimer was heated to 300°C in a capilliary tube. The compound melted at 125°C to give a purple-red liquid. Between 170° and 290°C, slow decomposition occurred with evolution of a gas. The residue was shown to contain largely unchanged dimer and some benzonitrile (a weak absorption at 2231 cm^{-1} was due to C≡N stretch).

8.2.3 Proton n.m.r. spectroscopy on $(PhCN_2S_2)_2$

Proton resonances were measured (relative to TMS) for solutions of the dimer in CCl_4, pentane and monoglyme (Table 8.1).

TABLE 8.1

Solvent	δ/ppm	Spectral Amplitude	δ/ppm (integrated ratio)
Monoglyme	3.26 (CH_3)	4,000	7.46 (2.5)
	3.42 (CH_2)		7.80 (1.0)
Pentane	0.89 (CH_3)	30,000	7.24 (3)
	1.25 (CH_2)		7.26 (1)
CCl_4	-	40,000	7.30
			7.70

8.2.4 Controlled hydrolysis of the RCN_2S_2 and $RCN_2S_2^+$ ring systems

(a) Distilled water (9.9 μL, 0.55 mmol) was added to $(PhCN_2S_2)_2$ (0.2 g, 0.55 mmol) in T.H.F. (30 ml) and the mixture stirred for 12 hours at room temperature. A white solid was isolated (0.11 g) which gave i.r. absorptions (Nujol mull) at 3400-3000(s,vbr), 1675(s,br), 1603(m), 1525(m,br), 1477(s), 1441(m), 1400(w,br), 1295(mw), 1268(mw), 1195(w,br), 1120(vs,vbr), 1050(m), 1022(m), 1015(m), 1005(m), 980(w), 969(w), 925(w,br), 781(s), 690(vs,br), 618(s), 528(w,br), 405(w), 387(w) cm^{-1}. Analysis found C, 47.91; S, 12.83; N, 13.82; H, 5.52 (80.08%). $(PhC(NH)N(H)SO)_2$ required C, 50.28; S, 19.19; N, 16.77; H, 4.19 (90.43%).

(b) A sample of $PhCN_2S_2Cl$ which had turned cream-white after storage for 5-10 years gave i.r. absorptions (Nujol mull) at 3450(m), 3420(m), 3210(m,br), 3100(m,br), 1695(sh), 1672(m), 1630(m), 1603(m), 1560(m), 1295(w), 1220(w,br), 1172(m), 1115(mw), 1094(w,br), 1030(mw), 1000(mw), 920(w), 870(mw), 840(mw), 780(ms), 757(ms,br), 685(vs), 600(w,br) and 520(w,br) cm^{-1}

(cf. spectrum of benzamidine•HCl section 8.2.1).

Analysis found C, 41.16; H, 5.98; N, 13.15; S, 18.73; Cl, 15.30 (94.32%). An 8:1 mixture of $PhCN_2H_4Cl$ and sulphur required C, 44.55; H, 4.77; N, 14.86; S, 16.97; Cl, 18.83 (99.98%).

(c) Distilled water (2.5 μL, 1.38 mmol) was added to $PhCN_2S_2Cl$ (0.3 g, 1.38 mmol) in T.H.F. (20 ml) and the mixture stirred for 2 hours at room temperature. A pale yellow solid (0.08 g) was isolated which had i.r. absorptions (KBr disc): 3400-3000(s,vbr), 1670(vs,br), 1602(s), 1582(m), 1520 (vs,br), 1477(s), 1440(m), 1400(w,br), 1293(m), 1257(w), 1158(w), 1127(sh), 1105(sh), 1095(ms), 1068(sh), 1025(m), 998(m), 927(mw), 920(mw), 842(w), 834(w), 782(s), 690(vs,br), 611(m), 515(m), 405(m) and 388(ms) cm^{-1}. Analysis found C, 44.14; S, 17.30; N, 14.09; Cl, 18.40; H, 4.81 (98.74%). The pale yellow filtrate was evaporated to dryness to give a dark brown sticky resin, which was not studied further.

(d) Distilled water (18 μL, 1.02 mmol) was added to Bu^t-CN_2S_2Cl (0.2 g, 1.02 mmol) in diethyl ether (20 ml) and the mixture stirred for 20 mins. at room temperature. A white solid (0.09 g) was isolated which gave i.r. absorptions (KBr disc) at 3400-3100(vs,vbr), 2970(s), 1670(vs,br), 1510(m), 1480(s,br), 1400(w), 1372(m), 1225(s,br), 1076(m), 1022(m), 945(w), 868(w), 810(m,br), 650(ms,vbr) and 540(m) cm^{-1}. Analysis found C, 34,06; S, 18.90; N, 14.72; Cl, 19.30; H, 8.92 (95.90%).

(e) A sample of Bu^t-CN_2S_2Cl when exposed to moist air for 12 hours became white in colour. The hydrolysed solid had i.r. absorptions (KBr disc) at 3400-3100 (vs,vbr), 2975(s), 2930(ms), 2775(mw), 2740(mw), 1675(vs,br), 1575(w), 1512(vs), 1468(m), 1400(sh), 1377(ms), 1370(ms), 1360(m), 1262(vs), 1233(vs,br), 1208(m), 1188(vs), 1109(m), 1080(vs,sh), 1025(vs), 948(m), 938(m), 868(m), 800(m,br), 650(vs,vbr), 620(s), 540(ms), 525(m), 497(w), 482(w) and 400(w,br) cm^{-1}. Analysis found C, 35.37; S, 21.20; N, 15.56; Cl, 17.85; H, 8.21 (98.19%). An 8:1 mixture of Bu^t-CN_2H_4Cl and sulphur required C, 35.60; S, 18.99; N, 16.62; Cl, 21.06; H, 7.71 (99.98%).

8.2.5 Attempted preparations of $(CH_3CN_2S_2)_2$

(a) $CH_3CN_2S_2Cl$ (0.3 g, 1.94 mmol) was stirred with NaNCS (0.16 g, 1.94 mmol) in monoglyme (40 ml) for 30 mins. at room temperature. The mixture was filtered to give a yellow-white solid (50 mg) (which was shown to be unreacted sodium thiocyanate) and a dark cherry red solution. The latter was reduced to low volume and cooled (-20°C) but no solid was precipitated. When the solution was evaporated in vacuo a red-orange product condensed in the cold trap (77K). This changed, reversibly between -55°C and room temperature into a pale yellow liquid, and decomposed instantly on exposure to the atmosphere.

(b) $CH_3CN_2S_2Cl$ (0.3 g, 1.94 mmol) was stirred with zinc/copper couple (0.13 g, 1.94 mmol) in T.H.F. (30 ml) for 1½ hours at room temperature. The red-brown solution was evaporated to dryness to give a brown sticky residue. A volatile orange species was trapped with the T.H.F. at 77K and this showed similar properties to the product isolated from (a) above.

Heating the brown sticky residue in vacuo ($80^{\circ}C/10^{-1}$mm Hg) removed the final traces of solvent to give a golden-brown product (0.15 g) which had i.r. absorptions (Nujol mull) at 1685(m), 1630(m,br), 1548(mw), 1260(w,br), 1240(w), 1165(w,br), 1115(br), 1068(w,br), 1040(sh), 1015(m), 920(w,br), 789(m), 630(w,br), 600(w,br) and 555(w,br) cm^{-1}.

(c) Sulphur dioxide (5.4 g) was condensed onto $CH_3CN_2S_2Cl$ (0.13 g, 0.84 mmol) and zinc/copper couple (0.05 g, 0.84 mmol) in an SO_2 reaction vessel[5] and the mixture warmed to room temperature. The red-brown solution was filtered and the SO_2 evaporated to leave a brown-black residue. I.r. absorptions (Nujol mull) were at 1675(s,vbr), 1230(ms,vbr), 1100(w,vbr), 1035(s,vbr), 1000(ms,br), 910(w), 870(vs), 842(vs), 787(s), 768(s), 620(m,br) and 540(ms) cm^{-1} (cf. underlined peaks with $CH_3CN_2S_2Cl$, Chapter 6, section 6.2.3). Analysis found S, 33.0; Cl, 25.6.

(d) Sulphur dioxide (11.5 g) was condensed onto $CH_3CN_2S_2Cl$ (0.4 g, 3.24 mmol) and NaNCS (0.53 g, 6.54 mmol) in an SO_2 reaction vessel and the mixture warmed to room temperature. The red-brown solution was filtered and the SO_2 evaporated to leave a brown-black residue. This had i.r. absorptions at (KBr disc) 3300-3100(m,br), 2080(vs), 2050(vs), 1670(vs,br), 1200(w,vbr), 1150(w,br), 1042(mw), 1015(m), 950(w,br), 755(m), 600(mw,vbr), 529(m), 479(ms), 470(m), 440(mw) cm^{-1} (underlined absorptions due to hydrolysis). Analysis found C, 20.93; N, 22.87; S, 41.80. $CH_3CN_2S_2 \cdot NCS$ required C, 20.31; N, 23.71; S, 54.28.

8.3 Reactions of the $PhCN_2S_2$ ring system

8.3.1 Reaction of $(PhCN_2S_2)_2$ with SO_2Cl_2

$(PhCN_2S_2)_2$ (0.13 g, 0.36 mmol) was stirred (1 hour, RT) with SO_2Cl_2 (30 ml and the mixture filtered to give a yellow solid which was washed with pentane (5 x 10 ml). I.r. absorptions (Nujol mull) were at 1670(m,br), 1594(mw), 1395(ms), 1292(mw), 1205(mw), 1170(w), 1150(m), 1065(w), 1028(m), 1000(w), 920(m), 890(s), 842(s), 792(w), 781(m), 698(vs), 620(w,br) and 544(m) cm^{-1} (cf. $PhCN_2S_2Cl$, Chapter 7, section 7.1.1). Underlined peaks were due to hydrolysis product. Analysis found S, 28.10; Cl, 16.90; C, 35.18; H, 2.11; N, 11.49 (92.98%). $PhCN_2S_2Cl$ required S, 29.56; Cl, 16.39; C, 38.79; H, 2.31; N, 12.93 (99.98%). Yield was 0.13 g (83% based on $(PhCN_2S_2)_2$).

8.3.2 Reaction between $(PhCN_2S_2)_2$ and boron trichloride

BCl_3 (2.5 ml) was vacuum distilled into a "Rotoflo" flask containing $(PhCN_2S_2)_2$ (0.1 g, 0.27 mmol). The dimer was recovered unreacted after 2 hours at room temperature. In a repeat reaction BCl_3 (43 μL, 0.5 mmol) was condensed into a "Rotoflo" flask containing $(PhCN_2S_2)_2$ (90 mg, 0.25 mmol) in pentane (10 ml). The solution was stirred for 12 hours at room temperature and evaporated to dryness. The brown residue had i.r. absorptions (Nujol mull) at 3200(ms,vbr), 1600(m,br), 1272(m), 1230(m), 1180(mw,br), 1125(m,br), 960(br), 750(m,br), 600(w), 535(sh) and 530(w,br) cm^{-1} (cf. hydrolysis product, page 247).

8.3.3 Reaction between $(PhCN_2S_2)_2$ and CCl_4

CCl_4 (30 ml) was condensed onto $(PhCN_2S_2)_2$ (0.2 g, 0.55 mmol) at 77K and the mixture stirred at room temperature for ⅔ hour. The yellow-orange solution was filtered to give a yellow-white solid which had i.r. absorptions (Nujol mull) at 1675(ms,br), 1505(m,br), 1400(w,br), 1100(mw,br), 1022(m,br), 1000(w), 970(w), 928(w), 784(m), 770(sh), 691(s) and 615(m,br) cm^{-1}. Analysis found C, 44.04; H, 4.45; N, 13.93; S, 17.70; Cl, 11.20(91.32%) equivalent to an empirical formula, $C_{12}H_{14}N_3S_2ClO_2$.

The i.r. spectrum of the solution contained absorptions due to CCl_4 and a few at 1447(w), 1371(mw), 1342(w), 1270(m), 1242(ms) and 690(m) cm^{-1} which were unidentified. CCl_4 was the only volatile component of the solution detected by G.l.c. (retention time was 3½ mins. using an O_{30} column (150°C) and N_2 carrier gas).

The CCl_4 solution was reduced to low volume, cooled (-20°C/3 days) and filtered to produce a white solid with i.r. absorptions (Nujol mull) at 3320(m,br), 3150(m,vbr), 1680(ms,br), 1630(m,br), 1608(mw), 1588(w), 1525(m,vbr), 1400(mw,br), 1298(w), 1225(ms,br), 1100(m,br), 1019(s), 970(w), 930(w,br), 786(s), 762(w,br), 732(w), 696(vs), 618(s,br) and 530(w,br) cm^{-1} (cf. section 8.2.1, page 247). Analysis found C, 41.34; H, 4.00; N, 14.38; S, 19.60; Cl, 9.56 (88.88%) equivalent to an empirical formula, $C_{13}H_{15}N_4S_2ClO_2$.

The CCl_4 solution was then evaporated to dryness and the residue heated in vacuo (80°C/10^{-2} mm Hg) to give a purple-black solid which had i.r. absorptions (Nujol mull) at 1675(w,br), 1595(w), 1400(w,br), 1320(w), 1240(w), 1220(w), 1137(m), 1073(mw), 1025(mw,br), 920(w), 899(w), 835(mw,br), 803(ms), 777(s), 769(s), 688(s), 685(sh), 660(w), 652(s), 615(w,br) and 509(ms) cm^{-1} (cf. $(PhCN_2S_2)_2$ section 8.2.1, page 246).

8.3.4 Reaction of $(PhCN_2S_2)_2$ with chlorobenzene

$(PhCN_2S_2)_2$ (0.2 g, 0.55 mmol) was stirred with chlorobenzene (30 ml) for 21 days at room temperature and filtered to give a sticky white-brown solid (0.1 g) and a pale yellow solution. The solid had i.r. absorptions (Nujol mull) at 3400-3100(m,u), 1680(m,vbr), 1647(s), 1582(mw), 1490(m), 1476(m), 1455(ms), 1419(ms), 1298(m), 1250(w,br), 1200(m), 1153(m), 1135(w), 1082(m,br), 1065(w), 1021(m), 1002(w), 981(m), 932(w), 900(w), 869(m), 790(w,br), 741(vs), 729(m), 702(m), 686(m), 621(mw), 563(mw) and 466(mw) cm^{-1} (cf. underlined peaks with chlorobenzene: 1582, 1477, 1445, 1090, 1068, 1021, 1000, 900, 740, 702, 682 and 468 cm^{-1}).

The solid was recrystallised from nitromethane and pale yellow crystals (2 mg) were isolated which gave i.r. absorptions at 1648 (m,br), 1597(w), 1582(w), 1530(w), 1488(m), 1420(m), 1298(mw), 1200(m), 1180(w), 1172(w), 1155(m), 1100(m,br), 1025(m), 997(mw), 980(m), 940(w), 932(w), 870(ms), 850(mw), 814(w), 802(w), 792(mw), 778(mw), 730(s), 700(m), 688(m), 650(m), 620(m), 562(m), 540(w), 528(w) and 455(w) cm^{-1} (Nujol mull).

The solution was evaporated to dryness to give a yellow solid (0.08 g) which after recrystallisation from CH_3NO_2 (5 ml) gave a pale lemon, microcrystalline solid (10 mg). This had an i.r. spectrum similar to that quoted above. Analysis found C, 39.31; H, 2.54; N, 13.78; S, 47.75 (103.38%). $(PhCN_2S_2)_2S_2$ required C, 39.39; H, 2.35; N, 13.14; S, 45.11 (99.99%).

8.3.5 Reaction between $(PhCN_2S_2)_2$ and chloramine, Me_2NCl

Chloramine (40 μL, 0.5 mmol) was condensed into a Schlenk tube containing $(PhCN_2S_2)_2$ (90 mg, 0.25 mmol) in pentane (5 ml), kept at -20°C (2 weeks) and filtered to give a brown solid and a pale yellow-brown solution. The solid had weak, broad i.r. absorptions at 1670, 1625, 1540, 1225, 1120, 1015, 832, 805, 780(sh), 768, 690, 650, 615 and 525 cm^{-1}. No evidence was obtained for the presence of $PhCN_2S_2Cl$. The solution was evaporated to low volume and the volatiles examined by gas phase i.r. spectroscopy. The absorptions were all assigned to pentane apart from one, at 675 cm^{-1} which was unidentified. Me_4N_2 was not detected in the pentane solution.

8.3.6 Reaction between $(PhCN_2S_2)_2$ and PCl_3

(a) PCl_3 (20 μL, 0.34 mmol) was condensed into an n.m.r. tube (modified for vacuum line connection) containing $(PhCN_2S_2)_2$ (60 mg, 0.17 mmol) in T.H.F. (1 ml) at 77K. The mixture was warmed to room temperature and examined by phosphorus n.m.r. A yellow solid formed rapidly but only one phosphorus resonance was detected, at -219.3 ppm. (cf. standard PCl_3 -219.3 ppm).

(b) When the reaction was done in neat PCl_3, some yellow solid had formed after 48 hours, but the dimer was mostly unchanged. One ^{31}P resonance was detected at -220.7 ppm.

(c) Reaction (a) was repeated using $(PhCN_2S_2)_2$ (70 mg, 0.19 mmol), PCl_3 (25 μL, 0.38 mmol) and T.H.F. (10 ml). The mixture was stirred at room temperature for 2 hours and filtered to give a yellow solid (40 mg). I.r. absorptions (Nujol mull) were at 1675(w,br), 1597(w), 1169(w), 1150(m), 1065(w,br), 1029(w), 970(w,br), 922(mw), 892(s), 845(ms), 794(m), 782(m), 696(vs), 620(w) and 548(ms) cm^{-1}. (cf. $PhCN_2S_2Cl$, Chapter 7, section 7.1.1). Analysis found Cl, 20.9; S, 27.5; $PhCN_2S_2Cl$ required Cl, 16.4; S, 29.6. A solution of this solid in nitrobenzene recorded no ^{31}P resonances in the range -300 to +500 ppm.

^{31}P n.m.r. on the T.H.F. solution showed two resonances (δ = -217.6 and -77.9 ppm) after 1 hour, only one after 10 hours (-219.6) and three after 200 hours (-219.3, -46.7 and -1.6). The latter resonances were present after a further 100 hours.

8.3.7 Reaction of $(PhCN_2S_2)_2$ with Ph_3P

(a) $(PhCN_2S_2)_2$ (94 mg, 0.26 mmol) was stirred in CCl_4 (20 ml) for five minutes at room temperature, to give an orange-red solution. Ph_3P (67 mg, 0.26 mmol) was added but no reaction occurred. The mixture was refluxed for 4 hours, cooled to -20°C and filtered to give a yellow-white solid which had i.r. absorptions at 3350(w,br), 3150(w,br), 1675(m), 1605(w), 1590(w), 1550(w,br), 1300(w), 1260(m), 1245(m,br), 1200(w,br), 1115(w,br), 1047(w), 1009(ms), 785(m), 735(m), 690(m), 620(w), 575(w) and 528(w) cm^{-1}. (cf. section 8.3.3, page 252). The solution was evaporated to dryness to give a sticky orange residue. Similar results were obtained when $(PhCN_2S_2)_2$ (0.15 g, 0.41 mmol) was reacted with Ph_3P (0.22 g, 0.82 mmol) in CCl_4 (40 ml) and the mixture refluxed for 1 hour.

(b) Solid $(PhCN_2S_2)_2$ (0.11 g, 0.30 mmol) and Ph_3P (0.16 g, 0.61 mmol) were heated (130°C/½ h) together in a Schlenk tube. The residue had major i.r. absorptions at 1150, 1143, 1100, 1070, 1025, 997, 970, 840, 805, 770, 748, 690, 652, 639, 614, 517 and 510 cm^{-1}. Underlined peaks were assigned to $(PhCN_2S_2)_2$ (——) and Ph_3P (----).

8.3.8 Vapour phase reaction of $(PhCN_2S_2)_2$ with Ag

$(PhCN_2S_2)_2$ (92 mg, 0.25 mmol) vapour was passed through silver wool (0.16 g, 1.53 mmol) in a pyrolysis tube (Apparatus C - Chapter 5, pages 128-9) under the following experimental conditions: T_1 = 50 - 120°C; T_2 = 180 - 240°C; T_3 = 5°C and P = 10^{-3} mm Hg.

The purple solid which formed on the coldfinger (T_1 = 60, T_2 = 200) had i.r. absorptions characteristic of $(PhCN_2S_2)_2$. Analysis found S, 33.83; N, 15.05; C, 46.05; H, 3.43 (98.36%). $(PhCN_2S_2)_2$ required S, 35.40; N, 15.46; C, 46.37; H, 2.76 (99.99%). No sulphur was detected in the silver catalyst.

8.3.9 Reaction between $(PhCN_2S_2)_2$ and $Mo(CO)_6$

$(PhCN_2S_2)_2$ (0.2 g, 0.55 mmol) was stirred (RT/4 weeks) with $Mo(CO)_6$ (0.28 g, 1.06 mmol) in T.H.F. (30 ml), and the mixture filtered to give a blue-grey solid (0.1 g) and a pale yellow-green solution. The former had i.r. absorptions at 3400(ms,br), 3200(ms,vbr), 1680(vs,br), 1611(mw), 1595(w), 1525(w,br), 1285(ms,br), 1230(s,br), 1170(s,br), 1068(mw), 1035(vs), 1003(w), 974(w), 940(w), 789(m), 694(m), 660(mw,br), 573(m) and 439(ms) cm^{-1}. Similar absorptions were recorded after washing the solid with CH_2Cl_2. Analysis found Mo, 1.90; S, 15.60; C, 36.28; H, 3.90; N, 13.71 (71.39%).

8.3.10 U.V. irradiation of $(PhCN_2S_2)_2$ in hexane

$(PhCN_2S_2)_2$ (0.2 g, 0.55 mmol) in hexane (40 ml) was irradiated with U.V. light (medium power, wide band spectrum) for 5 hours and filtered to give a pale orange solution and a dark brown solid. The solid had i.r. absorptions (at 1150, 1020, 856, 830, 802, 775, 768, 754, 690, 650 and 505 cm^{-1}) due to unreacted dimer and some (at 3400-3100(br), 1675, 1400, 1225 and 620 cm^{-1}) due to hydrolysis product.

8.4 Reactions of the $PhCN_2S_2^+$ ring system

8.4.1 Reaction between $PhCN_2S_2Cl$ and dimethylurea

$PhCN_2S_2Cl$ (0.4 g, 1.8 mmol) was refluxed with $(MeNH)_2CO$ (0.13 g, 0.9 mmol) in monoglyme (30 ml) for 2 hours and filtered to give a pale yellow solid and a yellow-orange solution. The solid contained unreacted $PhCN_2S_2Cl$ (strong i.r. absorptions at 1150, 920, 889, 842, 793, 781, 695 and 548 cm^{-1}).

8.4.2 Reaction between $PhCN_2S_2Cl$ and hydrogen sulphide

H_2S was bubbled through a solution of $PhCN_2S_2Cl$ (3.5 g, 15.7 mmol) in nitromethane (30 ml) for 1 hour. The mixture was filtered to give a cream-white solid which was washed with CS_2 (2 x 10 ml) and dried *in vacuo*. Yield 0.8 g. Analysis found C, 42.18; H, 4.97; N, 15.38; S, 18.69; Cl, 19.42 (100.64%). A mixture of benzamidine hydrochloride and sulphur (17% by weight) required C, 44.54; H, 4.77; N, 14.85; S, 17.00; Cl, 18.83 (99.99%). I.r. absorptions (KBr disc) were at 3400-3100(s,br), 1672(s,br), 1608(w), 1508(m), 1475(m), 1440(w), 1400(w,br), 1325(w,br), 1297(w), 1165(w), 1139(w), 1070(mw,vbr), 1021(mw), 925(w,br), <u>891(w)</u>, <u>841(w)</u>, 820(w), 787(m), <u>692(s)</u>, 620(w), <u>550(w)</u>, 530(w), 440(w,br), 410(w) and 390(w) cm^{-1}. (Underlined peaks indicated some unreacted $PhCN_2S_2Cl$).

8.4.3 Reaction between $PhCN_2S_2Cl$ and Raney nickel

$PhCN_2S_2Cl$ (1.1 g, 5.07 mmol) and Raney nickel (0.4 g, 10.14 mmol) were stirred in T.H.F. (40 ml) for 12 hours at room temperature. The solution was filtered to give a grey solid and an orange-brown solution. Analysis of the solid found N, 26.0; Cl, 27.3. It did not contain sulphur.

The solution contained three components, with R_f values (in CS_2) of 0.09 (brown, streaked from baseline), 0.23 (f) and 0.97(f). Evaporation to low volume produced a brown-black solid which was characterised as impure $(PhCN_2S_2)_2$ with strong i.r. absorptions (Nujol mull) at 840, 832, 805, 779, 770, 690, 685, 654 and 512 cm^{-1}.

8.4.4 Reaction between $PhCN_2S_2Cl$ and Ph_3P

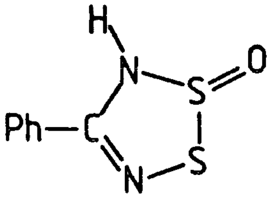
A solution of Ph_3P (1.08 g, 4.15 mmol) in CH_2Cl_2 (45 ml) was added to $PhCN_2S_2Cl$ (0.9 g, 4.15 mmol) and the mixture refluxed for 2 hours. A pale yellow solution formed, from which colourless crystals (10 mg) were formed by evaporation to low volume and cooling to $-20^{o}C$ (1 week). These had i.r. absorptions at 1583(w), 1570(vw), 1433(vs), 1335(br,u), 1307(mw), 1180(w), 1158(w), 1102(s), 1098(s), 1068(m), 1025(m), 998(m), 752(ms), 748(ms), 713(s), 690(s), 639(s), 614(m), 540(w), 518(ms), 511(ms), 470(mw), 457(mw) and 429(mw) cm^{-1}. Underlined absorptions were assigned to Ph_3P. The remaining solution was evaporated to dryness to produce a yellow-white solid which had i.r. absorptions at 1584(w,br), 1570(w,br), 1435(s), 1338(br,u), 1307(mw), 1195(mw,u), 1180(mw), 1158(mw), 1115(m,sh), 1102(ms), 1098(ms), 1068(mw), 1025(mw), 997(mw), 950(mw), 882(mw,br), 762(mw,sh), 752(m,sh), 748(m), 718(s), 690(s), 670(sh), 638(ms), 613(m), 569(mw,br), 543(sh) 532(m), 518(ms), 510(ms), 490(mw), 479(mw), 457(w) and 429(w) cm^{-1}. A solution of this residue in CH_2Cl_2 gave the following ^{31}P chemical shifts (relative to 85% H_3PO_4, downfield direction negative) = -43.63, -30.72, -17.81 and 4.9 ppm (cf. $Ph_3P = S$, -39 to -43; $Ph_3P = O$, -23 to -27 and Ph_3P, 5-8 ppm)[6]. Major mass spectral peaks were at 77(16.3)-Ph^+; 108(14.2)-PhP^+; 185(62.5)-Ph_2P^+; 201(6.2)-Ph_2PO^+; 217(6.1)-Ph_2PS^+; 262(27.2)-Ph_3P^+; 277(36.5)-Ph_3PNH^+; 278(21.3)-Ph_3PO^+; 294(100.0)-Ph_3PS^+.

8.5 Discussion

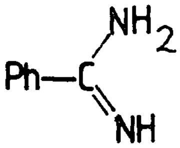
8.5.1 Purification and characterisation of $(PhCN_2S_2)_2$

Two methods of purifying $(PhCN_2S_2)_2$ were investigated (section 8.2.1), sublimation and Soxhlet extraction with pentane. The former gave small quantities of a high purity dimer. Pentane extraction was, however, the better method, giving a good yield of reasonably pure material.

Slow recrystallisation from pentane resulted in hydrolysis of the dimer. The yellow-orange solid, isolated after 3 weeks, was probably $PhCN_2S_2OH$ (V) with an impurity of sulphur (indicated by high S and low C, H and N analyses). I.r. absorptions correlated well with those reported by Fielder for pure $PhCN_2S_2OH$[4].



(V)



(VI)

The strong i.r. absorption at 1550 cm^{-1} was probably due to C=N stretch (compounds containing the C=N group are known to absorb in the region 1689 - 1471 cm^{-1})[7].

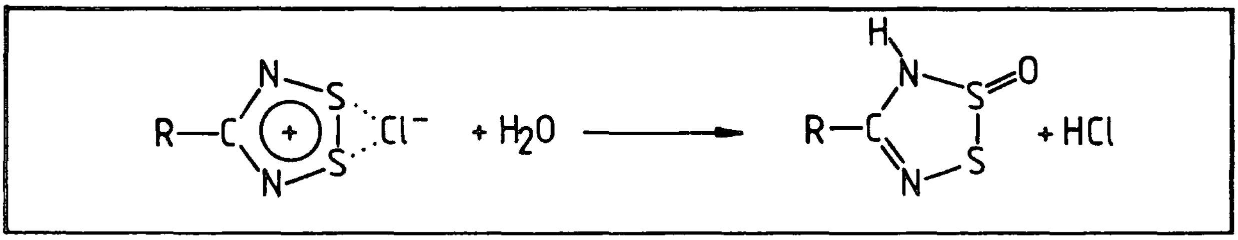
After 6 weeks a product was isolated which had an i.r. spectrum similar to benzamidine hydrochloride. It is likely therefore that further hydrolysis had occurred, ($V \rightarrow VI$)(see section 8.5.2). The strong absorptions at 1269 and 1227 cm^{-1}, in the first hydrolysis product, were probably due to NSO stretching vibrations, since they were absent from the spectrum of the second. Similar frequencies (1234 and 1215 cm^{-1}) were reported for the cyclic thionyl imide, $(HNSO)_4$ [8].

Only weak proton resonances were observed for $(PhCN_2S_2)_2$ because of its low solubility in suitable n.m.r. solvents. (The strongest solution was in monoglyme but even this required a spectral amplification factor of 4000). In order to check the validity of the results, therefore, measurements were made in several solvents.

Two resonances were observed (Table 8.1) with average chemical shifts of 7.35 ± 0.11 and 7.70 ± 0.10. Solutions of $(PhCN_2S_2)_2$ in the protonic solvents, monoglyme and pentane, showed deshielding and shielding effects (0.16 — 0.20 and 0.06 — 0.09 p.p.m. respectively) compared with CCl_4. The strong deshielding effect of monoglyme was probably caused by H-bonding interactions between solvent and dimer molecules. (These interactions also explain the higher solubility of $(PhCN_2S_2)_2$ in monoglyme). In contrast, the protons of $(PhCN_2S)_2$ would be shielded by the hydrogens of pentane. The aromatic protons of $(PhCN_2S_2)_2$ absorb at a position slightly downfield from those in benzene (δ = 7.25 p.p.m.)[9] and this reflects the electron-withdrawing nature of the $-CN_2S_2$ substituent. Benzonitrile (also downfield of benzene) has a similar chemical shift (7.55 p.p.m.)[9].

8.5.2 Hydrolysis of the RCN_2S_2 and $RCN_2S_2^+$ ring systems

It has been suggested[10] that hydrolysis of the $RCN_2S_2^+$ ring system occurs as follows:



However the i.r. spectrum of an old sample of $PhCN_2S_2Cl$ (section 8.4.2b) compared well with standard benzamidine hydrochloride, and the solid analysed as a mixture of $PhCN_2H_3 \cdot HCl$ and sulphur. Complete hydrolysis of the ring had therefore occurred. Similar results were observed for the $Bu^t-CN_2S_2Cl$ (section 8.2.4e) and a proposed mechanism is shown in Figure 8.1. No evidence was obtained for loss of HCl as required for mechanism (B).

In order to recognise the hydrolysis products invariably formed in reactions of $(PhCN_2S_2)_2$ (section 8.3) and $PhCN_2S_2Cl$ (section 8.4), a controlled hydrolysis of the $RCN_2S_2^+$ and RCN_2S_2 systems was carried out using the method described by Mueller.[11] In this way both $PhCN_2S_2Cl$ and $Bu^t-CN_2S_2Cl$ (sections 8.2.4c,d) were hydrolysed to an amidine hydrochloride, SO_2 and sulphur (Table 8.2).

FIGURE 8.1

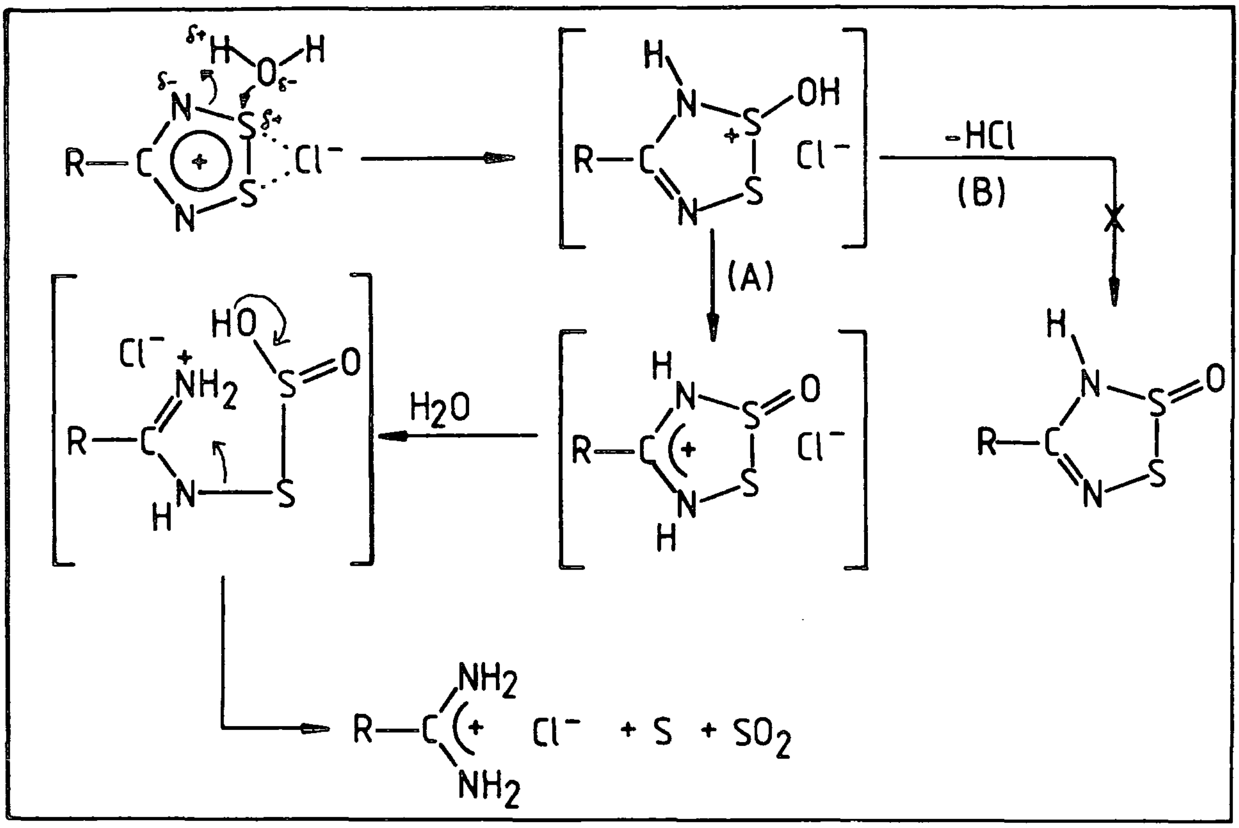


TABLE 8.2

	8.2.4c	Calc. for $PhCN_2H_4Cl$ and 17% S by weight	8.2.4d	Calc. for Bu^t-CN_2S_2Cl and 20% S by weight
C	44.14	44.55	34.06	35.02
H	4.81	4.77	8.92	7.59
N	14.09	14.86	14.72	16.35
S	17.30	16.97	18.90	20.32
Cl	18.40	18.83	19.30	20.72

Sulphur analysis of the product isolated from hydrolysis of $(PhCN_2S_2)_2$ (section 8.2.4a) was not consistent with the formation of $PhCN_2S_2OH$ (Table 8.3) and the possibility of a mixture of benzamidine and sulphur was ruled out because of the analytical evidence for the presence of oxygen. It is possible that $(PhC(NH)N(H)SO)_2$ (VII) was the major product of the reaction. It could be produced by dimerisation of the fragment formed by loss of sulphur from $PhCN_2S_2OH$ (Figure 8.2).

FIGURE 8.2

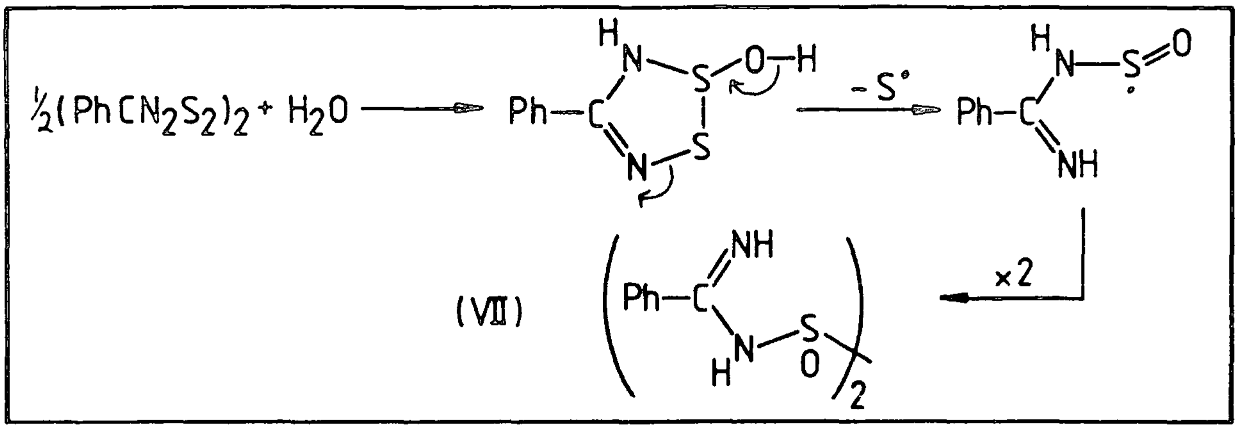


TABLE 8.3

	8.2.4a	Calc. for $PhCN_2S_2OH$	Calc. for $(PhC(NH)N(H)SO)_2$
C	47.91	42.39	50.28
H	5.52	3.03	4.19
N	13.82	14.14	16.77
S	12.83	32.36	19.19

Further support for structure (VII) came from the i.r. spectrum which had bands at ca. 3150, 1675 and 1120 cm^{-1} (assigned respectively to N-H, C=N and S=O* stretching vibrations) but which was significantly different to that recorded for $PhCN_2S_2OH$ [4] and standard benzamidine. Further purification and characterisation are required to confirm this possibility.

In summary, the $RCN_2S_2^+$ cation, being more susceptible to nucleophilic attack than RCN_2S_2, is completely hydrolysed to amidine hydrochlorides, sulphur and SO_2; whereas intermediates such as $PhCN_2S_2OH$ and possibly $(PhC(NH)N(H)SO)_2$ can be isolated from hydrolysis of $(PhCN_2S_2)_2$. $PhCN_2S_2OH$ can be further hydrolysed to benzamidine, sulphur and SO_2.

8.5.3 Attempted synthesis of dimers analogous to $(PhCN_2S_2)_2$

Of the known $RCN_2S_2^+$ systems (R = Ph-, Cl_3C-, and Bu^t-) only $PhCN_2S_2^+$ can be reduced to a dimeric thiadiazole. $(Cl_3C.CN_2S_2)_2$ and $(Bu^t-CN_2S_2)_2$ could not be prepared[12], presumably because steric crowding of the substituents prevented formation of a stable bonding S-S interaction between the $PhCN_2S_2$ molecules.

Reduction of $CH_3CN_2S_2Cl$ was attempted using NaNCS and Zn/Cu in monogylme, T.H.F. and SO_2 (section 8.2.5). A highly moisture sensitive red-orange volatile species was detected as a by-product of the reactions in monoglyme and T.H.F. This may have been a conjugated C-S-N heterocycle which dissociated on warming (cf. the known system $(NSCl)_{3(S)} \overset{50^oC}{\rightleftharpoons} 3NSCl_{(g)}$)[13]. Alternatively the compound could be thermochroic in nature (like S_4N_4), possessing an electronic transition which is blue shifted into the U.V. by heating from 77-298K.

Though its presence was inferred by the colour change from orange to purple (section 8.2.5a,b), $(CH_3CN_2S_2)_2$ did not crystallise from solution and evaporation to dryness produced sticky residues.

$CH_3CN_2S_2.NCS$ was formed by the room temperature reaction of $CH_3CN_2S_2Cl$ and NaNCS in SO_2 (section 5.2.5d). The crude salt had the i.r. absorptions characteristic of NCS^- [14]: 2080 and 2050 cm^{-1} (due to C≡N stretch), 479 and 470 cm^{-1} (NCS bending vibrations) and 755 cm^{-1} (C-S stretch) (cf. 2060(br), 475(br) and 750(br) cm^{-1} for anhydrous sodium thiocyanate). As well as absorptions at 1042, 1015, 529 and 440 cm^{-1}, which were probably due to complex vibrations of the $CH_3CN_2S_2^+$ cation (cf. 1029, 861, 848 and 535 cm^{-1} for the Cl^- salt, Chapter 6, page 203), there were some due to hydrolysis (section 8.2.5).

Hey synthesised $PhCN_2S_2.NCS$ in a room temperature reaction between $PhCN_2S_2Cl$ and NH_4NCS in liquid SO_2 [15]. In room temperature and refluxing monoglyme solutions, this salt was reduced to give $(PhCN_2S_2)_2$. He also showed that $(PhCN_2S_2)_2$ was produced by thermal decomposition of the solid thiocyanate. It may be worthwhile, therefore, to purify the $CH_3CN_2S_2.NCS$ salt and attempt a similar vapour phase conversion to $(CH_3CN_2S_2)_2$.

8.5.4 Reactions of the $PhCN_2S_2$ ring system

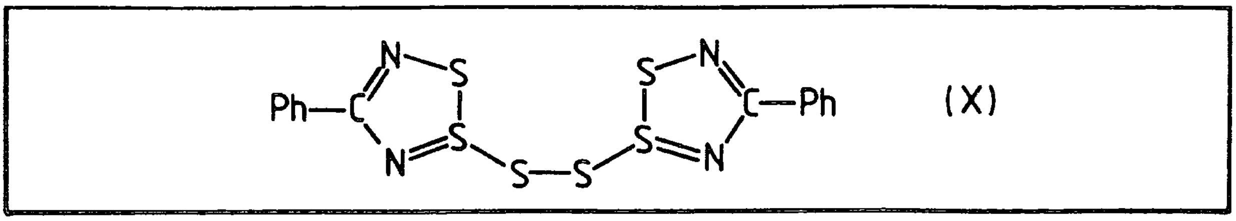
Hey[16] found that $(PhCN_2S_2)_2$ can be oxidised to $PhCN_2S_2^+$ salts by reaction with, for example, SO_2Cl_2. In fact the conversion is almost quantitative (section 8.3.1). It was therefore decided to investigate the ability of the dimer to abstract chlorine from reagents containing B-, C-, N- and P-Cl bonds (sections 8.3.2-8.3.6 respectively).

$(PhCN_2S_2)_2$ did not react with BCl_3 either neat or in pentane solution. In the latter case the dimer was partially hydrolysed. It is likely that the following equilibria exist for the dimer in solvents such as pentane, and that the monomeric species,(IX)is very reactive and readily hydrolysed.

$$(PhCN_2S_2)_2 \text{ (solid)} \rightleftharpoons \underset{\text{(VIII)}}{(PhCN_2S_2)_2} \text{ (solution)} \rightleftharpoons \underset{\text{(IX)}}{2PhCN_2S_2^{\bullet}} \text{ (solution)}$$

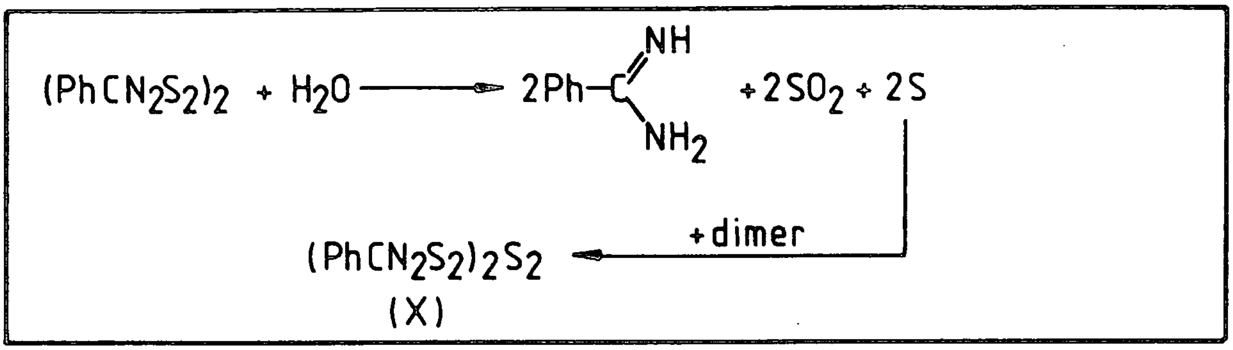
Although detection of chlorine in the solid product confirmed that a chlorine abstraction reaction had occurred between $(PhCN_2S_2)_2$ and CCl_4 (section 8.3.3), there was no i.r. evidence that $PhCN_2S_2Cl$ had been formed. The i.r. spectrum was similar to that reported on page 247 for the hydrolysis product from pentane solution. Clearly the monomeric species, $PhCN_2S_2^{\bullet}$ was more susceptible to hydrolysis in solution than oxidation by CCl_4. Since some $(PhCN_2S_2)_2$ was recovered unchanged (page 252) it is clear that the orange colour of the CCl_4 was due to $(PhCN_2S_2)_2$ (VIII) in solution and not a reaction product.

Some hydrolysis of $(PhCN_2S_2)_2$ also occurred in chlorobenzene (section 8.3.4) and there was no evidence of chlorine abstraction. However, the pale yellow crystals, isolated in low yield from solution (page 253) analysed as $(PhCN_2S_2)_2S_2$, for which structure (X)is postulated.


(X)

This compound could result from reaction of $(PhCN_2S_2)_2$ with the sulphur produced by hydrolysis of the dimer (Figure 8.3).

FIGURE 8.3



Structure (X) is supported by i.r. evidence, with a C=N stretching vibration at 1648 cm^{-1} and possible ring vibrations at 980, 870, 730, 688, 650 and 562 cm^{-1}. The absorption at 455 cm^{-1} could be due to ν(S-S) (cf. 430-520 cm^{-1} in aryl disulphides)[17]. Higher yields of this compound might be produced by reacting $(PhCN_2S_2)_2$ with sulphur in a solvent such as dry pentane.

Average thermochemical bond energies[18] were compared (Table 8.4) for the chlorine containing reagents used in Sections 8.3.1 - 6.

TABLE 8.4

Bond	Energy/kJ mol^{-1} (25°C)
B-Cl	548 (19)
C-Cl	327 (18)
N-Cl	193 (18)
P-Cl	319 (18)
S-Cl	255 (18)

The N-Cl bond in chloramine is very weak and readily hydrolyses, thus the brown solid isolated in section 8.3.5 was probably a mixture of chloramine and $(PhCN_2S_2)_2$ hydrolysis products.

$(PhCN_2S_2)_2$ was oxidised by PCl_3 (section 8.3.6) giving $PhCN_2S_2Cl$

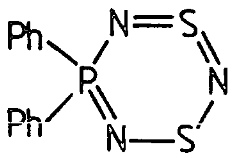
in good yield (56% based on $(PhCN_2S_2)_2$). The nature of the phosphorus species was not, however, clear from ^{31}P n.m.r. spectroscopy (section 8.3.6c). An intermediate was formed (δ = -77.9 ppm) which decomposed in solution to give two products, both containing phosphorus (δ = -46.7 and -1.6 ppm respectively). It is likely that one of the final products was $POCl_3$ (Table 8.5). Equation (XI) is the simplest representation of the reaction, however the absorptions at -77.9 and -46.7 ppm are both at higher field than would be expected for P_2Cl_4.

$$(PhCN_2S_2)_2 + 2PCl_3 \longrightarrow 2PhCN_2S_2Cl + P_2Cl_4 \qquad (XI)$$

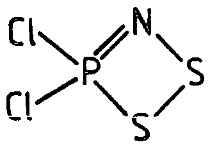
TABLE 8.5

Phosphorus compound	Shift (ppm)
$POCl_3$	-1.9 (20)
P_2Cl_4	-130.0*
$PhCN_2S_2^+ \; PCl_4^-$	-200.0*
P_4	+450.0 (6)
$PSCl_3$	-28.8 (20)
* estimated values (21)	

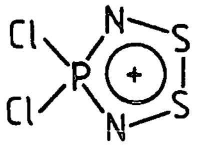
$Ph_2PS_2N_3$ (XII) was recently reported to have a ^{31}P n.m.r. shift of -21.2 ppm[22] thus it is possible that the absorption at -46.7 ppm represents a new 6π P-S-N compound (such as XIII or XIV).



(XII)



(XIII)



(XIV)

Conclusions

$(PhCN_2S_2)_2$, probably reacting in solution as the monomer $PhCN_2S_2^{\circ}$, will not abstract chlorine from strong bonds in excess of ca. 320 kJ mol^{-1} (such as B-Cl and possibly C-Cl). Oxidation (to $PhCN_2S_2^+$) occurred readily where the energetics were most favourable, for instance, with compounds containing a weak R-Cl bond, or where the reduction product was gaseous (XV) or involved the formation of a strong bond.

(XV) $(PhCN_2S_2)_2 + SO_2Cl_2 \rightleftharpoons 2PhCN_2S_2Cl + SO_2$ $\Delta G = \Delta H - T\Delta S$

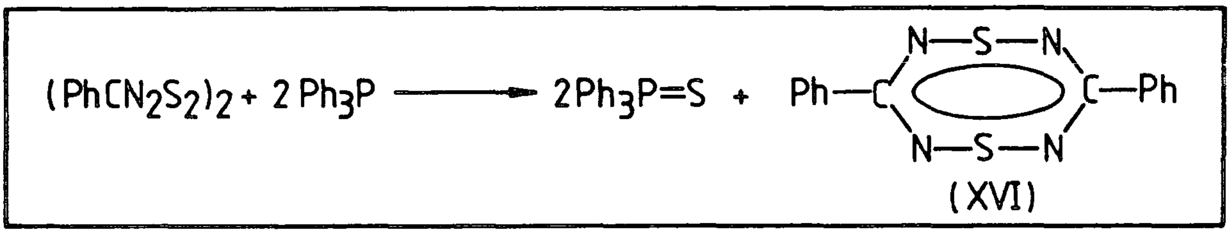
Reaction solvents should be carefully dried before use, since $PhCN_2S_2$ is very moisture sensitive.

In view of the strength of metal-metal bonds, it would be worthwhile to investigate the reactions of $(PhCN_2S_2)_2$ with metal carbonyl chlorides such as $Mn(CO)_5Cl$, $CpMo(CO)_5Cl$, $Re(CO)_5Cl$ and $CpFe(CO)_5Cl$. For example,

$$(PhCN_2S_2)_2 + 2Mn(CO)_5Cl \longrightarrow Mn_2(CO)_{10} + 2PhCN_2S_2Cl$$

8.5.5 Attempts to form new heterocycles from $(PhCN_2S_2)_2$

Attempts were made to synthesise new heterocycles (e.g. the 10π Hückel species, XVI) from $(PhCN_2S_2)_2$ by reacting with desulphurisation reagents such as Ph_3P (section 8.3.7) and hot silver wool (section 8.3.8).

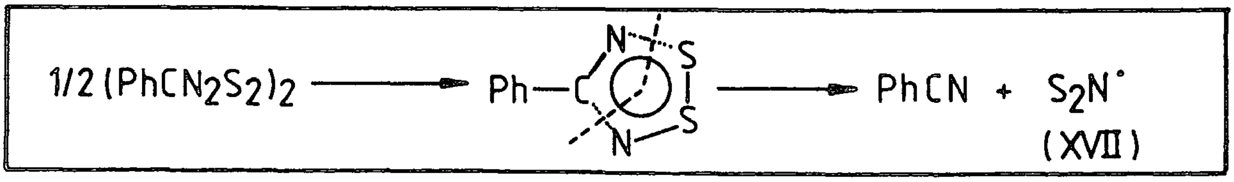


(XVI)

$(PhCN_2S_2)_2$ did not react with Ph_3P in CCl_4 solution but produced a hydrolysis product similar to that described in section 8.3.3. There was some evidence (an i.r. absorption at 639 cm^{-1} which could not be assigned to Ph_3P) that the dimer had been desulphurised by heating with solid Ph_3P (section 8.3.7b) (cf. 627 cm^{-1} P=S stretching frequency in Ph_3PS)^{23} It might therefore be worthwhile to investigate, with chromatography, an organic extract of the heated residue.

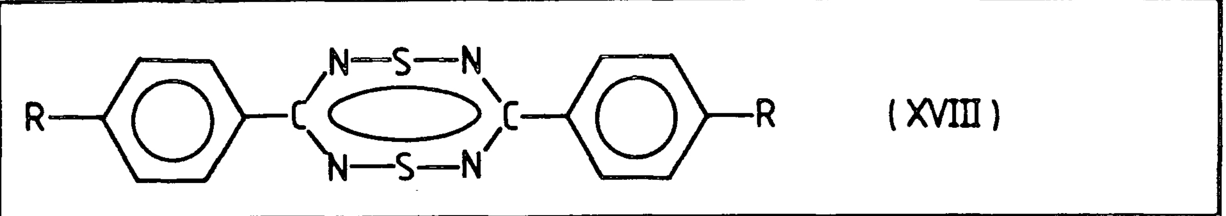
$(PhCN_2S_2)_2$, in contrast to vaporised $S_5N_5FeCl_4$ and silver (Chapter 5, section 5.2.4), was unaffected by hot silver wool.

$(PhCN_2S_2)_2$ was reacted with a transition metal carbonyl, $Mo(CO)_6$ (section 8.3.9) in an attempt to isolate a metal thionitrosyl involving the fragment, S_2N generated by decomposition of the dithiadiazole ring, (XVII).



(XVII)

The solid product, however, contained virtually no molybdenum, and analysed as $C_6H_8N_2S$ which (apart from a low carbon analysis) would be consistent with formation of the 10π species(XVIII)(R = H).



(XVIII)

As expected, the i.r. spectrum was similar to that recorded for $(PhC(NH)N(H)SO)_2$ (section 8.2.4a) except that the peak at 1120 cm^{-1} (assigned to S=O) was absent whilst there were additional strong peaks at 1230, 1170, 1035 and 439 cm^{-1}. Absorptions at 1285, 1230, 1170, 1003, 974, 940, 789 and 694 cm^{-1} had counterparts in the i.r. spectrum reported for compound (XVIII) which has recently been prepared from benzamidine, SCl_2 and diazabicycloundecene[24].

Conclusions

In general, the reactions of $(PhCN_2S_2)_2$ studied were not straightforward, but led to several products, invariably including hydrolysis compounds. Results suggested that members of a new heterocyclic system (XVIII) could be isolated if the purification problems were overcome. However, since $(PhCN_2S_2)_2$ itself has to be prepared in two stages from PhCN,SCl_2 and ammonium chloride, it is felt that the 1,5-dithia-2,4,6,8 tetrazocines are best prepared directly from benzamidine[24,25].

Also, the susceptibility of $(PhCN_2S_2)_2$ to moisture indicated that future reactions should be done in flamed out and sealed tubes.

8.5.6 Reactions of the $PhCN_2S_2^+$ ring system

Several attempts were made to synthesise new heterocycles from $PhCN_2S_2Cl$. Gaseous H_2S (section 8.4.2) caused ring degradation to benzamidine hydrochloride and sulphur (i.r. and analytical evidence). It was hoped that Raney nickel would act as a desulphurisation reagent, however it reduced the $PhCN_2S_2^+$ ring to $(PhCN_2S_2)_2$ in a reaction similar to the $PhCN_2S_2Cl$/metal reductions already known[3]. Strong ^{31}P nmr, i.r. and mass spectral evidence was obtained that Ph_3PS was a product of the reaction of $PhCN_2S_2Cl$ and Ph_3P (section 8.4.4). It is likely that once again ring breakdown occurred to give $PhCN_2H_4Cl$ (*i.e.* the benzamidine hydrochloride).

8.6 References

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APPENDIX

(a) Lectures and Seminars organised by the Department of Chemistry during the period 1978-1981

(* denotes those attended).

15 September 1978

Professor W. Siebert (University of Marburg, West Germany),
"Boron Heterocycles as Ligands in Transition Metal Chemistry".

22 September 1978

Professor T. Fehlner (University of Notre Dame, U.S.A.),
"Ferraboranes: Syntheses and Photochemistry".

* 12 December 1978

Professor C.J.M. Stirling (University of Bangor),
" 'Parting is such sweet sorrow' - the Leaving Group in Organic Reactions".

* 14 February 1979

Professor B. Dunnell (University of British Columbia),
"The Application of N.M.R. to the study of Motions in Molecules".

16 February 1979

Dr. J. Tomkinson (Institute of Laue-Langevin, Grenoble),
"Properties of Adsorbed Species".

14 March 1979

Dr. J.C. Walton (University of St. Andrews),
"Pentadienyl Radicals".

20 March 1979

Dr. A. Reiser (Kodak Ltd.),
"Polymer Photography and Mechanism of Cross-link Formation in Solid Polymer Matrices".

25 March 1979

Dr. S. Larsson (University of Uppsala),
"Some Aspects of Photoionisation Phenomena in Inorganic Systems".

25 April 1979

Dr. C.R. Patrick (University of Birmingham),
"Chlorofluorocarbons and Stratospheric Ozone: An Appraisal of the Environmental Problem".

1 May 1979

Dr. G. Wyman (European Research Office, U.S. Army),
"Excited State Chemistry in Indigoid Dyes".

2 May 1979

Dr. J.D. Hobson (University of Birmingham),
"Nitrogen-centred Reactive Intermediates".

* 8 May 1979

Professor A. Schmidpeter (Institute of Inorganic Chemistry,
University of Munich).
"Five-membered Phosphorus Heterocycles Containing Dicoordinate Phosphorus"

9 May 1979

Dr. A.J. Kirby (University of Cambridge),
"Structure and Reactivity in Intramolecular and Enzymic Catalysis".

9 May 1979

Professor G. Maier (Lahn-Giessen),
"Tetra-tert-butyltetrahedrane".

* 10 May 1979

Professor G. Allen, F.R.S. (Science Research Council).
"Neutron Scattering Studies of Polymers".

16 May 1979

Dr. J.F. Nixon (University of Sussex),
"Spectroscopic Studies on Phosphines and their Coordination Complexes".

23 May 1979

Dr. B. Wakefield (University of Salford)
"Electron Transfer in Reactions of Metals and Organometallic
Compounds with Polychloropyridine Derivatives".

13 June 1979

Dr. G. Heath (University of Edinburgh),
"Putting Electrochemistry into Mothballs - (Redox Processes
of Metal Porphyrins and Phthalocyanines)".

* 14 June 1979

Professor I. Ugi (University of Munich),
"Synthetic Uses of Super Nucleophiles".

20 June 1979

Professor J.D. Corbett (Iowa State University, Ames, Kowa, U.S.A.)
"Zintle Ions: Synthesis and Structure of Homo-polyatomic Anions
of the Post-Transition Elements".

27 June 1979

Dr. H. Fuess (University of Frankfurt),
"Study of Electron Distribution in Crystalline Solids by X-ray
and Neutron Diffraction".

21 November 1979

Dr. J. Muller (University of Bergen),
"Photochemical Reactions of Ammonia".

28 November 1979

Dr. B. Cox (University of Stirling)
"Macrobicyclic Cryptate Complexes, Dynamics and Selectivity".

5 December 1979

Dr. G.C. Eastmond (University of Liverpool),
"Synthesis and Properties of Some Multicomponent Polymers".

12 December 1979

Dr. C.I. Ratcliffe (University of London),
"Rotor Motions in Solids".

* 19 December 1979

Dr. K.E. Newman (University of Lausanne),
"High Pressure Multinuclear NMR in the Elucidation of the Mechanisms of Fast, Simple Reactions".

* 30 January 1980

Dr. M.J. Barrow (University of Edinburgh),
"The Structures of Some Simple Inorganic Compounds of Silicon and Germanium - Pointers to Structural Trends in Group IV".

* 6 February 1980

Dr. J.M.E. Quirke (University of Durham),
"Degradation of Chlorophyll-a in Sediments".

23 April 1980

B. Grievson B.Sc., (University of Durham),
"Halogen Radiopharmaceuticals".

* 14 May 1980

Dr. R. Hutton (Waters Associates, U.S.A.),
"Recent Developments in Multi-milligram and Multi-gram Scale Preparative High Performance Liquid Chromatography".

21 May 1980

Dr. T.W. Bentley (University of Swansea),
"Medium and Structural Effects in Solvolytic Reactions".

10 July 1980

Professor P. Des Marteau (University of Heidelberg),
"New Developments in Organonitrogen Fluorine Chemistry".

7 October 1980

Professor T. Felhner (Notre-Dame University, U.S.A.),
"Metalloboranes - Cages or Coordination Compounds?"

15 October 1980

Dr. R. Adler (University of Bristol),
"Doing Chemistry Inside Cages - Medium Ring Bicyclic Molecules".

12 November 1980

Dr. M. Gerloch (University of Cambridge),
"Magnetochemistry is about Chemistry".

19 November 1980

Dr. T. Gilchrist (University of Liverpool),
"Nitroso Olefins as Synthetic Intermediates".

3 December 1980

Dr. J.A. Connor (University of Manchester),
"Thermochemistry of Transition Metal Complexes".

18 December 1980

Dr. R. Evans (University of Brisbane, Australia),
"Some Recent Communications to the Editor of the Australian Journal of Failed Chemistry".

* 18 February 1981

Professor S.F.A. Kettle (University of East Anglia),
"Variations in the Molecular Dance at the Crystal Ball".

* 25 February 1981

Dr. K. Bowden (University of Sussex),
"The Transmission of Polar Effects of Substituents".

4 March 1981

Dr. S. Craddock (University of Edinburgh),
"Pseudo-Linear Pseudohalides".

11 March 1981

Dr. J.F. Stoddard (I.C.I. Ltd./University of Sheffield),
"Stereochemical Principles in the Design and Function of Synthetic Molecular Receptors".

* 17 March 1981

Professor W. Jencks (Brandsis University, Massechusetts),
"When is an Intermediate not an Intermediate?".

18 March 1981

Dr. P.J. Smith (International Tin Research Institute),
"Organotin Compounds - A Versatile Class of Organometallic Compounds".

* 9 April 1981

Dr. W.H.Meyer (RCA Zurich),
"Properties of Aligned Polyacetylene".

6 May 1981

Professor M. Szware, F.R.S.,
"Ions and Ion Pairs".

10 June 1981

Dr. J. Rose (I.C.I. Plastics Division),
"New Engineering Plastics".

17 June 1981

Dr. P. Moreau (University of Montpellier),
"Recent Results in Perfluoroorganometallic Chemistry".

(b) First year induction course (October-November 1977)

A series of one hour presentations on the services available in the Department.

i. Departmental organisation.
ii. Safety matters.
iii. Electrical appliances.
iv. Chromatography and microanalysis.
v. Library facilities.
vi. Atomic absorption and inorganic analysis.
vii. Mass spectrometry.
viii. Nuclear magnetic resonance spectroscopy.
ix. Glassblowing technique.