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**SOME CRYSTAL STRUCTURES OF  
SULPHUR NITROGEN AND CARBON BORON COMPOUNDS**

**By**

**I. Rayment, B.Sc.**

**A Thesis Submitted for the Degree of Doctor  
of Philosophy. Grey College, University of Durham.**

**July, 1975**



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I would like to express my sincere thanks to Dr H.M.M. Shearer under whose guidance this research was undertaken, for his excellent supervision and example.

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In conclusion I gratefully acknowledge the award of a Science Research Council Studentship.

Memorandum

This thesis describes research in chemical crystallography carried out in the Chemistry Department of the University of Durham between October 1972 and July 1975. This is the original work of the author except where acknowledged by reference, and has not been submitted for any other degree.

Part of the work described in this thesis has been the subject of the following publication:

The structure of thiodithiazyl chlorodisulphate,  $S_3N_2S_2O_6Cl$  and its preparation from thiodithiazyl monochloride,  $S_3N_2Cl$ , Banister, A.J., Clarke, H.G., Rayment, I. and Shearer, H.M.M. (1974). Inorg. Nucl. Chem. Letters 10, 647.

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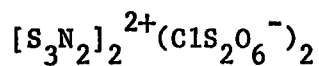
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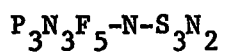
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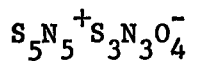
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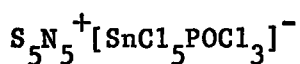


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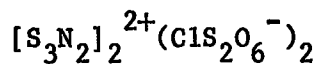
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(BCH<sub>3</sub>)<sub>6</sub>(CH)<sub>4</sub>

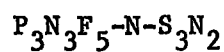
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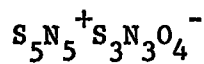
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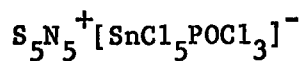
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$S_4N_4O_2$

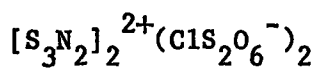
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$(BCH_3)_6(CH)_4$

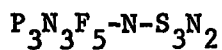
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SUMMARY

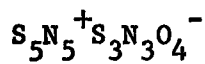
The crystal structures of five compounds containing cyclic sulphur-nitrogen species and one carbon-boron compound have been studied using X-ray diffraction methods. The sulphur-nitrogen compounds all contain two-coordinate nitrogen atoms and short S-N bonds which are characteristic of multiple bonding.



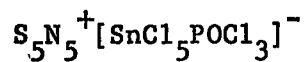
The cation consists of two, almost planar  $S_3N_2$  rings related by a centre of symmetry and held together by a four-centre S-S interaction. Each ring is thought to contain an aromatic  $6\pi$  system.



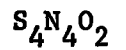
The molecule consists of an  $S_3N_2$  ring bonded at sulphur via a bridging nitrogen atom to a fluorophosphonitrilic ring. The  $S_3N_2$  ring is thought to contain a pseudo-aromatic  $6\pi$  system.



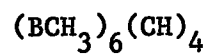
The cation is a roughly planar ten-membered ring of alternating sulphur and nitrogen atoms, and represents a  $14\pi$  inorganic aromatic Hückel compound. Its shape is that of azulene except that the molecule does not have a transannular N-N bond. The anion is an  $S_3N_3$  ring with two oxygen atoms on two of the sulphurs. The  $SO_2-N-SO_2$  part of the ring which carries the negative charge is bonded by single bonds to a sulphur diimide fragment.



The  $\text{S}_5\text{N}_5^+$  cation is essentially the same as in  $\text{S}_5\text{N}_5^+\text{S}_3\text{N}_3\text{O}_4^-$ . The anion consists of a tin atom bonded to five chlorine atoms and the oxygen of a  $\text{POCl}_3$  ligand in a roughly octahedral arrangement.



This molecule consists of a non-planar  $\text{S}_4\text{N}_4$  ring with both oxygen atoms attached to the same sulphur.



The molecule has a structure resembling that of adamantane. The framework of the molecule consists of a tetrahedron of carbon atoms held together by six boron atoms so that the molecular symmetry approximates to  $\bar{4}3m$ . Unlike normal carboranes the bonding can be described in terms of localised single B-C bonds.

**CHAPTER 1**

**Structure Determination By X-Ray Diffraction Methods**





## 1.1 Introduction.

The most important feature of the crystalline state is the three dimensional periodicity of the atomic or molecular arrangement within the crystals. Any position in a crystal is surrounded by a regular array of further positions which have exactly the same environment; this array defines the crystal lattice and gives a geometrical representation of the periodicity within a crystal. The lattice may be described in terms of any three non-coplanar vectors,  $\underline{a}$ ,  $\underline{b}$  and  $\underline{c}$  which represent unit translations between lattice points. These vectors define a parallelepiped which is referred to as the unit cell. This is described as primitive if there is one lattice point associated with it. In general there are elements of symmetry associated with the unit cell, and the entire set will correspond to one of the thirty two possible crystallographic point groups. The symmetry elements of the unit cell together with the translational elements of symmetry provided by the lattice define the space group of the crystal.

The faces and planes within a crystal may be indexed according to their relationship with the vectors  $\underline{a}$ ,  $\underline{b}$  and  $\underline{c}$ . A series of parallel planes which divide the vector  $\underline{a}$  into  $h$  parts,  $\underline{b}$  into  $k$  parts and  $\underline{c}$  into  $l$  parts is given the indices  $hkl$  and these are known as Miller indices. Crystal faces normally contain a high concentration of lattice points and consequently have small values for  $h$ ,  $k$ , and  $l$ .

## 1.2 Diffraction of X-rays and the Reciprocal Lattice.

In 1912 von Laue suggested that if X-rays were wave-like in nature and their wavelength was of the same magnitude as the distances between atoms, then it ought to be possible to observe X-ray diffraction effects. This suggestion was tested by Friedrich and Knipping who allowed a beam of white X-ray radiation to fall on a copper sulphate crystal and recorded the resulting diffraction pattern on photographic film. This established the wave properties of X-rays and started the science of X-ray crystallography.

Von Laue interpreted the results in terms of diffraction from a three-dimensional array of scattering centres according to the relationships

$$a (\cos \alpha - \cos \alpha_0) = h\lambda$$

$$b (\cos \beta - \cos \beta_0) = k\lambda$$

$$c (\cos \gamma - \cos \gamma_0) = l\lambda$$

where each expression represents the conditions necessary for diffraction to occur from a line of scatterers parallel to the axial directions.  $\alpha_0$ ,  $\beta_0$  and  $\gamma_0$  represent the angles of the incident radiation to the directions a, b and c, whereas  $\alpha$ ,  $\beta$  and  $\gamma$  represent the angles of diffraction. Whilst this approach is rigorous it is hard to visualise.

W.L. Bragg interpreted the diffraction patterns as being the result of the reflection of X-rays from planes within the crystal, and showed that for a set of planes with spacing  $d_{hkl}$  the necessary

condition for diffraction is,  $n\lambda = 2d_{hkl} \sin \theta$ , where  $\theta$  is the angle of the incident and diffracted radiation to the planes. This approach is much easier to understand but describes diffraction effects in terms of reflections.

A further concept of great value in interpreting diffraction patterns is that of the reciprocal lattice. This is defined by the three vectors  $\underline{a}^*$ ,  $\underline{b}^*$  and  $\underline{c}^*$  such that

$$\begin{array}{lll} \underline{a}^* \cdot \underline{a} = 1 & \underline{a}^* \cdot \underline{b} = 0 & \underline{a}^* \cdot \underline{c} = 0 \\ \underline{b}^* \cdot \underline{a} = 0 & \underline{b}^* \cdot \underline{b} = 1 & \underline{b}^* \cdot \underline{c} = 0 \\ \underline{c}^* \cdot \underline{a} = 0 & \underline{c}^* \cdot \underline{b} = 0 & \underline{c}^* \cdot \underline{c} = 1 \end{array}$$

i.e.  $\underline{a}^*$  is perpendicular to  $\underline{b}$  and  $\underline{c}$ . If  $\phi$  is the angle between  $\underline{a}$  and  $\underline{a}^*$  then

$$\underline{a} \cdot \underline{a}^* = |\underline{a}| |\underline{a}^*| \cos \phi$$

Hence

$$\begin{aligned} |\underline{a}^*| &= \frac{1}{|\underline{a}| \cos \phi} \\ &= \frac{1}{d_{100}} \end{aligned}$$

Each point in the lattice is related to a series of parallel planes in the crystal. For the planes of index  $hkl$ , the vector  $\underline{s}$  of magnitude  $\frac{1}{d_{hkl}}$  and direction perpendicular to the planes corresponds exactly to the vector  $h\underline{a}^* + k\underline{b}^* + l\underline{c}^*$ . The vector  $\underline{s}$  is known as the scattering vector.

### 1.3 The Structure Factor.

A crystal which contains  $N$  atoms in its unit cell may be viewed as  $N$  interpenetrating lattices, each centred on the position of one atom. The intensity of diffraction from that crystal may then be explained in terms of the sum of the diffraction from the individual lattices. The scattering from these arrays will differ in phase according to their separation.

Consider one atom,  $A$  in the cell; its position may be defined by the vector

$$\underline{r}_A = x\underline{a} + y\underline{b} + z\underline{c}$$

where  $x$ ,  $y$  and  $z$  are the coordinates in the fractions of the cell edges. The scattering from the array based on this atom with respect to one electron at the origin of each unit cell is given by the expression,  $f_A \exp(2\pi i \underline{r}_A \cdot \underline{s})$ , where  $f_A$  is the scattering factor for the atom  $A$  and  $\underline{s}$  is the scattering vector such that  $\underline{s} = h\underline{a}^* + k\underline{b}^* + l\underline{c}^*$ . Thus  $\underline{r}_A \cdot \underline{s}$  represents the perpendicular distance of the atom from the plane  $hkl$ . The exponential function,  $\exp(2\pi i \underline{r}_A \cdot \underline{s})$ , may be viewed as a rotation function in the complex plane and represents the difference in phase between the position  $\underline{r}_A$  and the origin i.e.

$$\frac{\phi_A}{2\pi} = \underline{r}_A \cdot \underline{s}$$

The expression for the scattering by the entire contents of the unit cell is given by

$$F(hkl) = \sum_{n=1}^N f_n \exp(2\pi i \underline{r}_n \cdot \underline{s})$$

Substituting for  $\underline{r}_n$  and  $\underline{s}$  gives

$$F(hkl) = \sum_{n=1}^N f_n \exp 2\pi i (x_n \underline{a} + y_n \underline{b} + z_n \underline{c}) \cdot (h \underline{a}^* + k \underline{b}^* + l \underline{c}^*)$$

which reduces to

$$= \sum_{n=1}^N f_n \exp[2\pi i (hx_n + ky_n + lz_n)]$$

this may be expressed in terms of its real and imaginary parts, i.e.

$$F(hkl) = A(hkl) + iB(hkl)$$

where

$$A(hkl) = \sum_{n=1}^N f_n \cos 2\pi (hx_n + ky_n + lz_n)$$

$$B(hkl) = \sum_{n=1}^N f_n \sin 2\pi (hx_n + ky_n + lz_n)$$

The scattering factors are calculated from the spatial distribution of electrons around the nucleus of the atom and are derived from the atom's atomic wave function.

Because the electrons associated with an atom occupy a finite volume, X-rays scattered from different parts of the atom differ increasingly in phase with increasing scattering angle. This results in destructive interference and consequently a decrease in the scattering factor with increasing scattering angle.

The quantity  $F(hkl)$  is known as the structure factor for the reflection  $hkl$ ; its modulus  $|F(hkl)|$  is known as the structure amplitude and is defined as the ratio of the amplitude of the radiation scattered by the contents of one unit cell, compared to that scattered by a single electron at the origin. The structure amplitude is given by

$$|F(hkl)|^2 = A(hkl)^2 + B(hkl)^2$$

and the phase angle for the scattered radiation is given by

$$\phi(hkl) = \tan^{-1} \frac{B}{A}$$

The presence of symmetry in the unit cell and lattice enables the structure factor calculation to be simplified. The most important element is the centre of symmetry, since this causes the  $B(hkl)$  terms to vanish. This occurs because  $\sin(-\theta) = -\sin \theta$  and for every atom at  $x, y, z$  there is a corresponding one at  $\bar{x}, \bar{y}, \bar{z}$ . As a consequence the phase angle is either 0 or  $\pi$  and the structure factors are either positive or negative. If further elements of symmetry are present then the structure factor may be simplified by collecting together all the terms arising from the equivalent positions and combining them trigonometrically. However when atoms are vibrating

anisotropically the scattering factors may not be the same for atoms in different equivalent positions and may not contribute equally to the structure factor. In these cases the general expression has to be used.

The observed structure factor corresponds to diffraction from the electron density throughout the cell, and the form just given calculated on the basis of spherically symmetrical atoms is an approximation to the actual electron density. If the diffraction of an infinitesimally small volume of electron density is considered, then the diffraction from the whole cell is given by the expression

$$F(hkl) \int_0^1 \int_0^1 \int_0^1 \rho(xyz) \exp[2\pi i(hx + ky + lz)] V dx dy dz$$

where  $V dx dy dz$  is the small volume and  $\rho(xyz)$  is the electron density at the point  $x, y, z$ .

#### 1.4 Temperature Factor.

The description of the structure factor just given is based on diffraction from a periodic array of stationary atoms; in reality the atoms in a crystal are subject to vibration about their mean position. The frequencies of vibration are very small compared to that of the X-rays i.e.  $\approx 10^{13}$  Hz for thermal vibration as compared to  $\approx 10^{18}$  Hz for X-rays, so that the X-rays effectively encounter a stationary model, in which the atoms are displaced slightly from their mean positions. As a consequence of destructive

interference the scattering factor falls off more rapidly with increasing  $\sin \theta/\lambda$  than for the atom at rest.

The scattering factor for an atom in thermal vibration is given by the product of  $f_0$  for the atom at rest multiplied by the transform  $q$  of the smearing function  $t$

$$\text{i.e.} \quad f_t(\text{hkl}) = f_0(\text{hkl}) q(\text{hkl})$$

For isotropic thermal motion  $q$  becomes

$$q = \exp[-B(\sin \theta/\lambda)^2]$$

$$\text{where} \quad B = 8\pi^2 \bar{u}^2$$

$B$  is known as the Debye factor and  $\bar{u}^2$  is the mean square amplitude of vibration.

In most cases the vibrations are not isotropic and the electron density time averages to ellipsoids. These may be described by a symmetrical tensor  $U$  with six independent components, such that the mean square amplitude of vibration in the direction of the unit vector  $\underline{l} = (l_1, l_2, l_3)$  is

$$\bar{U} = \sum_{i=1}^3 \sum_{j=1}^3 U_{ij} l_i l_j$$

$$\text{or} \quad \bar{U} = U_{11} l_1^2 + U_{22} l_2^2 + U_{33} l_3^2 + 2U_{23} l_2 l_3 + 2U_{31} l_3 l_1 + 2U_{12} l_1 l_2$$

$$\text{so that } q(\text{hkl}) = \exp[-2\pi^2 (U_{11} h^2 a^{*2} + U_{22} k^2 b^{*2} + U_{33} l^2 c^{*2} + 2U_{23} k l b^* c^* + 2U_{31} l h c^* a^* + 2U_{12} h k a^* b^*)]$$



For ease of computation these terms may be expressed as

$$q(hk1) = \exp[-(\beta_{11}h^2 + \dots + \beta_{23}k1 + \dots)]$$

where  $\beta_{11} = 2\pi^2 a^2 U_{11}$

$$\beta_{23} = 4\pi^2 b^* c^* U_{23}$$

It is often of value to have an estimate of the overall temperature factor and scale factor before the structure is known, and these can be estimated by a method due to Wilson (1942). He showed that the average of the square of the structure amplitude over a range of  $(\sin \theta/\lambda)^2$  tends to be given by

$$\overline{|F|^2} = \sum_j \overline{f_j^2}$$

Where  $\sum_j \overline{f_j^2}$  represents the sum of the squares of the atomic scattering factors for the atoms in the cell, and are calculated for the centre of the  $(\sin \theta/\lambda)^2$  range.  $\overline{|F_0|^2}$  is usually known on an arbitrary scale, so that

$$\overline{|F_0|^2} = K \overline{|F|^2}$$

and therefore

$$\overline{|F_0|^2} = K \sum_j \overline{f_j^2}$$

Assuming the Debye-Waller correction

$$f_j^2 = f_{0j}^2 \exp(-2 B \sin^2 \theta/\lambda^2)$$

Substituting and taking logarithms gives

$$\ln \left( \frac{|\overline{F_0}|^2}{\sum_j \overline{f_{0j}}^2} \right) = \ln K - \frac{2B}{\lambda^2} \sin^2 \theta$$

A plot of  $\sin^2 \theta$  against  $\ln |\overline{F_0}|^2 / \sum_j \overline{f_{0j}}^2$  gives from the intercept an estimate of the scale factor and from the slope an estimate of the temperature factor.

### 1.5 Anomalous Dispersion.

For both centrosymmetric and noncentrosymmetric crystals the intensities of the rays diffracted from the planes  $hkl$  and  $\overline{hkl}$  are identical (Friedel's law) unless one of the atoms has an absorption edge which lies close to but on the long-wavelength side of the radiation used for diffraction. In this case the wave scattered by that atom shows an anomalous phase shift. The scattering factor  $f$  can now be expressed in terms of the normal scattering factor  $f_0$  and two additional correction factors i.e.

$$f = f_0 + f' + if''$$

For noncentric crystals this produces a breakdown of Friedel's law and may be used to determine absolute configurations. In the case of centric crystals Friedel's law still holds, but the intensities are modified and unless a correction is made for this effect there may be systematic errors in the atomic parameters (Templeton, 1955).

### 1.6 Fourier Series

In X-ray diffraction a crystal may be described in terms of a periodic distribution of electron density which can be represented by a three-dimensional Fourier series

$$\rho(xyz) = \sum_{h'} \sum_{k'} \sum_{l'} C(h'k'l') \exp[2\pi i(h'x + k'y + l'z)]$$

where  $h'$ ,  $k'$  and  $l'$  are integers from  $-\infty \rightarrow +\infty$ . This expression for  $\rho(xyz)$  may be substituted into the expression for  $F(hkl)$

$$F(hkl) = \int_V \rho(xyz) \exp[2\pi i(hx + ky + lz)] dV$$

and becomes

$$F(hkl) = \int_V \sum_{h'} \sum_{k'} \sum_{l'} C(h'k'l') \exp 2\pi i[(h+h')x + (k+k')y + (l+l')z] dV$$

The individual terms in this integration are all zero except when  $h' = -h$ ,  $k' = -k$  and  $l' = -l$ , so that

$$F(hkl) = V C(\overline{hkl})$$

and therefore

$$\rho(xyz) = \frac{1}{V} \sum_h \sum_k \sum_l F(hkl) \exp[-2\pi i(hx + ky + lz)]$$

These relationships show that the structure factors are the Fourier transform of the electron density. It is significant that the

expression for the electron density, which is a real quantity, involves not only the magnitude of the structure factor but also its phase. This constitutes the phase problem, since only the magnitudes can be measured experimentally. So that before the electron density can be calculated from the observed structure factors, their phases must be found.

This form of the expression for  $\rho(xyz)$  is not the most convenient for computation. Remembering that  $F(hkl) = A(hkl) + iB(hkl)$  and since

$$A(hkl) = |F(hkl)| \cos \phi(hkl)$$

$$B(hkl) = |F(hkl)| \sin \phi(hkl)$$

$F(hkl)$  may be written as

$$F(hkl) = |F(hkl)| \exp[i \phi(hkl)]$$

so that  $\rho(xyz)$  may be written as

$$\rho(xyz) = \sum_{hkl} |F(hkl)| \exp[-2\pi i(hx + ky + lz) - \phi(hkl)]$$

but since  $|F(hkl)| = |F(\bar{h}\bar{k}\bar{l})|$  the contributions due to these terms may be collected together, and then the expression reduces to

$$\rho(xyz) = \frac{F_{000}}{V} + \frac{2}{V} \sum_{h=0}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F(hkl)| \cos[2\pi(hx + ky + lz) - \phi(hkl)]$$

This may be simplified considerably if there are additional elements of symmetry present in the unit cell. These simplified forms are given in International Tables Vol I for all space groups.

### 1.7 Patterson Function.

In an attempt to overcome the phase problem Patterson (1934) suggested calculating a Fourier synthesis using the squares of the structure amplitudes as Fourier coefficients. He defined a function

$$P(uvw) = V \int_0^1 \int_0^1 \int_0^1 \rho(xyz) \rho(x+u, y+v, z+w) dx dy dz$$

Substitution of the expression for  $\rho(xyz)$  gives

$$P(uvw) = \frac{1}{V} \sum_h \sum_k \sum_l |F(hkl)|^2 \exp[2\pi i(hu + kv + lw)]$$

where  $P(uvw)$  is known as the Patterson function and is real for all values of  $u$ ,  $v$  and  $w$ . This may be expanded to give

$$P(uvw) = \frac{1}{V} \sum_h \sum_k \sum_l |F(hkl)|^2 \cos[2\pi(hw + kv + lw)]$$

The magnitude of the Patterson function,  $P(uvw)$  for a point  $u$ ,  $v$ ,  $w$  in the Patterson vector map represents the summation of the product of the electron density at a point  $x$ ,  $y$ ,  $z$  and at a point  $x+u$ ,  $y+v$ ,  $z+w$  over the entire cell. Hence large peaks will be found in the vector map corresponding to the vectors between atoms, and their magnitude will be related to the product of their atomic numbers. There is always a large peak at the origin corresponding to the vector between each atom and itself.

Interpretation of these vector maps is greatly simplified by the presence of symmetry in the unit cell. In certain cases peaks

between atoms in equivalent positions are observed whose positions in the vector map are restricted to certain sections or lines. These were first discovered by Harker (1936) and bear his name. For example, if a cell contains a two-fold axis parallel to  $\underline{b}$ , then for an atom at  $x, y, z$  there will be a symmetry related atom at  $\bar{x}, y, \bar{z}$  and a maximum will occur in the vector map at  $u = 2x, v = 0, w = 2z$ . With this knowledge it is often possible to locate directly the position of an atom in the unit cell.

### 1.8 Heavy atom method.

The most important practical case where the Patterson function can be used to solve a structure fairly directly is when the crystal contains a relatively small number of heavy atoms. The Patterson peaks due to these atoms then stand out against a background of overlapping smaller peaks and give immediately the coordinates of the heavy atoms. The coordinates of the lighter atoms may then be determined by computing a Fourier synthesis based on the phases obtained from the heavy atom positions. The expression for the structure factor may be written in the form

$$F(hkl) = f_H \exp 2\pi i(hx + ky + lz) + \sum_j f_j \exp 2\pi i(hx_j + ky_j + lz_j)$$

where  $f_H$  is the scattering factor for the heavy atom. The heavy atom will tend to dominate the phases whenever its contribution to

the structure factor is greater than that of the remaining atoms. This technique has been found to be most effective if

$$\sum f_{\text{heavy atoms}}^2 \approx \sum f_{\text{light atoms}}^2$$

This is applicable since the contribution to the intensity by each atom depends approximately on the square of its scattering factor. If the atom is too heavy then the errors in the intensity measurement become comparable with the contribution from the lighter atoms.

### 1.9 Direct methods.

The second major approach to the phase problem uses the statistical relationships which exist between the magnitude and phases of the structure factors. Sayre (1952) showed that for a centrosymmetric space group the sign  $S_H$  of a reflection H could be derived from a simple product of the signs of algebraically related reflections,

$$\text{i.e.} \quad S_H \approx S_K \cdot S_{H-K}$$

This expression has a high probability of being correct if the magnitude of the three structure factors  $F_H$ ,  $F_K$  and  $F_{H-K}$  are all large.

Hauptman and Karle (1953) devised a statistical approach in which they used a normalised structure factor given by

$$|E_H|^2 = \frac{|F_H|^2}{N \epsilon \sum_{j=1} f_j^2(H)}$$

where  $\epsilon$  is a factor which takes into account space group extinctions.

They also introduced the  $\Sigma_2$  relationship expressed as

$$S_H \approx S \left[ \sum_K E_K \cdot E_{H-K} \right]$$

This is similar to that introduced by Sayre except that the relationship involves more than one interaction. The probability that a sign will be positive is given by (Cochran and Woolfson, 1955)

$$P(E_H)_+ = \frac{1}{2} + \frac{1}{2} \tanh(\sigma_3 \sigma_2^{-\frac{3}{2}} |E_H| \sum E_K \cdot E_{H-K})$$

where

$$\sigma_n = \sum_{j=1}^N Z_j^n$$

This shows that if the three reflections involved in a triple relationship have large E-values then the probability that the sign relationship will be correct will be large. So that by using probability relationships it is possible to start the assignment of phases from a few strong planes whose phases are either known or represented by symbols, and this is known as the symbolic addition procedure.

A strategy for using this method outlined by Karle and Karle (1966) first involves estimating a set of normalised structure factors and finding the triple relationships which exist amongst the stronger reflections. Next it is necessary to define the origin. This is required since in general there are a number of non-equivalent centres of symmetry and movement from one to another produces



systematic changes in the signs of the reflections. The origin is specified by choosing  $n$  linearly independent reflections and arbitrarily fixing their signs where  $n$  has a maximum value of three and depends upon the space group. These reflections are used to define the signs of further reflections using the  $\Sigma_2$  relationship. Subsequently several strong planes are given symbolic phases as necessary in order to phase all of the reflections. Signs are only accepted when the total probability for a predicted sign exceeds a specified value. The acceptance limit decreases as the symbolic addition procedure continues but high values initially reduce the number of incorrect sign allocations. At the end of this procedure each reflection may have its sign correctly determined or represented by more than one symbol or combination of symbols, and using these it is possible to predict the most likely signs for the symbols used.

An alternative strategy for using the  $\Sigma_2$  relationship involves the choice of a few strong reflections whose signs are systematically varied. Each of the possible sign combinations for these reflections, together with the origin determining reflections as before is used as a starting set for reiterative application of Sayre's relationship. This gives a series of solutions and is known as the multiresolution method. In the program described by Long (1968) the signs determined from the starting set, are used to predict more signs and redetermine those predicted before. The signs of the starting set are calculated at the end of each cycle but are not allowed to change.

A measure of the self consistency of the predicted signs is given by

$$C = \frac{\langle |E_A \sum_{A=B+C} E_B E_C| \rangle}{\langle |E_A| \sum_{A=B+C} |E_B| |E_C| \rangle}$$

where  $\langle \rangle$  means averaged over all values of A. The expression compares the observed  $\Sigma_2$  sum to that which would be observed if all the interactions were consistent. Usually the set with the largest consistency index represents the correct solution.

Sayre's equation applies equally well to noncentrosymmetric structures and in its general form refers to the addition of phases so that

$$\langle \phi_H \rangle \approx \langle \phi_H + \phi_{H-K} \rangle_K$$

where K ranges over reflections with large  $|E|$  values. In centrosymmetric structures the phases are 0 or  $\pi$  so that this expression simplifies to the product of the signs of the structure factors. This expression is suitable for direct use if the phases of only a few reflections are known. Where there is more than one term contributing to  $\langle \phi_H \rangle$  these may be combined by regarding each term as a vector of length  $|E_K \cdot E_{H-K}|$  and direction  $|\phi_K + \phi_{H-K}|$ . The most probable phase is then given by

$$\tan \phi_H = \frac{\sum_K |E_K E_{H+K}| \sin(\phi_K + \phi_{H-K})}{\sum_K |E_K E_{H-K}| \cos(\phi_K + \phi_{H-K})}$$

which is known as the tangent formula and represents the combination of the vectors by summation of their components parallel to the real and imaginary axes.

### 1.10 Structure Refinement.

The object of structure refinement is to find the model which gives the best fit to the experimental data. There are far more experimental measurements than parameters to be determined so that the problem is well suited to the method of least squares.

Consider an observable quantity  $q_i$  which is a linear function of a set of variables  $x, y, z, \dots$  then

$$q_i = a_i x + b_i y + c_i z + \dots$$

If there are errors involved in the measurement of  $q_i$  this may be expressed as

$$q_i + E_i = a_i x + b_i y + c_i z + \dots$$

or

$$E_i = a_i x + b_i y + c_i z + \dots - q_i$$

then for a series of measurements in which  $i = 1 \rightarrow n$  the optimum solution of these  $n$  equations for the parameters  $x, y, z, \dots$  requires

that  $\sum E_i^2$  is a minimum.

In the refinement of a structure it is desirable to make the calculated structure factors agree as closely as possible with those observed, so that using the method of least squares it is usual to minimise the square of the difference between the observed and calculated structure factors. The function most commonly used is

$$R = \sum_{hkl} w (|F_o| - |F_c|)^2$$

where  $w(hkl)$  reflects the reliability of that observation. For  $R$  to be a minimum

$$\frac{\partial R}{\partial p_j} = 0 \quad (j = 1 \rightarrow n)$$

where  $p_j$  is the  $j$ th parameter, and hence

$$\sum_{hkl} w \Delta \frac{\partial |F_c|}{\partial p_j} = 0 \quad \text{where } \Delta = |F_o| - |F_c|$$

This process applies to linear functions, however the structure factor is calculated from an exponential function of the form

$$F_c = \sum_r f_r \exp i2\pi(hx_r + ky_r + lz_r)$$

A linear expression relating  $F_c$  to its parameters may be obtained by

taking the first two terms in Taylor's series. This is a reasonable approximation if the differences between  $F_0$  and  $F_c$  are small. Taylor's series takes the form

$$f(x + \epsilon) = f(x) + \epsilon \frac{d(fx)}{dx} + \frac{\epsilon^2}{2!} \frac{d^2(fx)}{dx^2} \dots\dots$$

In the process of refinement  $|F_c| \rightarrow |F_c'|$  where  $|F_c'|$  is the structure factor based on the improved parameters  $(p_1 + \epsilon_1)$ ,  $(p_2 + \epsilon_2) \dots\dots (p_n + \epsilon_n)$

so that

$$\sum_{hkl} w(|F_0| - |F_c'|) \frac{\partial |F_c'|}{\partial p_j} = 0 \quad (j = 1 \rightarrow n)$$

But Taylor's theorem gives

$$F_c' = F_c + \sum_{i=1}^n \epsilon_i \frac{\partial |F_c|}{\partial p_i}$$

so that

$$|F_0| - |F_c'| = |F_0| - |F_c| - \sum_{i=1}^n \epsilon_i \frac{\partial |F_c|}{\partial p_i}$$

Substituting this into  $\frac{\partial R}{\partial p_j} = 0$  and letting  $|F_0| - |F_c| = \Delta$  gives

$$\sum_{hkl} w \Delta \frac{\partial |F_c|}{\partial p_j} - \sum_{i=1}^n \left[ \sum_{hkl} w \frac{\partial |F_c|}{\partial p_i} \frac{\partial |F_c|}{\partial p_j} \right] \epsilon_i = 0$$

$$j = (1 \rightarrow n)$$

This may be rearranged and expanded to give the so called normal equations,

$$\sum_{hkl} w \left( \frac{\partial |F_c|}{\partial p_1} \right)^2 \epsilon_1 + \sum_{hkl} w \left( \frac{\partial |F_c|}{\partial p_2} \right) \left( \frac{\partial |F_c|}{\partial p_1} \right) \epsilon_2 \dots = \sum_{hkl} w \Delta \frac{\partial |F_c|}{\partial p_1}$$

$$\sum_{hkl} w \left( \frac{\partial |F_c|}{\partial p_1} \right) \left( \frac{\partial |F_c|}{\partial p_2} \right) \epsilon_1 + \sum_{hkl} w \left( \frac{\partial |F_c|}{\partial p_2} \right)^2 \epsilon_2 \dots = \sum_{hkl} w \Delta \frac{\partial |F_c|}{\partial p_2}$$

$$\begin{array}{ccc} \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \end{array}$$

Alternatively these n equations may be expressed in matrix notation

$$\sum_i a_{ij} \epsilon_i = b_j$$

where

$$a_{ij} = \sum_{hkl} w \frac{\partial |F_c|}{\partial p_i} \cdot \frac{\partial |F_c|}{\partial p_j}$$

$$b_j = \sum_{hkl} w \Delta \frac{\partial |F_c|}{\partial p_j}$$

In a structure containing many atomic parameters it is frequently impractical to calculate all the terms  $a_{ij}$  of the normal equations. The simplest approximation is to ignore all off-diagonal terms, ( $i \neq j$ ) but this approach converges slowly and does not yield the best solution. The block-diagonal approximation neglects all off-diagonal elements between different atoms. So that

a 9 x 9 matrix is used for the positional and anisotropic thermal parameters for each atom, or a 4 x 4 if the atom is refined with an isotropic temperature factor. A 2 x 2 matrix is used for the scale and overall isotropic temperature parameter. This method requires a larger number of iterations than the full matrix method. In the work described here the block-diagonal approximation was used initially but the refinement was completed using full matrix least squares methods.

### 1.11 The Accuracy of Parameters derived from Least Squares Methods

In order to obtain a reliable estimate of the accuracy of the atomic parameters the weighting scheme used in the refinement should correspond to  $w = \frac{1}{\sigma^2(F_o)}$  where  $\sigma^2(F_o)$  is the variance for the observation. In this case the variance of the parameter  $p_i$  is given by

$$\sigma^2(p_i) = (a^{-1})_{ii}$$

where  $(a^{-1})_{ii}$  is diagonal element of the inverse matrix to the normal equation matrix. Generally  $\sigma(F_o)$  is not known exactly so that relative weights of the form  $w = \frac{k_o}{\sigma^2(F_o)}$  are used, in which case the estimated standard deviation is given by

$$\sigma^2(p_i) = (a^{-1})_{ii} \cdot (\sum w \Delta^2) / (m-n)$$

where  $m-n$  is the number of degrees of freedom. The variances estimated from the block-diagonal approximation underestimate the

true variances because of the neglect of the interatomic correlations (Hodgson and Rollett, 1963).

The accuracy of interatomic distances and angles depends upon the estimated standard deviation (e.s.d.) of the atomic coordinates involved (Cruickshank and Robertson, 1953) thus if a molecular parameter  $m = \sum l_i x_i$  is a linear function of a number of atomic parameters then

$$\sigma^2(m) = \sum_i \sum_j l_i l_j \text{cov}(x_i, x_j)$$

If the atomic parameters are assumed to be independent the covariances between different atoms are taken as zero. So that for a bond  $l$  between two independent atoms having variances of  $\sigma^2(a)$  and  $\sigma^2(b)$  in the direction of the bond,  $\sigma^2(l) = \sigma^2(a) + \sigma^2(b)$ .

For an angle at B between two bonds AB and BC

$$\sigma^2(\beta) = \frac{\sigma^2(A)}{AB^2} + \sigma^2(B) \left( \frac{1}{AB^2} - \frac{2\cos\beta}{AB \cdot BC} + \frac{1}{BC^2} \right) + \frac{\sigma^2(C)}{BC^2}$$

It is often desirable to compare bond lengths or angles so that a criterion of significance is required. If it is assumed that the errors in the observed structure factors are random and if the number of degrees of freedom  $\nu$  in estimating a parameter  $l$  is large ( $\nu > 30$ ) then the observed parameter will have a normal distribution about its unknown real position  $\lambda$ . For  $\nu > 30$  the estimated standard deviation  $s$  is a good estimate of the unknown



standard deviation. Then  $t = (\ell - \lambda)/s$  where  $t$  is a random variable which has a Student distribution for  $\nu$  degrees of freedom.

It is often necessary to test the hypothesis that a theoretical value  $\lambda_0$  is compatible with an observed value  $\ell_0$ . In this case  $t_0 = (\ell_0 - \lambda_0)/s$  and from tables of the Student distribution it is possible to give an estimate of the probability that the hypothesis is correct. If the value of the probability  $P$  is small then the hypothesis may be neglected. A larger value of  $P$  means that the experimental measurement  $\ell_0$  is not inconsistent with  $\lambda_0$  but does not prove that  $\lambda_0$  is the correct value. For  $\nu > 30$  the values of  $t_0$  for the usual significance points are

$P = 0.05$	$t_0 = 1.960$
$P = 0.01$	$t_0 = 2.576$
$P = 0.001$	$t_0 = 3.291$

so that if  $t_0 = 2.576$  then the difference between  $\ell_0$  and  $\lambda_0$  is said to be significant at the 1% level. A difference is often taken as significant if  $t > 3.0$ .

If it is required to compare the difference between two bond lengths  $\ell_1$  and  $\ell_2$  with estimated standard deviations of  $s_1$  and  $s_2$  then for independent bond lengths  $t_0 = (\ell_1 - \ell_2) / (s_1^2 + s_2^2)^{\frac{1}{2}}$ . So that the difference may be taken as significant if  $t_0 > 3.0$ . If the two bonds are not independent i.e. they depend upon the common position of one atom then estimated standard deviation for the

difference,  $(s_1^2 + s_2^2)^{\frac{1}{2}}$  will be an underestimate of the true value. This may be corrected by including the covariance of the two bonds in the calculation of the e.s.d. of their difference. Cruickshank and Robertson (1953) suggest that the covariance takes the form

$$\text{cov}(l_1, l_2) = \sigma^2(B) \cos\beta$$

where B is the common atom,  $\sigma^2(B)$  is the variance of B in the direction of the tangent to the circle through A, B and C and  $\beta$  is the angle between  $l_1$  and  $l_2$ .

#### 1.12 Diffractometer Geometry.

The introduction of diffractometers has considerably improved the ease and speed of data collection whilst also improving the reliability of the data. The geometry of the Hilger and Watts Y290 four-circle diffractometer as shown in figure 1.1 is similar to that used by W.H. Bragg in his spectrometer. The counter, crystal and incident beam lie in the equatorial plane of the instrument so that the first requirement for diffraction from a plane hkl is that its scattering vector  $\underline{s} = h\underline{a}^* + k\underline{b}^* + l\underline{c}^*$  should lie in the equatorial plane. This may be attained by rotating the crystal about the  $\phi$  axis until  $\underline{s}$  lies in the plane of the  $\chi$  circle; rotation using this circle brings  $\underline{s}$  into the equatorial plane. The plane may then be brought into the diffracting position by rotating the crystal using the  $\omega$  circle until the scattering vector touches the sphere of reflection, so that the diffracted beam may be collected by placing

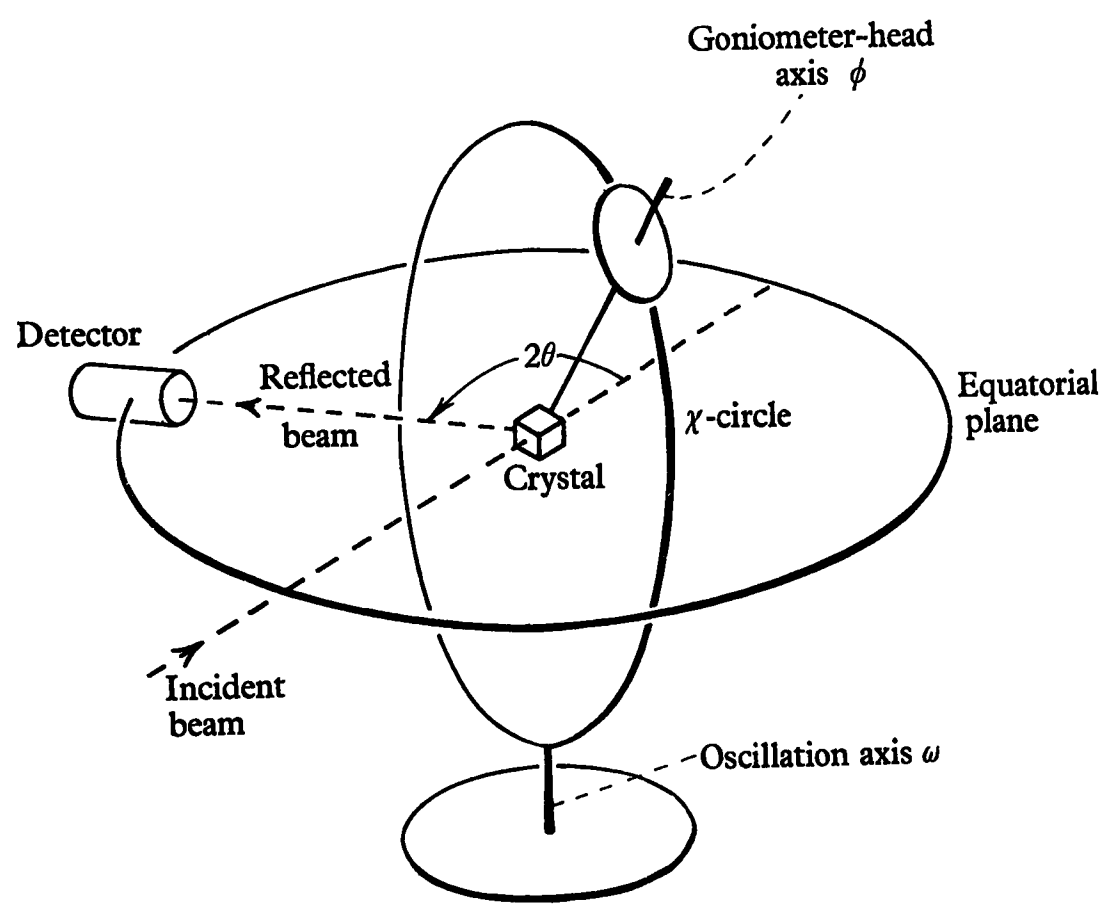


Figure 1.1

the counter mounted on the  $\theta$  circle at twice the angle on the  $\omega$  circle. This is known as the bisecting geometry since the  $hkl$  plane is orthogonal to the plane of the  $\chi$  circle which bisects the angle between the incident and diffracted beams. At large angles of  $\theta$  the  $\chi$  circle obstructs the diffracted beam so that it is necessary to change to perpendicular geometry in which the scattering vector is perpendicular to the  $\chi$  circle and  $\theta = 90 - \omega$ .

### 1.13 Lorentz and Polarisation corrections.

The Lorentz factor is introduced to account for the different times that different planes in the crystal spend in the reflecting position, or alternatively how long the reciprocal lattice points remain in contact with the sphere of reflection. For real crystals reflection occurs over a finite angular range, which means that the reciprocal lattice point has a finite size. The time that a reciprocal lattice point takes to cut the sphere of reflection will depend upon the distance of the point from the origin and the way in which it moves through the sphere of reflection.

The Lorentz factor for data collected on a four-circle diffractometer is given by

$$L = \frac{1}{\sin 2\theta}$$

The incident X-ray beam is unpolarised, which means that the azimuth of the electric vector assumes all directions with time. The beam reflected from a crystal is partially polarised and this

leads to a reduction in intensity by a factor  $p$  which is given by

$$p = \frac{1}{2} (1 + \cos^2 2\theta)$$

this depends only on the angle of diffraction and is independent of the mode of data collection.

CHAPTER 2

Unsaturated Cyclic Sulphur-Nitrogen Compounds

## 2.1 Introduction.

Research into sulphur-nitrogen chemistry was started early in the 19th century. Indeed many of the simpler compounds were discovered before 1900, although the exact nature of the majority of these has not been elucidated until more recently. Early structural work using the techniques of chemical degradation was mostly inconclusive because of problems of analysis and instability of the reaction products. The most successful analyses have been completed using diffraction methods. The more usual techniques of spectroscopy are of great value in this field, but the structural information that they yield is often inconclusive. Sulphur-nitrogen compounds usually lack the structural probes necessary for the satisfactory application of n.m.r. spectroscopy and their infrared spectra are difficult to interpret because of the wide variety of bonding found in these compounds.

Cyclic sulphur-nitrogen compounds may be broadly classified into two groups according to whether they contain a saturated or unsaturated ring system. The chemistry of these compounds has been reviewed recently (Banister, 1974) so that the major emphasis in this review will be placed on the unsaturated species since they are more relevant to the work described later. These are characterised by containing nitrogen atoms which are two-coordinate.

## 2.2 Tetrasulphur tetranitride.

The most well known unsaturated sulphur-nitrogen compound is tetrasulphur tetranitride,  $S_4N_4$  which was first prepared by Gregory

in 1835 by the reaction of disulphur dichloride with ammonia. Early work established its molecular formula, but attempts to deduce its structure from infrared and early X-ray diffraction studies were unsuccessful. Its correct molecular structure was first deduced by electron diffraction (Lu and Donohue, 1944) and has been subsequently confirmed by X-ray diffraction studies (Clarke, 1952 and Sharma and Donohue, 1963). As shown in figure 2.1 the molecule consists of a ring of alternating sulphur and nitrogen atoms which is buckled such that the sulphur atoms lie at the corners of a slightly distorted tetrahedron. There are two main features of interest in this structure. Firstly all the S-N bond distances are the same within experimental error and their mean distance of  $1.62\text{\AA}$  is considerably shorter than the normal single bond distance of  $1.73\text{\AA}$  found in  $\text{S}_7\text{NH}$  (Weiss and Neubert, 1965). Secondly the S---S distance of  $2.58\text{\AA}$  across the ring is much shorter than the S---S van der Waals distance of  $3.60\text{\AA}$  (Bondi, 1964).

Several models have been proposed in order to describe the bonding in  $\text{S}_4\text{N}_4$ . The short S---S cross-ring contacts have been attributed to the presence of a  $\sigma$ -bond composed primarily of p orbitals (Lindqvist, 1958), which would be consistent with the observation that the S---S contact is approximately perpendicular to the S-N bonds. Sulphur-sulphur single bond lengths vary considerably with the hybridisation of the sulphur atoms. The  $\text{sp}^3\text{-sp}^3$  single bond distance is normally taken as about  $2.048\text{\AA}$  as is found in  $\text{S}_8$  (Cooper, Bond and Abrahams, 1961), however longer



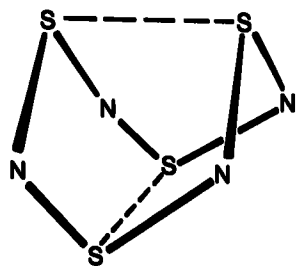
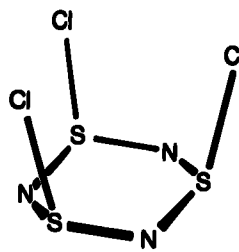
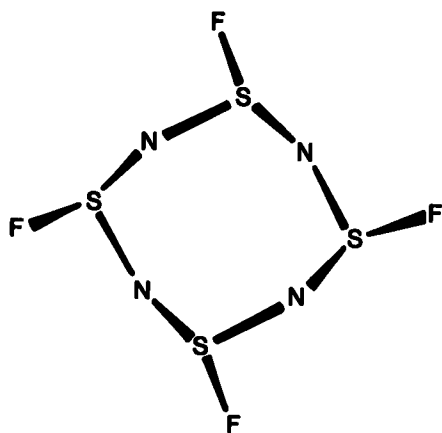
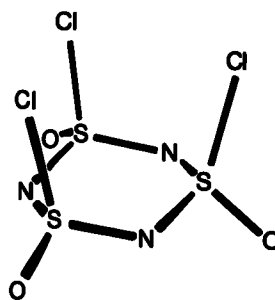
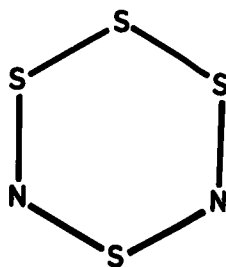
 $S_4N_4$  $(NSCl)_3$  $(NSF)_4$  $(NSOCl)_3$  $S_4N_2$ 

Figure 2.1

single bond distances of  $2.15\text{\AA}$  and  $2.39\text{\AA}$  are seen in  $\text{S}_2\text{O}_6^{2-}$  and  $\text{S}_2\text{O}_4^{2-}$  (Lindqvist and Mortzell, 1958). The length of these bonds is attributed to an increase in p character; from which it was deduced that an S-S bond composed entirely of p orbitals would be of the same magnitude as the S---S separation in  $\text{S}_4\text{N}_4$ .

The length of the S-N bonds and the two-fold coordination at the nitrogen atoms suggest that there is considerable delocalisation in these bonds. Gleiter (1970) using symmetry arguments and extended Hückel calculations concluded that the structure consists of eight single S-N bonds and two cross-ring S-S bonds. This necessitates a positive charge on each sulphur atom and a negative charge on each nitrogen atom. However there is considerable evidence for delocalisation in  $\text{S}_4\text{N}_4$ . The e.s.r. spectrum of the  $\text{S}_4\text{N}_4^-$  radical anion, produced in liquid ammonia by reduction with sodium or potassium, indicates that the unpaired electron is delocalised over the whole molecule and provides direct evidence for delocalisation in the bonding (Braterman, 1965). Further experimental evidence is provided by its high diamagnetic susceptibility which probably arises from a ring current analogous to those in aromatic compounds. On the basis of CNDO/2 calculations it was concluded that the S-N bond order is about 1.5 and also that there is a strong S-S transannular interaction (Cassoux et al. 1972). The authors interpreted their results in terms of islands of delocalisation over the S-N-S fragments so that this bonding description is analogous to that proposed by Dewar, et al, 1960 for cyclophosphazenes.

### 2.3 Cyclothiazenes.

$S_4N_4$  is exothermic with respect to decomposition to its elements. (Enthalpy of formation =  $500 \text{ kJ mol}^{-1}$ ); consequently it is a very reactive compound and the starting material for many syntheses. Some of the first compounds prepared from  $S_4N_4$  were the cyclothiazenes which are six- or eight-membered heterocycles of the type  $(NSX)_n$ . The structures of two trimeric cyclothiazenes and one tetrameric cyclothiazene have been determined, ie  $(NSCl)_3$ ,  $(NSF)_3$  and  $(NSF)_4$ .

The trichlorocyclotrithiazene,  $(NSCl)_3$  may be prepared in high yield by the action of chlorine on a solution of  $S_4N_4$  in chloroform (Demarcay, 1880). The mechanism for this reaction is unknown, but since it results in contraction of the  $S_4N_4$  ring it is thought to involve monomeric SN and ClSN units. Its structure has been determined by X-ray diffraction methods (Wieggers and Vos, 1966). The molecule as shown in figure 2.1 consists of a puckered  $S_3N_3$  ring with the chlorine atoms attached to the sulphur atoms in an equatorial conformation. The nitrogen atoms are situated no more than  $0.18 \text{ \AA}$  away from the plane of the sulphur atoms such that the molecule shows  $3m$  symmetry within experimental error. All of the S-N distances are equivalent and their mean of  $1.605 \text{ \AA}$  is considerably shorter than the normal single bond distance of  $1.73 \text{ \AA}$ . These points may be explained by  $Np\pi-Sd\pi$  delocalised bonding within the ring which is in agreement with the angle of  $124.3^\circ$  found at nitrogen. Also the ring is roughly planar although this is not a necessity for  $p\pi-d\pi$  bonding. This description is similar to that used for phosphonitrilic compounds such as  $P_3N_3F_6$  in which the  $P_3N_3$  ring is exactly planar. An alternative explanation of the bonding is to

consider the shortness of the S-N bond to be a consequence of the bond polarity, ie.  $\overset{+}{S}-\overset{-}{N}$ ; however this would require an angle of  $109^{\circ}28'$  at the nitrogen atoms.

The d orbitals on sulphur atoms are normally too diffuse to participate in the bonding and need to be contracted in order to interact effectively with say the p orbital on a  $sp^2$  hybridised nitrogen. This contraction may be provided by the attachment of an electronegative element to the sulphur atom as in  $(NSCl)_3$  or by a formal positive charge as in  $S_4N_3^+$  (section 2.5).

It is significant that all the chlorines in  $(NSCl)_3$  are axial in orientation, whereas they might have been expected to be equatorial in order to minimise the repulsions between the lone pairs on the chlorine atoms. The probable explanation for this, is that the interactions between the lone pairs on the nitrogen atoms and those on the chlorine atoms are greater than the chlorine-chlorine lone pair interactions.

The second trimeric cyclothiazene,  $(NSF)_3$  can be prepared by fluorinating  $(NSCl)_3$  using  $AgF_2$  (Glemser, 1964). Its structure has been determined by X-ray diffraction (Krebs, Pohl and Glemser, 1972) which showed it to be the fluorine analogue of  $(NSCl)_3$ . The molecular symmetry is close to  $3m$  with the nitrogen atoms lying  $0.23\text{\AA}$  away from the plane of the sulphur atoms. The mean S-N bond length of  $1.593\text{\AA}$  is shorter, though not significantly than that observed in  $(NSCl)_3$ . Some shortening of the S-N bonds is expected on account of the higher electronegativity of fluorine. The angles

within the ring are similar to those seen in  $(\text{NSCl})_3$ . However the average N-S-F angle of  $101.5^\circ$  is less than the corresponding N-S-Cl angle of  $113.7^\circ$  in  $(\text{NSCl})_3$  and this is probably a result of smaller lone pair interactions between the axial fluorine atoms. A bond order of 1.4 has been estimated for the S-N bonds in this compound from studies of the correlation between force constants and bond lengths in sulphur-nitrogen compounds (Glemser et.al. 1968).

These are the only halide derivatives of the trimeric cyclothiazenes. A preparation of  $(\text{NSBr})_x$  reported in 1896 has not been confirmed (Zborilova et al, 1972), however esters of the general composition  $(\text{NSOR})_3$  have been prepared where for example  $\text{R} = \text{CH}(\text{CH}_2\text{Cl})_2$  but their structures have not been studied (Banister and Bell, 1972 ).

There is only one known tetrameric cyclothiazene, namely  $(\text{NSF})_4$ , which may be prepared by fluorination of  $\text{S}_4\text{N}_4$  using  $\text{AgF}_2$  in carbon tetrachloride (Glemser, 1964). The molecule, as shown in figure 2.1 consists of a puckered eight-membered  $\text{S}_4\text{N}_4$  ring, however in contrast to the trimeric thiazenes there are two types of S-N bonds of length  $1.540\text{\AA}$  and  $1.660\text{\AA}$  (Weegers and Vos, 1963). This is usually interpreted as a system of alternating single and double bonds. The bond angles at sulphur and at nitrogen are similar to those seen in  $(\text{NSF})_3$ .

The lack of bond equalisation in  $(\text{NSF})_4$  cannot be attributed to an effect of the fluorine atoms attached to the sulphur atoms, as was first thought, before the structure of  $(\text{NSF})_3$  was known;

since in the latter compound bond equalisation is seen to occur. The puckering of the  $S_4N_4$  ring has been ascribed to the steric effects of the equatorial sulphur and nitrogen lone pairs (Krebs, Pohl and Glemser, 1972). Alternatively the puckering may be a consequence of the  $\sigma$ -bonding in the ring. In  $(NSF)_3$  the bonding involves  $sp^3$  hybridised sulphur and  $sp^2$  hybridised nitrogen atoms and by comparison  $(NSF)_4$  would seem to have a similar  $\sigma$  framework, which is attained by puckering of the ring. A planar eight-membered ring would require angles at sulphur and nitrogen of  $135^\circ$  and it would appear that the additional delocalisation possible does not outweigh the changes in the  $\sigma$ -bonding. The adoption of  $\bar{4}$  symmetry in preference to  $4m$  symmetry may be a consequence of lone pair interactions.

#### 2.4 Sulphanuric chloride.

In the cyclothiazenes just mentioned the sulphur is formally in oxidation state IV, however there is another group of sulphur-nitrogen heterocycles in which the sulphur is formally in oxidation state VI. The best known of these is sulphanuric chloride,  $(NSOCl)_3$  and as shown in figure 2.1 it consists of a puckered six-membered  $S_3N_3$  ring with a chlorine and oxygen atom bonded to each sulphur atom. The S-N bond distances are all the same within experimental error and their mean of  $1.564\text{\AA}$  indicates that there is considerable multiple bonding within the ring (Hazell, Wieggers and Vos, 1966). Many other sulphanuric derivatives are known in which

chlorine atoms have been replaced by fluorine atoms, secondary amines,  $R_2N-$ , esters  $RO-$  or phenyl groups, (Banister, 1974).

### 2.5 Aromatic Sulphur-Nitrogen Compounds

One of the first sulphur-nitrogen compounds prepared was  $S_4N_3Cl$  which was made in 1880 by heating  $S_4N_4$  with  $S_2Cl_2$  (Demarcay and Hebel, 1880). It occurs as bright yellow crystals which are remarkably stable in dry air.  $S_4N_3Cl$  itself is insoluble in most solvents however many derivatives of the form  $S_4N_3X$  have been prepared and several of these have been studied by X-ray diffraction, for example  $S_4N_3NO_3$  (Cordes, Kruh and Gordon, 1965),  $S_4N_3BiCl_4$  (Kruss and Ziegler 1972a) and  $(S_4N_3)_2SbCl_5$  (Kruss and Ziegler 1972b). All of these determinations have shown that the sulphur-nitrogen species consists of a cationic planar seven-membered ring as illustrated in figure 2.2. The dimensions given are taken from the determination of the structure of  $(S_4N_3^+)_2SbCl_5$ .

The features of significance in this ion are firstly that the ring is planar and shows  $2m$  symmetry within experimental error, and secondly that the S-N bonds which range from 1.548-1.566 Å are much shorter than the normal single bond distance of 1.73 Å. The latter suggests that there is a high degree of multiple bonding within this ion. It was found that the u.v. spectrum for this cation could only be interpreted in terms of a delocalised  $10\pi$  system, to which each sulphur contributes two electrons and each nitrogen one electron

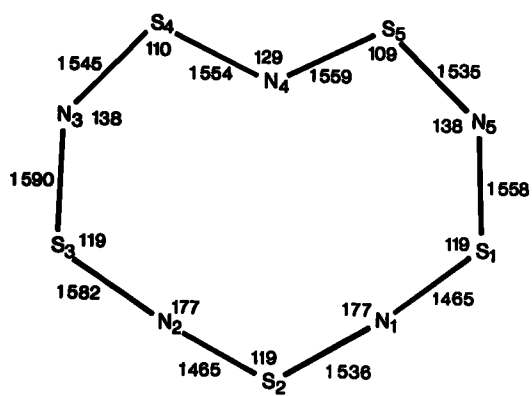
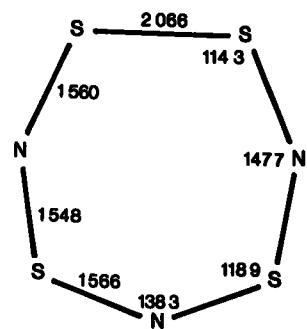
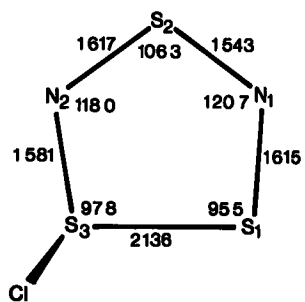
 $S_5N_5^+$  $S_4N_3^+$  $S_3N_2Cl^+$ 

Figure 2.2



(Friedman, 1969). This ion is the first known member of a series of cyclic sulphur-nitrogen compounds which are approximately planar and show short S-N bond distances. They are characterised by containing  $(4n + 2)\pi$  electrons and represent inorganic analogues of the organic aromatic Hückel series.

The second example of this type of compound was found in  $S_3N_2Cl_2$  which has been known since 1881 (Demarcay, 1881). The crystal structures of  $S_3N_2Cl_2$  (Zalkin, Hopkins and Templeton, 1966) and also a derivative,  $S_3N_2ClFeCl_4$  (Shearer, 1972) have been studied; both of which have been found to contain the cation  $S_3N_2Cl^+$ . As shown in figure 2.2 it consists of a five membered  $S_3N_2$  ring with an exocyclic chlorine atom attached to one sulphur atom. This sulphur lies  $0.2\text{\AA}$  above the plane of the remaining  $S_2N_2$  fragment which is almost exactly planar. The S-N bond distances which range from  $1.543 - 1.617\text{\AA}$  indicate a considerable degree of multiple bonding in this ion. Because of the lack of planarity  $S_3N_2Cl^+$  is considered to be a pseudo-aromatic species. The number of  $\pi$  electrons available in these cations can be estimated by presuming that each sulphur atom is in an oxidation state IV so that it can contribute two electrons to the  $\pi$  system and that each nitrogen atom can contribute one electron. When a sulphur atom is bonded to an exocyclic group as in  $S_3N_2Cl^+$  then that sulphur atom can only contribute one electron to the  $\pi$  system. Hence formally the addition of an  $Cl-S^+$  unit to the  $S_2N_2$  fragment contributes no electrons to the  $\pi$  system, so that in  $S_3N_2Cl^+$  there are  $6\pi$  electrons available.

The third example found was the cation  $S_5N_5^+$  in the salt  $S_5N_5^+AlCl_4^-$  (Hazell and Hazell, 1972) and as shown in figure 2.2 it consists of a roughly planar heart-shaped ten-membered ring. This molecule shows remarkably short S-N bond distances which vary from 1.465 - 1.590Å and formally possesses a  $14\pi$  system. This electron counting formalism has been supported by theoretical calculations which confirmed, using an all valence SCF MO treatment, the existence of a  $6\pi$  system in  $S_3N_2Cl^+$ , a  $10\pi$  system in  $S_4N_3^+$  and a  $14\pi$  system in  $S_5N_5^+$ . (Adams et al. 1971) A measure of the  $\pi$  bonding between two atoms is given by the total  $\pi$  bond overlap populations and for  $S_3N_2Cl^+$ ,  $S_4N_3^+$  and  $S_5N_5^+$  the average values were calculated to be 0.86 (0.50), 1.08 (0.60) and 1.05 (0.58) respectively. The figures in parentheses refer to the contribution from the d orbitals on sulphur, although this theoretical treatment over-emphasizes the d orbital participation. These figures indicate extensive  $\pi$  bonding between the sulphur and nitrogen atoms. These calculations also showed that there is appreciable  $\pi$  bonding in the S-S bond in  $S_4N_3^+$ , whereas comparison of its bond length of 2.066Å with the normal single bond distance of 2.048Å found in  $S_8$  would have suggested that this was essentially a single bond. This again illustrates the hazards in correlations of bond length with bond order. The positive charge in these ions makes an important contribution to their stability, since it contracts the orbitals on the sulphur atoms and enables them to bond more effectively to the nitrogen atoms.

The electron counting formalism mentioned above may be used to predict the number of  $\pi$  electrons available in any  $S_x N_y$  species (Banister, 1972) a summary of which is shown in table 2.1. Compounds with an excess of nitrogen are likely to be explosive since they will contain a N-N bond, whereas neutral species containing a high sulphur content are likely to be unstable or will exist as S(II) compounds because of insufficient contraction of the orbitals on the sulphur atoms. The number of possible unsaturated cyclic sulphur-nitrogen compounds may be extended by including an atom or group which formally does not contribute any electrons to the  $\pi$  system. An example of this is the Cl-S<sup>+</sup> group in  $S_3 N_2 Cl^+$  which has the effects of relieving the strain present in an  $S_3 N_2$  ring and stabilising the  $\pi$  system by its positive charge.

The only two neutral cyclic sulphur-nitrogen compounds known are  $S_2 N_2$  and  $S_4 N_2$ . The first of these which formally contains a  $6\pi$  system has been shown to be a planar four-membered ring with alternating sulphur and nitrogen atoms from its infrared spectrum. Its crystal structure has not been examined for reasons of its thermal instability however an adduct  $S_2 N_2 (SbCl_5)_2$  has been studied (Patton and Raymond, 1969). The  $S_2 N_2$  ring in this adduct shows *mmm* symmetry within experimental error and has S-N distances of 1.619 Å which are short taking into account the angles of 95.1° at nitrogen and 84.9 at sulphur. These features are consistent with delocalised multiple bonding. The structure of the  $S_2 N_2$  ring in the adduct is thought to be close to that of the free  $S_2 N_2$  molecule because of the similarities of their infrared spectra and also because of the ease with which the  $SbCl_5$  may be removed from the adduct.

Table 2.1

$\pi$ -electron counts for neutral  $S_x N_y$  species.

x	2	3	4	5	6
y					
2	6*	8	10*		
3	7	9	11†	13	
4	8	10	12	14	16
5		11	13	15†	17
6			14	16	18
7				17	19

\* Existing neutral  $S_x N_y$  species.

† Existing cationic  $S_x N_y$  species.

The second neutral compound  $S_4 N_2$  exists as a thermally unstable deep red liquid freezing at  $24^\circ$  and has been shown to be a cyclic compound with the basic configuration shown in figure 2.1. This was deduced from its dipole moment, mass spectrum, u.v. spectrum and vibrational spectra, using both Raman and infrared methods. These measurements were unable to determine whether the ring is planar or whether it has a boat or chair conformation. This compound formally contains a ten  $\pi$  system and if the orbitals on the sulphur atoms are sufficiently contracted the molecule would be expected to be planar (Nelson and Heal, 1971).

Other unsaturated cyclic sulphur-nitrogen compounds.

A compound of formula  $S_3N_3Cl$  has been prepared (Zborilova et al., 1972) and is thought to contain an S-Cl bond although its crystal structure has not been studied. A derivative  $S_3N_3NP(Ph)_3$  has been studied and, as shown in figure 2.3 it consists of an  $S_3N_3$  ring bonded at sulphur to a triphenyl phosphine group via an exocyclic nitrogen atom (Holt and Holt, 1970). Except for the three-coordinate sulphur atom the  $S_3N_3$  ring is roughly planar. Likewise the S-N bond lengths in the ring except for those involving the substituted sulphur atom are quite short which suggest that there is considerable multiple bonding in this part of the ring.

A compound containing an N-substituted  $S_3N_3$  ring has also been reported, namely  $S_3N_3POF_2$  (Roesky and Grimm, 1972). The structure was proposed on the basis of the compound's infrared and  $^{31}P$  and  $^{19}F$  n.m.r. spectra but has yet to be confirmed by crystallographic studies.

Sulphur-nitrogen compounds may also act as chelating ligands thus forming a ring system. Earlier work on these complexes has been the subject of a review by Weiss, 1966. The most well known chelating ligands contain an S-N-S-N fragment, in which the terminal sulphur and nitrogen atoms bond to the metal atom to form a five-membered ring. These compounds fall into two groups; those in which the ligand is the  $S_2N_2$  fragment itself and those in which there is a group attached to the terminal nitrogen atom.

An example of the first type is  $PbS_2N_2NH_3$  whose structure has been studied by X-ray diffraction (Neubauer, 1958). The bond lengths as

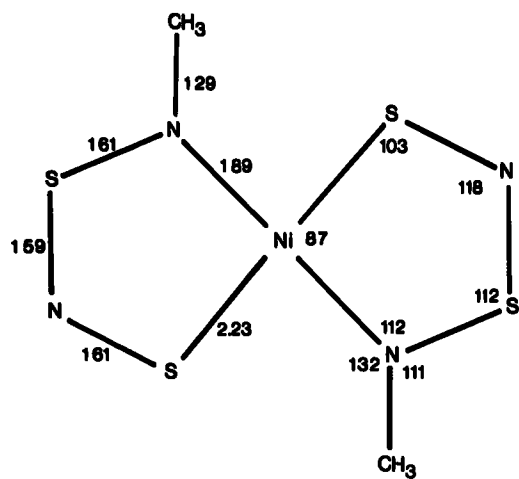
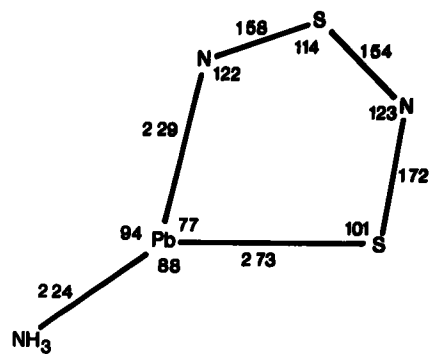
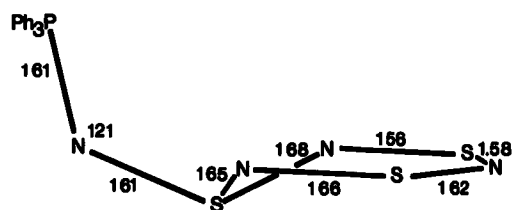

 $\text{Ni}(\text{S}_2\text{N}_2\text{CH}_3)$ 

 $\text{Pb}(\text{S}_2\text{N}_2)\text{NH}_3$ 

 $\text{S}_3\text{N}_3\text{-N-Ph}_3\text{P}$ 

Figure 2.3

shown on figure 2.3 would suggest that the five-membered ring consists of a sulphur diimide fragment, N=S=N connected by single bonds to a lead and sulphur atom.

The substituted  $S_2N_2$  chelating groups are of interest because of the effects of substitution on the bond lengths in the sulphur-nitrogen ligand. In the compound  $Ni(CH_3N_2S_2)_2$  all the S-N bonds are shorter than the normal single bond length of  $1.73\text{\AA}$  as shown in figure 2.3 (Ziegler, 1963). Since the coordination at the substituted nitrogen atom is roughly planar there would appear to be delocalised bonding encompassing the entire sulphur nitrogen fragment.

CHAPTER 3

The Crystal Structure of  $[\text{S}_3\text{N}_2]^{2+}(\text{ClS}_2\text{O}_6^-)_2$



### 3.1 Introduction.

The compound of empirical formula  $S_3N_2Cl$  has been known since 1880 (Demarcay, 1880). It may be conveniently prepared by heating  $S_3N_2Cl_2$  in vacuo at 80-90° (Banister et al., 1974). This gives a dark green powder which is virtually insoluble in all common solvents, so that little was known of its chemistry and no crystals suitable for structure analysis had been prepared.

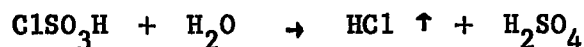
This compound was of interest because it could contain another pseudo-aromatic sulphur-nitrogen system.  $S_3N_2Cl$  itself would be an odd electron species, but magnetic susceptibility measurements carried out on a solid sample showed the material to be diamagnetic. This indicated that in the solid the  $S_3N_2Cl$  units are associated with formulation  $[S_3N_2Cl]_{2n}$  where n is probably 1. Hereafter this compound will be referred to as  $[S_3N_2Cl]_2$ .

N.q.r. measurements on this material failed to show a chlorine resonance (Lynch and Waddington, 1973), which would have been expected if the chlorine was covalently bound to the sulphur-nitrogen fragment. This suggested that the material is ionic and contains a sulphur-nitrogen cation. At this stage the most likely description for the cation was in terms of a large ring with formula  $S_6N_4^{2+}$ , which would contain a  $14\pi$  system as in  $S_5N_5^+$ .

The u.v. spectra of the sulphur-nitrogen species present in  $[S_3N_2Cl]_2$  was recorded in 100% sulphuric acid, which is a technique generally applicable to sulphur-nitrogen cations (Clarke, 1974). This showed firstly that the material could be dissolved giving the possibility of preparing crystalline derivatives, and secondly that the

species present in solution is different from any previously examined sulphur-nitrogen cation. The wavelengths and intensities of the absorptions indicated  $\pi$ -delocalisation similar to that seen in  $S_4N_3^+$  or  $S_3N_2Cl^+$ .

The material was slowly hydrolysed by this solvent and it was impossible to isolate a derivative. Chlorosulphuric acid was tried as an alternative, since this is self-dehydrating.



The  $[S_3N_2Cl]_2$  dissolved rapidly with the evolution of HCl gas, to give a dark brown solution. Excess solvent was pumped off at room temperature over a period of several days, whereupon small plate-like crystals formed at the bottom of the flask. These were separated and sealed in thin walled quartz capillary tubes to prevent decomposition. At this stage it was believed that the chlorosulphate derivative had been prepared.

### 3.2 Crystal Data.

The crystals were obtained directly from the reaction of  $(S_3N_2Cl)_2$  and chlorosulphuric acid as dark green irregular plates showing prominent  $\{10\bar{1}\}$  faces. The crystal used for intensity measurements had dimensions 0.6 x 0.4 x 0.25mm. Initial measurements using precession methods showed the unit cell to be triclinic, with possible space groups of P1 or  $P\bar{1}$ . The normalised structure factors showed a centrosymmetric distribution corresponding to  $P\bar{1}$  as shown in table 3.1, and this was confirmed by solution of the structure.

Accurate cell dimensions were obtained from a least squares treatment of the positions of twelve high order reflections (Busing and Levy, 1967) measured on a diffractometer.

$$\begin{array}{rcl}
 [\text{S}_3\text{N}_2]_2^{2+}(\text{ClS}_2\text{O}_6^-)_2 & M = & 639.56 \\
 & a = & 7.689(1) \text{ \AA} \quad \alpha = 101.00^\circ \\
 & b = & 10.726(1) \text{ \AA} \quad \beta = 114.42^\circ \\
 & c = & 6.614(1) \text{ \AA} \quad \gamma = 90.35^\circ \\
 & z = & 1 \\
 & U = & 485.38 \text{ \AA}^3 \\
 & D_c = & 2.19 \text{ gm cm}^{-3}
 \end{array}$$

Absorption coefficient for MoK $\alpha$  radiation ( $\lambda = 0.7107\text{\AA}$ ) =  $14.27\text{cm}^{-1}$   
 The density of the crystals was not measured due to the small number available from the preparation.

### 3.3 Data Collection.

The intensity data were collected on a Hilger and Watts Y290 four-circle diffractometer (section 1.12) using Zr-filtered MoK $\alpha$  radiation. A  $2\theta - \omega$  scan was employed using 80 steps of  $0.01^\circ$ . A counting time of 3 seconds per step, together with a background count of 40 seconds at the beginning and end of each scan were chosen. Three standard reflections were measured every fifty reflections. These showed no systematic change throughout data measurement, indicating that the crystal neither decomposed nor moved significantly during the experiment. These standard reflections were used to compute a scale factor which was applied to the data to place the measurements on a common scale.

The whole sphere of reflection was recorded to a limit of  $\theta = 25^\circ$ , yielding two equivalent sets of reflections. These gave, after averaging, a total of 1707 independent reflections of which 1337 reflections were considered to be observed having net counts  $> 3$  esd's.

The intensities were corrected for Lorentz and polarisation effects (section 1.13) but no corrections were made for absorption.

### 3.4 Solution and Refinement.

An attempt was made to solve the structure using the symbolic addition procedure. This led to the correct solution which was not recognised at that time, because the cation was different in shape from the ten-membered ring expected and the anion was  $\text{ClS}_2\text{O}_6^-$  and not  $\text{ClSO}_3^-$ . In addition the peak due to the chlorine atom in the E-map was small so there was no evidence of chlorine bonded to sulphur. Also the analytical data for this compound were unreliable because of the small sample prepared, and for the same reason the density was not measured.

Prior to attempting the symbolic addition procedure, an overall temperature factor and scale were estimated using the Wilson plot method described earlier, these are given in table 3.1.

The structure was solved from its Patterson function which, for the space group  $\text{P}\bar{1}$ , takes the form

$$P(u,v,w) = \frac{2}{v} \sum_h \sum_k \sum_l \{ |F(hkl)|^2 \cos 2\pi(hu + kv + lw) + |F(\bar{h}k\bar{l})|^2 \cos 2\pi(-hu + kv + lw) + |F(h\bar{k}l)|^2 \cos 2\pi(hu - kv + lw) + |F(hk\bar{l})|^2 \cos 2\pi(hu + kv - lw) \}$$

this function was computed for half the unit cell from

$u = 0 \rightarrow 1$	at intervals of	$0.27558\text{\AA}$
$v = 0 \rightarrow 1$	"	$0.25630\text{\AA}$
$w = 0 \rightarrow \frac{1}{2}$	"	$0.26815\text{\AA}$

the coefficients used were  $|F_{\text{obs}}|^2$  weighted by  $(Lp)^{-1}$  for each reflection. This increased the importance of the higher order reflections and thus enhanced the magnitude of the sulphur-sulphur vectors in the map.

A single weight sulphur-sulphur peak was found by observing that the vector 0.467, -0.05, 0.083 occurred between six pairs of the twenty larger peaks in the map. There was a small peak corresponding to this vector. This was tried as a possible single weight peak, corresponding to there being a sulphur atom at 0.233, -0.025, 0.042. One application of the superposition method yielded possible positions for six further atoms. All possible vectors between these seven positions were calculated, but only five of these positions gave vectors corresponding to those seen in the vector map. These positions were,

u	v	w
0.233	-0.025	0.042
0.200	0.100	0.250
0.300	0.225	0.042
-0.167	0.219	0.573
0.633	0.533	0.792

these coordinates were refined by two cycles of least squares refinement using the block-diagonal approximation when R became 0.45. The sulphur atoms were given isotropic temperature factors of  $2.65\text{\AA}^2$ , as calculated from the Wilson plot. An electron density map was calculated in which the additional peaks were all of about the same height, so that once again the S-Cl fragment could not be picked out. The peak corresponding to the chlorine atom was small due to its high temperature factor. Five further atoms were included in the refinement and the R value fell to 0.28. During this process the temperature factor of one of the additional atoms, which were taken as oxygens, became negative indicating that this was the chlorine atom. At this stage the structure became clear and the inclusion of the remaining atoms caused R to fall to 0.16. With anisotropic thermal parameters for all the atoms R became 0.0338. Further refinement using the full matrix least squares method saw R converge on its final value of 0.0307. The parameter shifts in the last cycle were all  $< 0.3 \sigma$ . A difference synthesis was calculated at the end of refinement and showed no peaks greater than  $0.3e.\text{\AA}^{-3}$  in general areas of the map; however there were negative regions of about  $-1.1e.\text{\AA}^{-3}$  associated with the sulphur positions.

The weighting scheme used throughout the block-diagonal refinement was of the form

$$\sqrt{w} = 1/[P_1 + |F_o| + P_2 |F_o|^2]^{\frac{1}{2}}$$

where

$$P_1 = 10.0 \quad \text{and} \quad P_2 = 0.01$$

this scheme was replaced in the final stages of refinement by one based on counting statistics. This was of the form

$$\sqrt{w} = \frac{1}{\sigma F_0}$$

where  $\sigma F_0$  represents the standard deviation of  $F_0$ .  $\sigma F_0$  may be derived thus

$$F_0 = \frac{k \cdot \sqrt{N}}{\sqrt{L_p}}$$

where  $k$  is the scale and  $L_p$  is the Lorentz-polarisation factor. Then using the approximation  $dF_0 \approx \sigma F_0$  and  $dN \approx \sigma N$  and differentiating gives

$$\begin{aligned} \sigma F_0 &= \frac{1}{2} \cdot \frac{k \cdot \sigma N}{\sqrt{L_p} \cdot \sqrt{N}} \\ &= \frac{1}{2} \cdot F_0 \cdot \frac{\sigma N}{N} \end{aligned}$$

the expression used for  $\sigma N$  was

$$\sigma N = [T + B.G. + (P.N)^2]^{\frac{1}{2}}$$

where  $B$  is the ratio between the total background count ( $G$ ) and the total peak count ( $T$ ). The term  $(T + B.G.)^{\frac{1}{2}}$  represents the standard deviation based on counting statistics. This underestimates the error in the very intense reflections, so the term  $(P.N)^2$  is introduced

Table 3.1  $[\text{S}_3\text{N}_2]_2^{2+} (\text{ClS}_2\text{O}_6^-)_2$ Final Least Squares Totals †

$\Sigma F_o $	$\Sigma F_c $	$\Sigma \Delta $	R
22421.95	22415.61	688.79	0.0307

Weighting Analysis

$ F_o $ Ranges	N	$\Sigma w\Delta^2/N$	R
0 - 5	76	0.03	0.142
5 - 7	222	0.03	0.085
7 - 10	172	0.03	0.050
10 - 15	293	0.02	0.029
15 - 20	216	0.03	0.023
20 - 45	299	0.02	0.021
45 - 70	50	0.02	0.022
70 - upwards	8	0.03	0.030

† Excluding reflection(2 1 1)

The Statistical Distribution of Normalised Structure Factors and the Estimated Scale and Temperature Factor.

	Observed	Centrosymmetric	Noncentrosymmetric
$\langle  E  \rangle$	0.799	0.798	0.886
$\langle  E ^2 \rangle$	1.000	1.000	1.000
$\langle  E^2 - 1  \rangle$	0.968	0.968	0.736
$ E  > 3$	0.41%	0.3%	0.01%
$ E  > 2$	4.69%	5.0%	1.8 %
$ E  > 1$	31.75%	32.0%	37.0 %

Overall Temperature Factor  $B = 2.65$ Overall Scale  $k = 0.1396$



Table 3.2  $[\text{S}_3\text{N}_2]_2^{2+} (\text{ClS}_2\text{O}_6^-)_2$ 

Final Atomic Coordinates with their Estimated Standard Deviations  
( $\times 10^5$ ) and Isotropic Temperature Factors ( $\text{\AA}^2$ ).<sup>†</sup>

Atom	x/a	y/b	z/c	B
Cl	0.16310 (18)	-0.40500 (13)	-0.11392 (18)	4.10
S(1)	0.30556 (13)	0.23302 ( 9)	0.03092 (16)	2.42
S(2)	0.18355 (13)	0.09889 ( 9)	0.26863 (15)	2.40
S(3)	0.24138 (12)	-0.02176 ( 8)	0.00940 (15)	2.31
S(4)	0.16996 (13)	-0.21259 ( 9)	0.42716 (15)	2.45
S(5)	0.36104 (13)	-0.38092 ( 8)	0.20389 (16)	2.48
O(1)	0.11388 (35)	-0.15639 (23)	0.23129 (42)	2.64
O(2)	0.01382 (42)	-0.25515 (30)	0.46755 (51)	4.24
O(3)	0.33641 (42)	-0.15420 (28)	0.61780 (45)	3.75
O(4)	0.23706 (36)	-0.35827 (22)	0.34008 (42)	3.32
O(5)	0.48091 (39)	-0.27070 (25)	0.24602 (49)	3.86
O(6)	0.43640 (49)	-0.49782 (26)	0.23149 (54)	4.95
N(1)	0.24028 (41)	0.23254 (27)	0.22712 (48)	2.85
N(2)	0.30665 (39)	0.09103 (27)	-0.08086 (48)	2.66

<sup>†</sup> The temperature factors given by the last cycle of isotropic refinement.

Table 3.3  $[\text{S}_3\text{N}_2]_2^{2+} (\text{ClS}_2\text{O}_6^-)_2$ 

Anisotropic Thermal Parameters with their Estimated Standard Deviations (Both  $\text{\AA}^2 \times 10^5$ ) †

Atom	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{23}$	$\beta_{13}$	$\beta_{12}$
C1	2592 (21)	1794 (9)	1886 (30)	- 90 (38)	1443 (51)	684(37)
S(1)	1477 (21)	614 (9)	2197 (30)	402 (25)	1927 (41)	92(21)
S(2)	1395 (20)	692(10)	1585 (27)	204 (24)	1549 (37)	92(21)
S(3)	1234 (20)	577 (9)	2062 (29)	320 (24)	1858 (39)	253(20)
S(4)	1476 (21)	724(10)	1566 (27)	384 (24)	1491 (39)	600(22)
S(5)	1724 (23)	583 (9)	2113 (29)	314 (25)	2289 (42)	295(22)
O(1)	1648 (61)	809(28)	2270 (85)	1194 (76)	1815 (117)	633(64)
O(2)	2110 (71)	1488(39)	3546(112)	2030(107)	4052 (152)	1201(84)
O(3)	2092 (74)	1109(34)	2376(100)	- 700 (91)	327 (138)	662(80)
O(4)	2163 (67)	583(25)	2587 (88)	691 (74)	3189 (131)	401(64)
O(5)	2061 (71)	858(30)	3648(111)	265 (90)	3334 (151)	- 272(72)
O(6)	3345 (89)	802(31)	3792(118)	987 (94)	4211 (173)	1521(85)
N(1)	1399 (69)	650(31)	1815 (94)	- 10 (83)	1528 (131)	- 41(71)
N(2)	1198 (64)	681(31)	2070 (97)	526 (85)	1817 (132)	215(68)

† Where  $\beta_{ij}$  refers to the expression

$$\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2kl\beta_{23} + 2hl\beta_{13})]$$

to down weight these reflections.  $P$  was varied to make  $w\Delta^2$  as uniform as possible over the whole range of  $|Fo|$ . The optimum value was 0.06. One reflection ( $2\bar{1}1$ ) was excluded from the refinement because of its unusually large  $\Delta$ . The unobserved reflections were not included in the refinement. The final least squares totals and weighting analysis are given in table 3.1. The final atomic parameters and thermal parameters are given in tables 3.2 and 3.3 respectively.

The scattering factors used in this refinement were taken from International Tables Vol. III. The chlorine and sulphur atoms were corrected for anomalous dispersion, the correction factors also being taken from International Tables Vol. III. The final structure factors are shown in table 3.8.

### 3.5 Results and Discussion.

The compound is ionic and contains  $[S_3N_2]_2^{2+}$  cations and chlorodisulphate anions,  $ClS_2O_6^-$ . The bond distances and angles are given in tables 3.4 and 3.5 respectively.

#### 3.5.a The Structure of $[S_3N_2]_2^{2+}$

The  $[S_3N_2]_2^{2+}$  cation consists of two  $S_3N_2$  rings held together by a four-centre S-S interaction, as shown in figure 3.1. The two rings which are separated by S-S distances of  $3.027\text{\AA}$  are related to one another by a centre of symmetry and are inclined at an angle of  $108^\circ$  to the plane of the four sulphur atoms involved in the interaction. The individual  $S_3N_2$  rings are nearly planar (table 3.6), the maximum

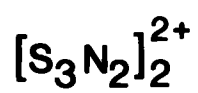
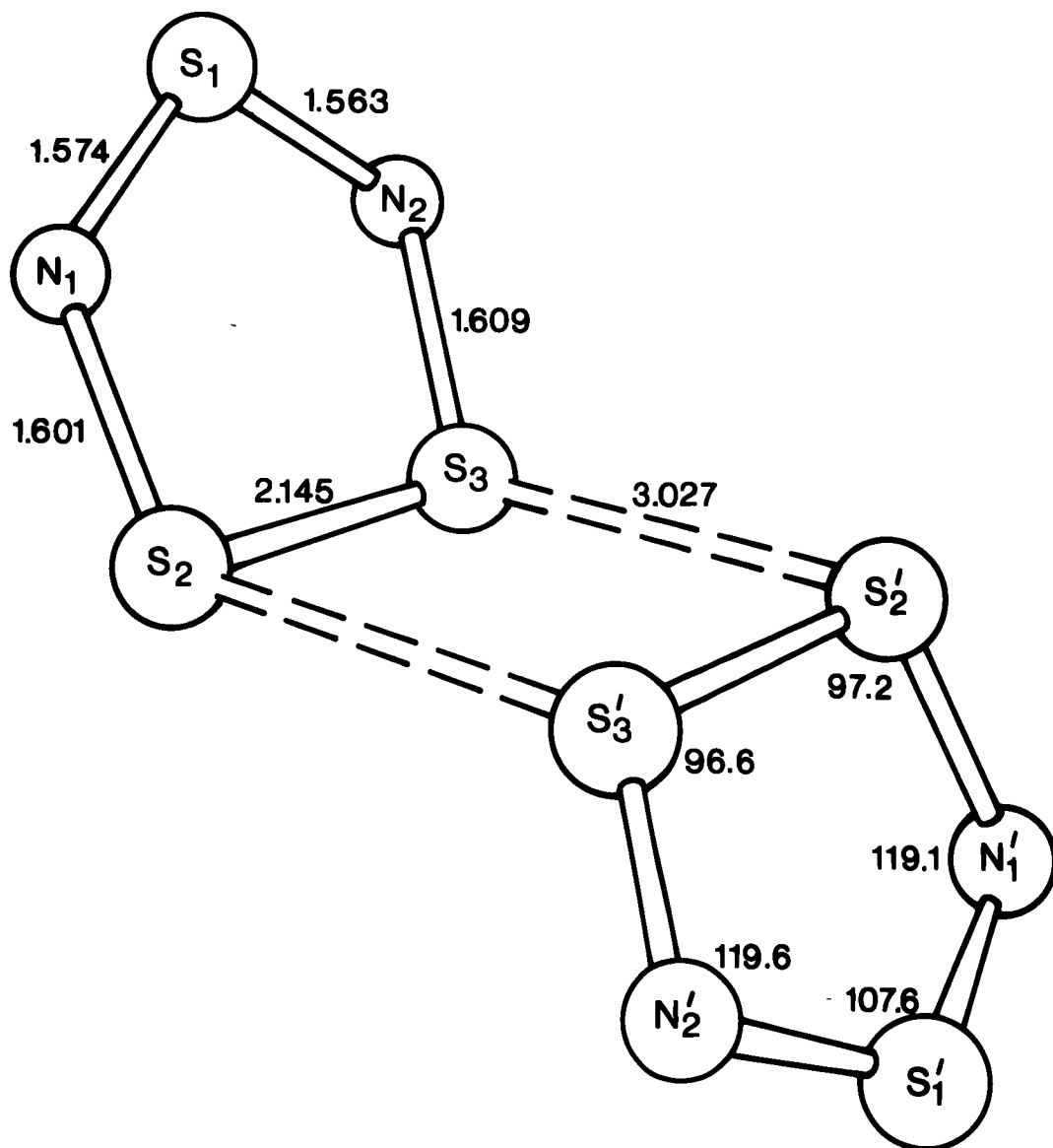


Figure 3.1

Table 3.4  $[\text{S}_3\text{N}_2]_2^{2+} (\text{ClS}_2\text{O}_6^-)_2$ 

Bond Distances ( $\text{\AA}$ ) and their Estimated Standard Deviations  
( $\text{\AA} \times 10^3$ )

S(1) - N(1)	1.574(3)
S(1) - N(2)	1.563(3)
S(2) - S(3)	2.145(1)
S(2) - S(3')	3.027(1)
S(2) - N(1)	1.601(3)
S(3) - N(2)	1.609(3)
S(4) - O(1)	1.438(3)
S(4) - O(2)	1.423(4)
S(4) - O(3)	1.405(3)
S(4) - O(4)	1.718(3)
S(5) - Cl	1.986(2)
S(5) - O(4)	1.552(3)
S(5) - O(5)	1.405(3)
S(5) - O(6)	1.396(3)

Some Non-Bonding Intramolecular Distances and their Estimated  
Standard Deviations ( $\text{\AA} \times 10^3$ ).

S(1) - S(2)	2.736(1)
S(1) - S(3)	2.740(1)
S(2) - N(2)	2.825(3)
S(3) - N(1)	2.833(3)
N(1) - N(2)	2.530(4)
Cl - O(1)	3.297(3)
O(1) - O(5)	3.056(4)
O(3) - O(5)	3.154(4)

' represents the equivalent position  $\bar{x} \bar{y} \bar{z}$

Table 3.5  $[\text{S}_3\text{N}_2]_2^{2+} (\text{ClS}_2\text{O}_6^-)_2$ 

Final Bond Angles and their Estimated Standard Deviations  
 (Deg. x  $10^2$ )

N(1) - S(1) - N(2)	107.56(17)
S(3) - S(2) - N(1)	97.19(12)
S(2) - S(3) - N(2)	96.58(12)
O(1) - S(4) - O(2)	114.21(18)
O(1) - S(4) - O(3)	116.17(18)
O(1) - S(4) - O(4)	103.36(15)
O(2) - S(4) - O(3)	117.22(20)
O(2) - S(4) - O(4)	99.02(17)
O(3) - S(4) - O(4)	103.26(16)
Cl - S(5) - O(4)	101.69(12)
Cl - S(5) - O(5)	107.03(14)
Cl - S(5) - O(6)	107.39(16)
O(4) - S(5) - O(5)	111.09(17)
O(4) - S(5) - O(6)	107.11(18)
O(5) - S(5) - O(6)	120.83(20)
S(1) - N(1) - S(2)	119.08(20)
S(1) - N(2) - S(3)	119.55(20)
S(4) - O(4) - S(5)	124.86(17)

deviation from the mean plane being  $0.02\text{\AA}$ .

The sulphur-nitrogen bond lengths, S(2) - N(1) of  $1.601(3)\text{\AA}$  and S(3) - N(2) of  $1.609(3)\text{\AA}$  are the same within experimental error using the criterion described in section 1.11. For these bonds

$$t = \frac{1.609 - 1.601}{(0.003^2 + 0.003^2)^{\frac{1}{2}}} = 1.9$$

so that  $P \approx 0.05$  and the difference is not significant. Similarly the bonds S(1) - N(1) of  $1.574(3)\text{\AA}$  and S(1) - N(2) of  $1.563(3)\text{\AA}$  do not differ from one another significantly. The angles S(1) - N(1) - S(2) of  $119.08(20)^\circ$  and S(1) - N(2) - S(3) of  $119.55(20)^\circ$  are also the same within experimental error. The angles S(3) - S(2) - N(1) of  $97.19(12)^\circ$  and S(2) - S(3) - N(2) of  $96.58(12)^\circ$  both depend upon the common positions of S(1) and S(2) so that, allowing for this, the difference between these angles does not appear to be significant, and consequently the ring approaches  $mm$  symmetry.

The mean S-N distances of  $1.569\text{\AA}$  and  $1.605\text{\AA}$  are characteristic of a  $\pi$ -delocalised sulphur-nitrogen cation. They may be compared with the distances of  $1.548 - 1.566\text{\AA}$  in  $S_4N_3^+$  (Kruss and Ziegler, 1972b) which formally contains a  $10\pi$  system or  $1.543 - 1.617\text{\AA}$  in  $S_3N_2Cl^+$  (Zalkin, Hopkins and Templeton, 1966) which formally contains a  $6\pi$  system. The S-S distance of  $2.145\text{\AA}$  within the ring is similar to that of  $2.066\text{\AA}$  in  $S_4N_3^+$  or  $2.136\text{\AA}$  in  $S_3N_2Cl^+$ .

### 3.5.b The Bonding in $[S_3N_2]_2^{2+}$

The lengths of the S-N bonds and the angles at nitrogen of  $119.3^\circ$

show that there is considerable delocalisation within the ring. S-S distances are dependent upon hybridisation as noted earlier (section 2.2) so that from bond lengths alone it is not possible to deduce the bond order of the S-S bond. A  $\pi$  bond order of 0.35 has been calculated for the S-S bond in  $S_3N_2Cl^+$  and of 0.83 for the S-S bond in  $S_4N_3^+$  (Adams et al., 1971). Since the S-S bond in  $[S_3N_2]_2^{2+}$  is similar in length and environment to those seen in  $S_4N_3^+$  and  $S_3N_2Cl^+$ , it is reasonable to expect substantial  $\pi$ -bonding across this bond.

An isolated  $S_3N_2^+$  ring would contain a  $7\pi$  system using the electron counting rule. (i.e. Each sulphur donates two electrons and nitrogen one electron to the  $\pi$  system, together with the subtraction of one to allow for the positive charge gives  $7\pi$  electrons). Thus an isolated  $S_3N_2^+$  cation will be paramagnetic. However the solution obtained by dissolving  $[S_3N_2Cl]_2$  in chlorosulphuric acid was found to contain no paramagnetic ions using n.m.r. techniques. No line broadening or shifts were observed for the proton resonances of tertiary butyl alcohol in chlorosulphuric acid on the addition of  $[S_3N_2Cl]_2$ . Under these conditions the presence of paramagnetic ions would cause line broadening and shifts to high field of the proton resonances. Hence the  $S_3N_2$  rings are associated in solution sufficiently to allow spin pairing to occur.

No magnetic measurements were performed on solid  $[S_3N_2]_2^{2+} (ClS_2O_6^-)_2$  but since spin pairing occurs in solution it is expected to occur also in the solid. The distance between the rings of  $3.027\text{\AA}$  is far longer



than a normal S-S bond distance and yet is considerably shorter than the van der Waals distance for sulphur of  $3.60\text{\AA}$  (Bondi, 1964). The nature of the association is not clear, yet it must be strong enough to hold two positively charged ions together in solution. The bonding may be described in terms of two  $\text{S}_3\text{N}_2$  rings each containing an aromatic  $6\pi$  system held together by a four-centre two electron bond. This cation probably occurs in  $[\text{S}_3\text{N}_2\text{Cl}]_2$  also; evidence for this is seen in the similarities of the infrared spectra of  $[\text{S}_3\text{N}_2\text{Cl}]_2$  and  $[\text{S}_3\text{N}_2]_2^{2+}(\text{ClS}_2\text{O}_6^-)_2$  and because both compounds give the same electronic spectrum in concentrated sulphuric acid.

Another compound containing an  $\text{S}_3\text{N}_2$  ring is described in the following chapter so that a discussion of  $\text{S}_3\text{N}_2$  ring compounds is deferred until then.

### 3.5.c The $\text{ClS}_2\text{O}_6^-$ anion.

This is the first structure determination of this anion. It was first observed in infrared and Raman studies on solutions of  $\text{SO}_3$  in  $\text{ClSO}_3\text{H}$  (Gillespie and Robinson, 1961). Several alkali metal salts containing this anion have been isolated, (Auger, Wartell and Heubel, 1970) but none has been studied crystallographically.

The anion as shown in figure 3.2 is a chlorine substituted disulphate ion. The most striking feature of the ion is the asymmetry of its S-O-S bridge. The bond distances are  $1.552(3)\text{\AA}$  for S(5) - O(4) and  $1.718(3)\text{\AA}$  for S(4) - O(4). The length of

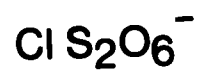
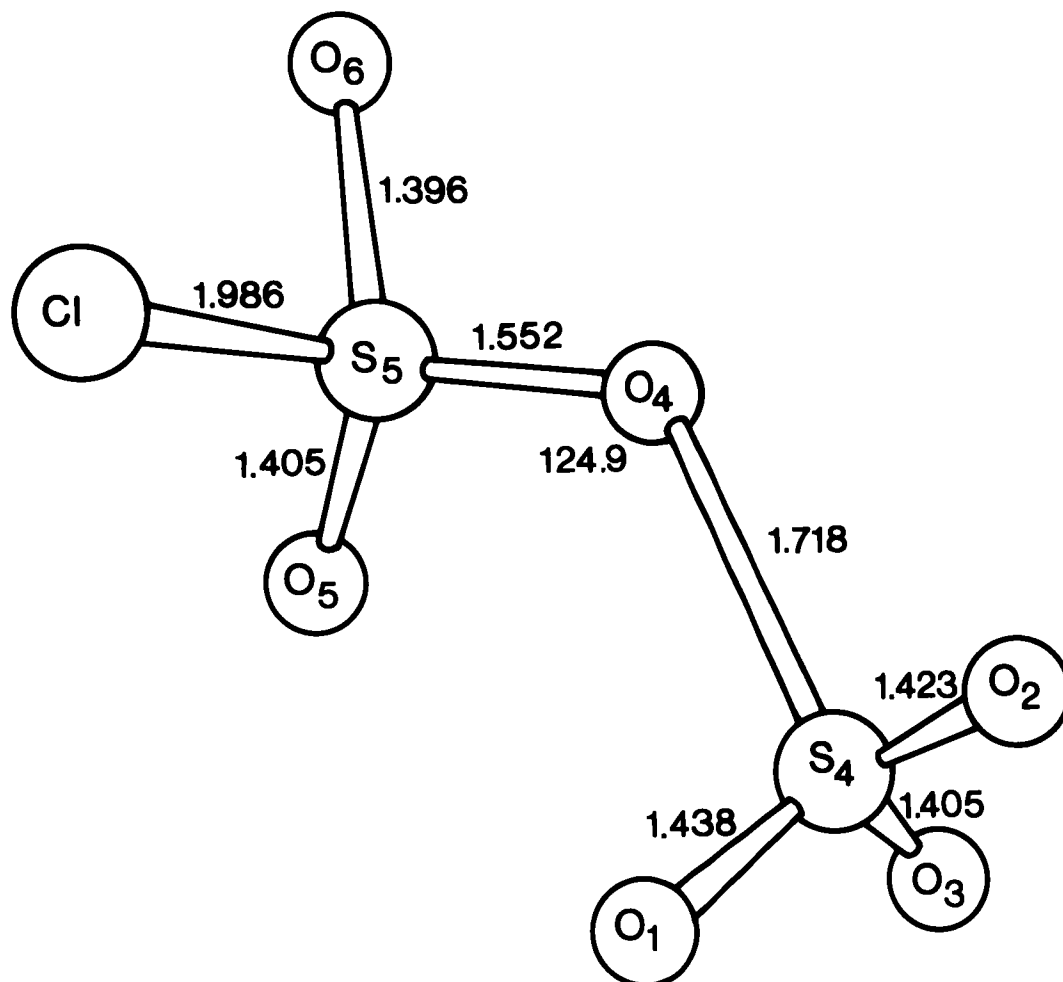


Figure 3.2

1.718Å is one of the longest S-O distances known. A similar value of 1.72Å has been reported in  $(\text{NO}_2)_2\text{S}_2\text{O}_{10}^{2-}$  (Cruickshank, 1964b). This distance is longer than the single bond distance of 1.70Å calculated from Pauling's covalent radii (Pauling, 1960) or the value of 1.69Å from the Schomaker Stevenson rule (Schomaker and Stevenson, 1941). The other distance in the bridge (1.552Å) lies between the S-O single bond distance of 1.70Å and the double bond distance of 1.43Å as seen in  $\text{SO}_3$  (McDonald and Cruickshank, 1967), and indicates substantial multiple bonding in this bond, as is confirmed by the angle of 124.9° at the bridging oxygen. There is no steric requirement for such a large angle since the nonbonding contacts between terminal atoms on S(4) and S(5) are all greater than the normal van der Waals distances.

This asymmetry is substantially larger than that seen in  $\text{HOS}_2\text{O}_6^-$  in which the bond lengths corresponding to S(5) - O(4) and S(4) - O(4) are 1.59Å and 1.67Å (Brown, Crump and Gillespie, 1971). The S-O-S bridges in these anions may be compared with the symmetrical bridge found in  $\text{S}_2\text{O}_7^{2-}$  in which the S-O distance is 1.645Å (Lynton and Truter, 1960).

The asymmetry of the bridge in  $\text{ClS}_2\text{O}_6^-$  is probably caused by preferential multiple bonding of O(4) to S(5) which carries the chlorine, leaving S(4) - O(4) as essentially a single bond. A chlorine atom bonded to sulphur will lower the energy and contract the orbitals on sulphur more effectively than an oxygen carrying a formal negative charge. Hence O(4) will  $\pi$  bond to S(5) more successfully than to S(4). Further evidence that the length of the S(4) - O(4)

bond is due to the chlorine on S(5) rather than the negative charge on S(4) is shown by the S-O bridging length of  $1.58\text{\AA}$  in  $\text{CH}_3\text{OSO}_3^-$  which is short even though there is a negative charge on the ion (Marsau and Cam, 1973).

The terminal S-O distances lie within the range  $1.396 - 1.438\text{\AA}$  which are similar to the terminal distances of  $1.43\text{\AA}$  in  $\text{HS}_2\text{O}_7^-$  (Brown, Crump and Gillespie, 1971) or  $1.407\text{\AA}$  in  $\text{CH}_3\text{OSO}_3^-$  (Marsau and Cam, 1973) and indicate a high degree of multiple bonding.

The terminal S-O distances to S(5) are, S(5) - O(5)  $1.405\text{\AA}(3)$  and S(5) - O(6)  $1.396(3)\text{\AA}$  and are the same within experimental error. Their mean of  $1.401\text{\AA}$  is shorter than the average terminal S-O distance of  $1.422\text{\AA}$  in the  $\text{SO}_3^-$  unit, which is partly due to the presence of chlorine in place of an oxygen carrying a negative charge.

The terminal S-O distances for the  $\text{SO}_3^-$  part are, S(4) - O(1)  $1.438(3)\text{\AA}$ , S(4) - O(2)  $1.423(4)\text{\AA}$  and S(4) - O(3)  $1.405(3)\text{\AA}$ . This range in bond length is greater than can be ascribed to experimental error, and may be caused by secondary bonding. All the terminal oxygens on the anion participate in short intermolecular contacts (section 3.6) to the sulphur atoms of the  $(\text{S}_3\text{N}_2)_2^{2+}$  cation. The shortest of these involve O(1) and are, S(2) --- O(1)  $2.731\text{\AA}$  and S(3) --- O(1)  $2.680\text{\AA}$ . These are well below the normal sulphur-oxygen van der Waal contact of  $3.32\text{\AA}$  (Bondi, 1964) and the lengthening of S(4) - O(1) may be a consequence of this.

The S(5) - Cl bond distance was found to be  $1.986(2)\text{\AA}$  which is within the range of S-Cl bond distances observed in sulphur oxyhalides and sulphur halides, eg.  $1.99\text{\AA}$  in  $\text{S}_2\text{Cl}_2$  (Palmer, 1950) and

2.011Å in  $\text{SOCl}_2$  (Hargittai, 1968).

The coordination about S(4) and S(5) is approximately tetrahedral. At S(5) the largest deviations are shown by O(5) - S(5) - O(6), ( $120.8^\circ$ ) and Cl-S(5) - O(4) ( $101.7^\circ$ ). The magnitude of O(5) - S(5) - O(6) may be a consequence of the extensive multiple bonding in S(5) - O(5) and S(5) - O(6). This will result in shorter bonds with more s character and hence increase the angle between themselves and decrease the Cl-S(5) - O(4) angle which is observed. The remaining angles would be less affected by this change and range from  $107.0^\circ$  -  $111.1^\circ$ .

At S(4) the angles involving the terminal oxygen atoms are all greater than  $109^\circ 28'$ , i.e. O(1) - S(4) - O(2)  $114.2^\circ$ , O(1) - S(4) - O(3)  $116.2^\circ$  and O(2) - S(4) - O(3)  $117.2^\circ$ , whereas the angles at S(4) involving the bridging oxygen are all less than  $109^\circ 28'$ . The terminal bonds are shorter due to the multiple bonding and hence contain a higher s character, making the angles between themselves larger. The increased proportion of p character in S(4) - O(4) increases the bond length and decreases the angles at S(4) between O(4) and the terminal oxygen atoms. A similar effect is seen in the disulphate ion  $\text{S}_2\text{O}_7^{2-}$  (Lynton and Truter, 1960) in which the average angle between terminal oxygen atoms is  $113.9^\circ$  and the average angle between the terminal and bridging oxygen is  $104.5^\circ$ .

### 3.6 Intermolecular Contacts.

The packing of  $[\text{S}_3\text{N}_2]_2^{2+}$  and  $\text{ClS}_2\text{O}_6^-$  is characterised by the presence of many short sulphur-oxygen intermolecular contacts. Those

less than the normal S---O van der Waals distance of  $3.32\text{\AA}$  are shown in table 3.7.

The shortest contacts involve O(1) and the basal sulphurs of the  $\text{S}_3\text{N}_2$  ring as just mentioned. This is shown in figure 3.3

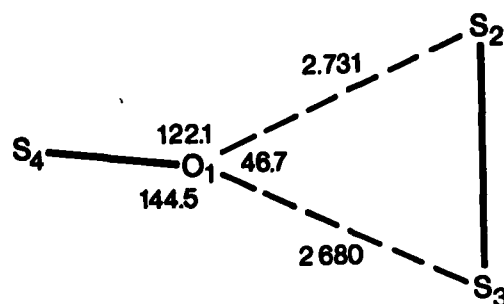


Figure 3.3

In cationic sulphur-nitrogen compounds the sulphur atoms carry a net positive charge, whilst in this compound there is a negative charge spread over the three terminal oxygen atoms attached to S(4); so that part of this interaction could be ionic. However it has been shown that many short intermolecular contacts seen in compounds of the main group elements have a specific orientation with respect to the rest of the molecule (Alcock, 1972) and that they can be explained by the overlap of a lone pair on one atom with vacant orbitals on the other. It is significant therefore that the oxygen atom O(1) lies only  $0.06\text{\AA}$  away from the plane of the  $\text{S}_3\text{N}_2$  ring, so that the interaction may involve the overlap of a lone pair orbital on O(1) with a vacant orbital on S(2) and S(3).

Table 3.7  $[\text{S}_3\text{N}_2]_2^{2+} (\text{ClS}_2\text{O}_6^-)_2$ 

Sulphur-Oxygen intermolecular contacts  $< 3.35\text{\AA}$  and their  
Estimated Standard Deviations ( $\text{\AA} \times 10^3$ ).

Atom A	Atom B	Equivalent	Cell	A---B $\text{\AA}$
O(1)	S(1)	2	(0,0,0)	2.980(3)
O(1)	S(2)	1	(0,0,0)	2.731(3)
O(1)	S(3)	1	(0,0,0)	2.680(3)
O(2)	S(1)	2	(0,0,0)	3.251(3)
O(2)	S(2)	2	(0,0,1)	3.043(4)
O(3)	S(1)	2	(1,0,1)	3.030(3)
O(3)	S(3)	1	(0,0,1)	3.071(3)
O(5)	S(1)	2	(1,0,0)	2.996(3)
O(6)	S(1)	1	(0,-1,0)	2.917(3)

This type of interaction is common in compounds in which the sulphur atoms carry a positive charge. The best example is seen in the structure of  $\text{S}_4\text{N}_3\text{Cl}$  (Hazel, 1974) which contains three crystallographically independent units of  $\text{S}_4\text{N}_3\text{Cl}$  per unit cell. Each of these has a chloride ion situated close to (within  $0.4\text{\AA}$ ) the mean plane of the ring opposite to the S-S bond. The average S---Cl distance of  $2.868\text{\AA}$  is very short compared with the van der Waals distance of  $3.55\text{\AA}$ .

Further examples are to be found in a wide range of organic dithiolium compounds of the general formula  $[\text{S}_2(\text{CR})_3]^+\text{X}^-$  which contain an unsaturated five membered cyclic disulphide, where X = I, Br, Cl or N

(Hordvick, 1970). In all of these compounds, X is situated close to the plane of the ring and suggests that the interaction involves orbital overlap.

The other contacts in  $[\text{S}_3\text{N}_2]_2^{2+}(\text{ClS}_2\text{O}_6^-)_2$  are less directional and may be primarily ionic in nature. A projection along  $\underline{c}$  given in figure 3.4, shows the packing of the  $[\text{S}_3\text{N}_2]_2^{2+}$  cations and the  $\text{ClS}_2\text{O}_6^-$  anions and suggests that the shape and size of the cation may be the reason why the chlorodisulphate crystallises out in preference to the chlorosulphate.

Table 3.6.  $[\text{S}_3\text{N}_2]_2^{2+}(\text{ClS}_2\text{O}_6^-)_2$

The equation for the weighted mean plane  
of the  $\text{S}_3\text{N}_2$  ring.

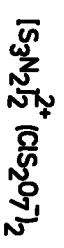
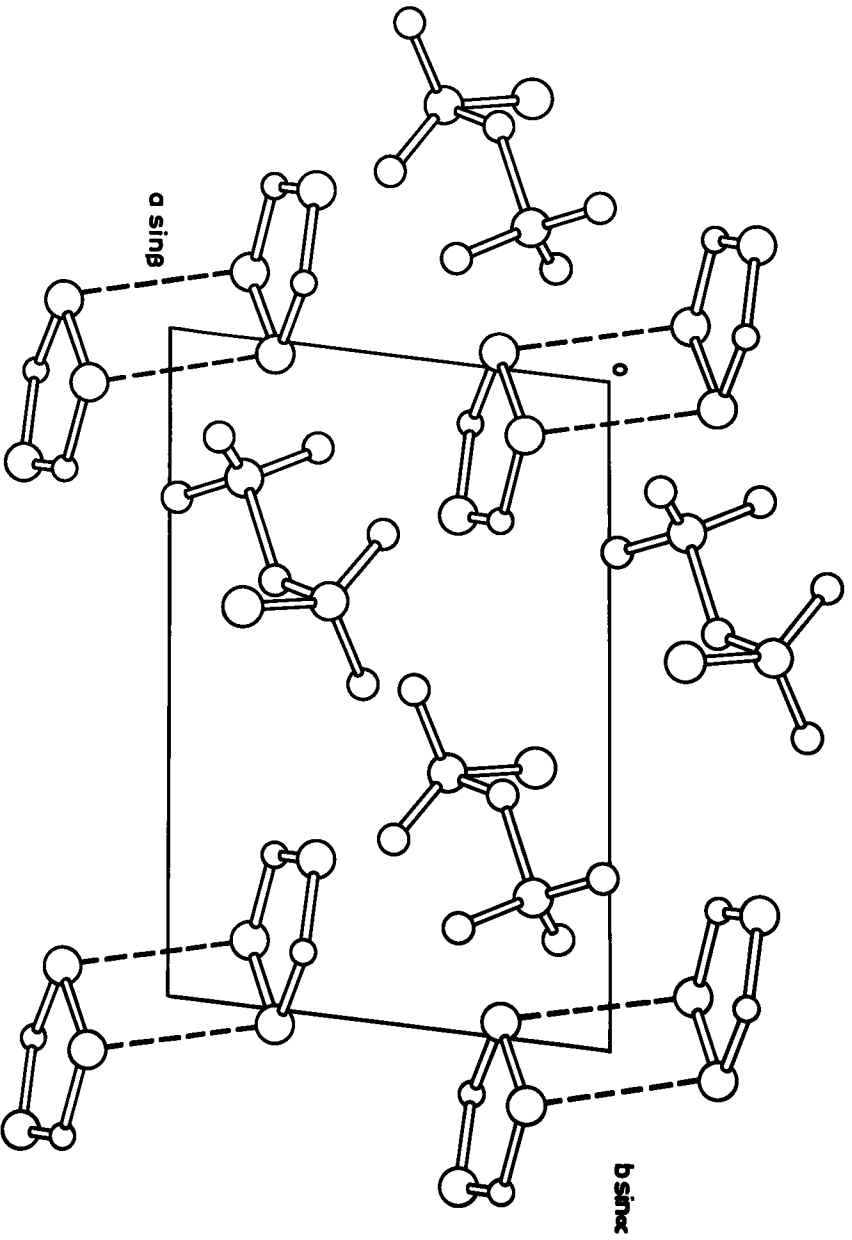
$$- 0.7411X + 0.1460Y - 0.6553Z + 1.4294 = 0$$

Atom	S(1)	S(2)	S(3)	N(1)	N(2)	O(1) <sup>†</sup>
P	0.0020	0.0014	-0.0003	-0.0224	-0.0081	0.0616
$\sigma(P)$	0.0010	0.0010	0.0010	0.0032	0.0031	0.0027

Where P and  $\sigma(P)$  are the distance and its estimated standard deviation of an atom from the mean plane. The plane is calculated with respect to the orthogonal axes X, Y and Z defined such that X lies along  $\underline{a}$ , Z lies along  $\underline{c}^*$ , and Y lies in the plane  $\underline{b}^*\underline{c}^*$  perpendicular to  $\underline{c}^*$ .

† This atom was not included in the calculation.





projection on the  $[001]$  plane

Figure 3.4

Table 3.8  $[\text{S}_3\text{N}_2]_2^{2+} (\text{ClS}_2\text{O}_6^-)_2$

Final Calculated and Observed Structure Factors

H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC	
0	1	0	18.4	19.2	0	-4	4	5.6	5.9	1	10	-5	0.0	-1.5	1	7	-1	14.4	-14.3	
0	2	0	34.2	-37.2	0	-3	4	8.9	-6.8	1	11	-5	6.5	7.1	1	8	-1	42.5	42.6	
0	3	0	11.7	-11.2	0	-2	4	-2.6	-7.0	1	-9	-4	5.3	5.1	1	9	-1	3.9	3.8	
0	4	0	4.8	4.6	0	-1	4	57.1	56.6	1	-8	-4	12.5	-12.1	1	10	-1	5.4	-5.5	
0	5	0	35.4	37.5	0	0	4	30.7	29.8	1	-7	-4	11.4	-11.5	1	11	-1	19.9	20.1	
0	6	0	26.1	-25.9	0	0	1	-9.1	-5.6	1	-6	-4	6.0	6.1	1	12	-1	12.1	10.9	
0	7	0	23.6	-23.9	0	0	2	-2.8	1.3	1	-5	-4	22.4	-22.3	1	-12	0	-3.1	-2.9	
0	8	0	35.8	35.7	0	0	3	6.6	8.2	1	-4	-4	10.0	-10.5	1	-11	0	15.1	-14.1	
0	9	0	8.1	7.9	0	0	4	31.8	33.1	1	-3	-4	-2.2	3.3	1	-10	0	4.9	3.7	
10	10	0	10.7	10.9	0	0	5	16.0	-10.4	1	-2	-4	6.2	-6.5	1	-9	0	-3.0	-0.9	
11	11	0	0.0	-1.1	0	0	6	10.5	-16.1	1	-1	-4	50.8	50.3	1	-8	0	44.2	-45.1	
12	12	0	-3.3	-1.8	0	0	7	9.2	8.5	1	0	-4	20.0	-19.2	1	-7	0	19.3	-19.8	
13	13	1	7.6	7.0	0	0	8	17.4	17.8	1	1	-4	11.9	11.5	1	-6	0	43.6	-44.2	
14	14	1	9.2	-8.7	0	0	10	-0.8	0.6	1	2	-4	18.6	18.0	1	-5	0	40.6	39.9	
15	15	1	13.3	13.0	0	0	-9	-2.5	0.6	1	3	-4	2.9	-3.1	1	-4	0	19.1	19.4	
16	16	1	11.2	-10.9	0	0	-8	0.0	-3.1	1	4	-4	7.5	7.4	1	-3	0	40.4	-42.4	
17	17	1	-2.7	3.4	0	0	-7	15.3	-15.4	1	5	-4	18.8	-19.8	1	-2	0	44.9	49.6	
18	18	1	-0.7	0.9	0	0	-6	7.7	8.4	1	6	-4	-1.9	1.6	1	-1	0	3.0	-3.5	
19	19	1	29.7	-29.7	0	0	-5	23.8	23.4	1	7	-4	36.1	35.7	1	0	0	5.0	2.8	
20	20	1	36.5	35.9	0	0	-4	26.9	27.1	1	8	-4	15.6	16.1	1	1	0	54.1	54.3	
21	21	4	9.7	9.9	0	0	-3	4.7	4.0	1	9	-4	13.7	13.6	1	2	0	65.2	-67.4	
22	22	1	48.1	49.6	0	0	-2	5.6	-5.7	1	10	-4	7.3	-7.6	1	3	0	25.3	25.3	
23	23	1	83.2	87.8	0	0	-1	-3.5	3.8	1	11	-4	8.9	7.8	1	4	0	34.1	-33.7	
24	24	1	15.0	-14.1	0	0	0	18.8	18.5	1	12	-4	15.4	14.9	1	5	0	18.2	-18.3	
25	25	0	44.0	43.6	0	0	1	10.2	9.7	1	-10	-3	6.4	-6.8	1	6	0	28.1	28.8	
26	26	1	22.9	23.4	0	0	2	12.5	-12.3	1	-9	-3	-2.5	-1.2	1	7	0	27.9	28.4	
27	27	1	10.6	10.2	0	0	3	-1.3	0.2	1	-8	-3	20.3	-20.3	1	8	0	20.3	20.5	
28	28	1	16.3	17.0	0	0	4	6.9	6.6	1	-7	-3	39.5	-39.1	1	9	0	22.3	23.0	
29	29	1	9.8	9.4	0	0	5	15.8	15.3	1	-6	-3	18.6	19.2	1	10	0	0.0	0.2	
30	30	1	-1.7	1.6	0	0	6	13.1	12.8	1	-5	-3	20.5	21.0	1	11	0	13.6	12.9	
31	31	1	7.7	7.7	0	0	7	-4.3	3.5	1	-4	-3	16.1	16.2	1	12	0	5.3	5.0	
32	32	1	14.5	14.2	0	0	-9	-1.4	-1.1	1	-3	-3	6.6	-6.5	1	-12	1	-2.7	-2.3	
33	33	1	22.7	22.5	0	0	-8	4.7	-3.1	1	-2	-3	11.6	-11.6	1	-11	1	6.0	-4.7	
34	34	1	11.1	11.5	0	0	-7	10.9	10.0	1	-1	-3	40.9	40.6	1	-10	1	11.8	-11.7	
35	35	1	11.6	-11.3	0	0	-6	8.9	9.2	1	0	-3	46.4	-44.1	1	-9	1	17.0	-17.5	
36	36	1	-2.4	1.1	0	0	-5	17.6	17.1	1	1	-3	50.6	-49.3	1	-8	1	52.0	-53.6	
37	37	2	-4.1	-3.3	0	0	-4	-2.6	1.8	1	2	-3	4.1	-4.6	1	-7	1	6.8	6.1	
38	38	2	-13.7	-13.7	0	0	-3	11.2	-10.8	1	3	-3	34.8	32.6	1	-6	1	22.4	22.3	
39	39	2	5.7	5.5	0	0	-2	19.2	18.7	1	4	-3	48.0	47.2	1	-5	1	8.4	8.0	
40	40	2	19.2	19.0	0	0	-1	-2.4	-1.5	1	5	-3	-2.0	1.1	1	-4	1	19.8	-20.4	
41	41	2	18.1	-18.2	0	0	0	12.4	-11.7	1	6	-3	10.4	10.1	1	-3	1	21.3	-21.5	
42	42	2	-1.1	0.0	0	0	1	-1.7	-1.0	1	7	-3	26.6	25.8	1	-2	1	49.7	51.2	
43	43	2	18.3	17.8	0	0	2	-2.4	-3.0	1	8	-3	15.4	15.1	1	-1	1	42.4	42.8	
44	44	2	56.1	55.2	0	0	3	37.0	36.8	1	9	-3	13.5	13.2	1	0	1	89.0	-90.8	
45	45	2	34.3	35.1	0	0	4	11.2	10.2	1	10	-3	4.9	4.7	1	1	1	62.0	-66.9	
46	46	2	11.6	-12.2	0	0	-5	7	6.6	6.0	1	11	-3	9.6	-9.1	1	2	1	36.9	39.1
47	47	2	46.6	-45.3	0	0	-4	5.7	6.7	1	12	-3	0.0	2.5	1	3	1	30.0	31.3	
48	48	2	59.5	59.3	0	0	-3	16.1	-16.0	1	-11	-2	15.3	-14.3	1	4	1	6.6	-5.8	
49	49	2	11.4	-10.5	0	0	-2	5.3	4.9	1	-10	-2	14.6	-14.1	1	5	1	10.0	-9.9	
50	50	2	6.4	6.0	0	0	-1	7.3	6.9	1	-9	-2	9.5	-10.3	1	6	1	10.7	11.1	
51	51	2	19.9	19.1	1	-1	-7	-4.3	-4.1	1	-8	-2	12.2	12.0	1	7	1	56.9	58.1	
52	52	2	30.9	31.5	1	1	-6	18.0	19.3	1	-7	-2	-2.7	-0.3	1	8	1	7.3	7.9	
53	53	2	65.3	66.4	1	1	-7	8.9	-9.9	1	-6	-2	3.5	3.0	1	9	1	-4.0	-5.1	
54	54	2	14.4	14.4	1	1	-7	-2.8	2.7	1	-5	-2	12.1	-12.5	1	10	1	0.0	-1.4	
55	55	2	13.9	-13.4	1	1	-6	-2.4	-2.4	1	-4	-2	27.7	25.9	1	11	1	-1.2	-0.3	
56	56	2	6.3	6.4	1	1	-5	5.5	-4.4	1	-3	-2	15.2	-14.7	1	-12	2	20.4	-19.6	
57	57	2	-1.3	1.9	1	1	-4	18.4	18.0	1	-2	-2	32.6	-31.6	1	-11	2	-4.0	-4.6	
58	58	2	17.8	17.9	1	1	-3	5.0	3.2	1	-1	-2	46.2	-45.3	1	-10	2	-3.0	-3.1	
59	59	2	15.0	-14.4	1	1	-2	10.9	10.6	1	0	-2	0.0	0.8	1	-9	2	-1.5	2.2	
60	60	2	9.8	-9.4	1	1	-1	10.4	-10.7	1	1	-2	0.0	-0.3	1	-8	2	3.6	3.5	
61	61	2	-3.6	-5.0	1	1	-1	-1.0	0.2	1	2	-2	9.3	10.5	1	-7	2	31.3	-31.8	
62	62	2	7.6	-7.5	1	1	-2	-2.7	2.8	1	3	-2	28.4	28.0	1	-6	2	-2.3	-0.8	
63	63	2	13.6	-13.2	1	1	-1	10.0	-9.9	1	4	-2	43.0	40.2	1	-5	2	9.8	-9.4	
64	64	2	31.3	31.0	1	1	0	7.9	7.6	1	5	-2	72.5	71.2	1	-4	2	15.7	-16.3	
65	65	2	29.8	31.0	1	1	-1	18.9	-18.5	1	6	-2	18.8	17.5	1	-3	2	14.0	12.8	
66	66	2	-1.1	1.1	1	1	-2	0.0	-0.2	1	7	-2	11.9	12.0	1	-2	2	40.4	-41.4	
67	67	2	9.5	9.2	1	1	-3	26.9	26.1	1	8	-2	17.8	17.4	1	-1	2	13.4	-11.6	
68	68	2	19.4	-19.5	1	1	-4	24.7	26.1	1	9	-2	75.8	-76.0	1	0	2	40.0	39.2	
69	69	2	0.0	-0.8	1	1	-5	9.7	9.8	1	10	-2	7.5	6.6	1	1	2	59.0	-58.4	
70	70	2	18.1	17.1	1	1	-6	0.0	1.3	1	11	-2	12.4	12.6	1	2	2	35.0	36.4	
71	71	2	32.9	-32.8	1	1	-7	-2.3	-0.6	1	12	-2	8.9	8.3	1	3	2	15.4	15.4	
72	72	2	41.5	39.8	1	1	-8	13.5	12.5	1	-12	-1	14.3	-13.6	1	4	2	22.4	23.2	
73	73	2	9.2	8.7	1	1	-9	-1.8	-1.2	1	-11	-1	9.6	-9.0	1	5	2	22.6	23.3	
74	74	2	33.3	33.8	1	1	-10	6.1	-7.2	1	-10	-1	13.7	13.3	1	6	2	16.9	-17.6	
75	75	2	42.8	42.7	1	1	-11	-3.4	-4.5	1	-9	-1	-3.7	-3.4	1	7	2	3.2	4.4	
76	76	2	0.0	-1.0	1	1	-12	10.1	10.0	1	-8	-1	19.1	-19.4	1	8	2	5.0	-3.7	
77	77	2	30.5	31.2	1	1	-13	0.0	-0.6	1	-7	-1	4.4	-3.9	1	9	2	4.9	-5.5	
78	78	2	8.3	8.6	1	1	-14	32.1	-32.0	1	-6	-1	6.2	5.7	1	10	2	18.9	18.8	
79	79	2	5.8	6.4	1	1	-15	27.9	-28.2	1	-5	-1	5.1	-4.6	1	-12	3	8.5	-8.1	
80	80	2	5.4	3.1	1	1	-16	17.5	17.8	1	-4	-1	57.0	-59.4	1	-11	3	5.2	4.4	
81	81	2	20.0	-19.6	1	1	-17	20.0	19.8	1	-3	-1	67.2	-72.2	1	-10	3	4.9	5.4	
82	82	2	-4.1	2.5	1	1	-18	23.9	23.6	1	-2	-1	71.0	74.1	1	-9	3	24.0	-24.3	
83	83	2	-3.0	2.9	1															

H	K	L	PO	PC	H	K	L	PO	PC	H	K	L	PO	PC	H	K	L	PO	PC
22.7				21.7	0.0				0.5	-2	-1		19.7	-13.6	2	-7	3	16.0	16.4
-2.1				-2.5	17.4	1	-5		-17.7	2	-6	3	63.3	62.4	2	-6	3	23.2	-23.7
39.3				39.8	32.3	2	-5		32.4	2	0	-1	48.8	-48.8	2	-5	3	10.6	-10.6
-2.4				-2.2	24.8	3	-5		-24.4	2	1	-1	29.0	27.9	2	-4	3	19.0	-19.5
24.3				-24.7	37.9	4	-5		-37.5	2	2	-1	42.5	-42.7	2	-3	3	-2.8	-1.6
11.8				-12.1	14.4	5	-5		-14.8	2	3	-1	25.3	-27.4	2	-2	3	32.4	32.3
-3.5				-3.7	9.8	6	-5		-9.3	2	4	-1	35.8	-33.5	2	-1	3	4.4	-4.0
15.3				15.3	18.9	7	-5		19.0	2	5	-1	45.4	-44.4	2	0	3	29.9	-25.6
10.6				10.9	12.4	8	-5		-13.2	2	6	-1	21.5	20.8	2	1	3	18.5	-19.0
-3.4				-1.7	8.4	9	-5		-8.1	2	7	-1	-1.4	2.2	2	2	3	18.8	-19.9
-3.0				-3.4	19.7	10	-5		19.6	2	8	-1	18.8	-19.0	2	3	3	12.4	-12.2
8.9				9.0	10.6	11	-5		10.4	2	9	-1	15.2	14.8	2	4	3	21.3	-22.3
15.1				-15.0	31.1	-9	-4		-30.1	2	10	-1	4.6	3.7	2	5	3	12.0	-13.1
28.6				-26.4	8.0	-8	-4		-8.0	2	11	-1	0.0	1.2	2	6	3	0.0	-1.3
17.1				-17.2	16.0	-7	-4		-15.4	2	12	-1	-1.2	-0.6	2	7	3	-3.7	4.0
4.4				-4.1	9.8	-6	-4		9.8	2	12	0	7.0	7.0	2	8	3	-0.5	-0.2
10.9				10.9	10.2	-5	-4		-10.2	2	-5	4	5.8	6.9	2	-10	4	11.9	-11.1
-4.4				-23.3	37.9	-4	-4		-38.2	2	-4	4	22.4	-22.5	2	-9	4	-3.4	-4.6
15.4				-15.2	26.3	-3	-4		26.2	2	-3	4	18.7	-19.0	2	-8	4	9.2	-9.0
9.0				8.2	-1.5	-2	-4		1.6	2	-2	4	5.2	-4.6	2	-7	4	7.9	-7.3
34.8				34.3	22.9	-1	-4		-22.0	2	-1	4	8.1	8.3	2	-6	4	-1.2	-0.3
3.7				3.5	9.1	-1	-4		-8.6	2	-2	4	4.9	-4.2	2	-5	4	-3.6	4.7
17.5				-17.4	51.0	1	-4		-50.1	2	-4	0	56.6	-58.2	2	-4	4	18.2	18.4
15.8				-15.9	22.3	2	-4		22.1	2	-3	0	40.5	41.0	2	-3	4	-3.1	3.6
5.3				-5.3	9.7	-3	-4		-9.3	2	-3	0	17.6	19.3	2	-2	4	34.9	-34.5
-2.4				-2.7	29.4	-2	-4		-28.5	2	-2	0	12.3	-12.9	2	-1	4	16.1	-15.7
7.8				-0.7	24.9	-2	-4		-23.3	2	-1	0	65.2	-68.7	2	0	4	4.9	-4.7
5.5				7.6	6.4	-2	-4		-6.4	2	0	0	88.7	-91.5	2	1	4	12.3	-12.0
9.3				9.3	20.3	1	-4		19.9	2	1	0	16.0	-16.1	2	2	4	7.8	-7.5
10.3				10.4	16.8	2	-4		16.5	2	2	0	-1.8	-1.2	2	3	4	31.6	-32.3
8.0				-8.2	10.2	3	-4		-10.0	2	3	0	38.7	-39.6	2	4	4	-2.5	-2.4
-7.0				-6.9	0.0	4	-4		1.7	2	4	0	17.2	-17.2	2	5	4	6.0	6.5
12.9				-12.7	0.0	11	-4		1.1	2	5	0	9.7	-9.5	2	6	4	-3.3	3.1
-3.9				1.8	5.0	-10	-3		5.2	2	6	0	21.2	21.4	2	7	4	-4.3	4.4
-2.2				2.5	13.5	-9	-3		-14.1	2	-7	0	24.0	23.8	2	-9	5	7.5	-8.2
9.0				-8.8	-0.7	-8	-3		3.9	2	-8	0	15.1	-14.9	2	-8	5	12.0	12.4
-2.0				1.5	4.4	-7	-3		-3.4	2	-9	0	21.1	-21.5	2	-7	5	5.5	4.5
-2.8				3.4	4.6	-6	-3		-4.7	2	10	0	9.9	9.6	2	-6	5	5.5	4.6
5.9				-6.2	-2.0	-5	-3		-3.6	2	11	0	-4.0	-3.4	2	-5	5	21.2	-21.0
12.3				-11.9	19.2	-4	-3		-19.0	2	-12	1	7.3	-7.9	2	-4	5	13.4	-12.9
37.7				-37.7	8.8	-3	-3		-8.4	2	-11	1	7.9	8.0	2	-3	5	17.3	17.1
8.8				9.0	18.6	-2	-3		-18.6	2	-10	1	-3.5	-0.8	2	-2	5	14.5	-14.4
15.2				15.2	47.3	-1	-3		-46.1	2	-9	1	21.2	-20.5	2	-1	5	19.4	-18.9
6.9				7.7	40.9	0	-3		-38.7	2	-8	1	6.6	-6.9	2	0	5	16.7	-16.7
-3.1				2.4	9.9	-1	-3		-10.3	2	-7	1	6.4	5.7	2	1	5	5.8	-5.6
8.7				-8.2	-1.9	-2	-3		-1.9	2	-6	1	30.3	30.1	2	2	5	16.3	17.9
19.1				18.9	19.4	-2	-3		-18.8	2	-5	1	12.2	-11.7	2	3	5	13.0	-13.1
-3.2				2.7	8.5	-3	-3		7.9	2	-4	1	23.0	-24.4	2	4	5	-3.4	-2.2
11.2				10.7	12.7	2	-3		12.7	2	-3	1	-1.0	-2.5	2	-5	6	5.9	-5.6
-5.6				-17.1	16.6	2	-3		16.5	2	-2	1	12.4	-13.2	2	-4	6	7.2	-6.3
12.2				-12.6	21.5	-2	-3		-21.8	2	-1	1	91.7	-105.3	2	-3	6	0.0	0.4
18.9				-18.9	21.9	-2	-3		-22.6	2	0	1	42.8	-40.7	2	-2	6	13.5	-12.9
5.5				-3.8	10.1	-2	-3		-10.1	2	1	1	36.7	-38.2	2	-1	6	4.7	3.3
10.7				9.9	6.1	-3	-3		5.8	2	2	1	21.4	21.6	2	0	6	8.8	8.3
16.3				-16.3	7.9	-3	-3		7.5	2	3	1	16.5	16.3	2	0	6	6.8	6.3
7.3				6.3	8.4	-2	-3		-7.6	2	4	1	19.1	-20.1	2	-3	7	-3.3	-3.1
10.7				9.5	9.0	-1	-3		-1.6	2	5	1	22.5	22.4	2	-1	7	1.5	-0.1
7.9				8.3	-3.5	-10	-2		0.1	2	6	1	12.5	-12.1	2	0	7	8.4	-7.7
10.3				10.4	-3.5	-9	-2		0.9	2	7	1	22.8	-23.2	2	1	7	24.2	-24.6
24.9				-25.3	-2.8	-8	-2		-2.2	2	8	1	-3.4	2.2	2	2	7	-2.9	-3.2
16.9				-17.2	23.3	-7	-2		-7.7	2	9	1	15.7	-15.2	2	3	7	-3.2	3.4
7.1				-7.0	7.7	-6	-2		-7.7	2	10	1	5.1	4.3	2	3	7	5.1	4.1
8.1				-8.6	55.8	-5	-2		-55.2	2	11	1	5.9	-5.2	2	4	7	-2.6	1.1
10.8				10.3	40.2	-4	-2		-40.4	2	11	2	-2.7	-0.9	2	5	7	5.4	-5.4
11.1				-10.6	14.3	-3	-2		-14.4	2	-12	2	6.2	-6.8	2	6	7	-1.9	-1.7
3.1				-4.4	18.3	-2	-2		-17.0	2	-11	2	-1.8	-0.9	2	7	7	0.0	-0.4
15.2				14.5	17.5	-1	-2		-18.4	2	-10	2	-2.8	-1.8	2	8	7	0.0	1.3
4.9				3.4	91.2	0	-2		-91.7	2	-9	2	24.2	24.2	2	-6	8	-2.9	-2.3
-2.2				-2.2	37.8	1	-2		37.7	2	-8	2	11.7	12.1	2	-5	8	4.9	-5.1
24.0				-24.0	19.1	2	-2		19.6	2	-6	2	49.4	-49.8	2	-4	8	9.8	-9.7
29.5				-30.0	17.2	3	-2		16.9	2	-5	2	8.6	-8.3	2	-3	8	7.9	-7.7
0.0				-0.9	14.1	4	-2		-14.1	2	-4	2	28.5	-28.9	2	0	8	23.4	23.3
6.5				6.5	28.3	5	-2		-28.5	2	-3	2	6.1	-6.2	2	1	8	-2.2	-0.5
12.0				-11.6	-1.3	6	-2		-0.4	2	-2	2	2.9	1.3	2	2	8	-3.3	-2.7
9.0				-8.2	21.0	7	-2		-20.5	2	-1	2	88.3	-88.2	2	3	8	19.8	-19.8
4.2				-2.6	21.4	8	-2		-21.1	2	0	2	24.4	23.8	2	4	8	16.2	-16.6
4.5				4.3	5.7	9	-2		-4.4	2	1	2	19.3	19.5	2	5	8	8.2	8.7
7.0				7.4	6.8	-10	-2		-7.2	2	2	2	26.9	-28.3	2	6	8	18.5	-18.9
9.6				-9.2	21.3	11	-2		21.1	2	3	2	11.5	-11.4	2	7	8	16.8	-16.9
14.0				-14.5	6.7	-12	-2		6.6	2	4	2	41.8	-44.2	2	8	8	-3.3	-3.8
0.0				2.9	-3.5	-11	-1		1.4	2	5	2	15.6	15.9	2	9	8	5.6	-6.5
9.8				-10.1	10.4	-11	-1		10.6	2	6	2	7.6	8.1	2	8	8	11.4	11.2
-3.1				2.4	0.0	-10	-1		-1.0	2	7	2	27.5	-28.1	2	7	8	7.5	7.5
17.1				-16.7	6.5	-9	-1		6.1	2	8	2	12.8	-13.0	2	8	8	15.6	-15.6
9.7				-9.8	30.3	-8	-1		-30.1	2	9	2	-2.9	-1.7	2	9	8	0.0	-0.7
20.0				-19.6	9.2	-7	-1		-10.2	2	10	2	7.9	8.5	2	10	8	4.2	-4.2
24.0				-24.2	9.5	-6	-1		9.0	2	-11	3	-2.8	2.9	2	11	8	31.3	31.4
4.2				3.9	19.4	-5	-1		-20.1	2	-10	3	4.5	1.1	2	12	8	24.6	24.6
15.7				-15.7	34.7	-4	-1		-33.7	2	-9	3	1						

H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC
3	1	-3	5.1	-6.0	3	2	-1	6.3	-6.8	3	2	3	10.5	-19.2	4	4	-4	59.4	59.7
3	2	-3	7.5	-7.4	3	3	-1	78.8	-77.5	3	3	3	11.4	-11.6	4	5	-4	26.8	27.0
3	3	-3	19.9	-20.4	3	4	-1	11.7	-11.8	3	4	3	7.7	8.0	4	6	-4	24.9	-25.0
3	4	-3	57.5	-58.4	3	5	-1	2.7	2.5	3	5	3	10.7	10.5	4	7	-4	5.7	-4.4
3	5	-3	-1.3	0.3	3	6	-1	6.9	-7.1	3	6	3	12.7	-12.4	4	8	-4	4.3	-3.2
3	6	-3	12.8	13.1	3	7	-1	13.0	-12.7	3	7	3	-3.4	1.5	4	9	-4	-3.7	-1.3
3	7	-3	5.6	-5.4	3	8	-1	4.3	-4.2	3	8	4	8.5	8.7	4	10	-4	5.3	-3.6
3	8	-3	5.7	5.2	3	9	-1	-4.0	1.6	3	9	4	22.1	21.4	4	11	-4	15.0	-15.0
3	9	-3	8.5	-9.4	3	10	-1	6.1	4.8	3	10	4	-2.8	-0.9	4	-10	-3	-4.6	4.1
3	10	-3	0.0	-0.1	3	11	-1	17.3	-16.9	3	-6	4	0.0	0.0	4	-9	-3	13.1	13.0
3	11	-3	0.0	-0.8	3	-12	0	10.9	11.0	3	-5	4	23.7	23.8	4	-8	-3	25.4	25.0
3	-8	-4	8.8	-8.0	3	-11	0	4.9	3.9	3	-4	4	10.9	11.2	4	-7	-3	4.8	-5.8
3	-9	-4	0.0	-2.9	3	-10	0	6.1	-6.6	3	-3	4	11.5	11.3	4	-6	-3	10.4	10.4
3	-6	-4	15.8	15.6	3	-9	0	4.4	-4.1	3	-2	4	18.5	-18.5	4	-5	-3	4.3	4.4
3	-5	-4	-11.5	-11.7	3	-8	0	22.5	22.1	3	-1	4	30.3	-29.9	4	-4	-3	11.2	-10.8
3	-4	-4	28.3	28.4	3	-7	0	22.9	23.8	3	0	4	11.3	11.4	4	-3	-3	26.4	26.3
3	-3	-4	13.4	12.6	3	-6	0	8.7	9.1	3	1	4	6.2	-5.5	4	-2	-3	16.4	15.5
3	-2	-4	14.4	14.4	3	-5	0	-0.9	1.7	3	2	4	6.1	7.0	4	-1	-3	12.2	11.4
3	-1	-4	13.1	13.0	3	-4	0	17.0	18.1	3	3	4	5.3	4.4	4	0	-3	47.7	45.9
3	0	-4	38.9	-38.8	3	-3	0	21.1	20.5	3	4	4	-4.4	-3.3	4	1	-3	31.6	-30.0
3	1	-4	18.5	-18.5	3	-2	0	24.8	-24.1	3	5	4	14.7	15.0	4	2	-3	42.1	40.8
3	2	-4	3.5	-3.9	3	-1	0	35.8	-35.6	3	-7	5	7.3	7.7	4	3	-3	23.8	22.8
3	3	-4	40.0	-39.0	3	0	0	22.3	-21.6	3	-6	5	0.0	-1.3	4	4	-3	-0.8	0.4
3	4	-4	12.5	-12.0	3	1	0	27.6	25.3	3	-5	5	12.3	12.7	4	5	-3	6.6	6.8
3	5	-4	5.4	5.6	3	2	0	0.0	-1.5	3	-4	5	11.7	-11.5	4	6	-3	21.7	-21.4
3	6	-4	14.1	14.3	3	3	0	-0.9	-1.4	3	-3	5	-2.1	-3.2	4	7	-3	7.1	7.1
3	7	-4	6.3	-6.4	3	4	0	12.3	-11.9	3	-2	5	-2.0	3.0	4	8	-3	12.2	12.7
3	8	-4	-25.7	-25.7	3	5	0	7.3	6.6	3	-1	5	0.0	0.3	4	9	-3	14.3	-14.4
3	9	-4	8.6	-8.9	3	6	0	4.1	-3.9	3	0	5	12.4	12.2	4	10	-3	-3.6	1.3
3	10	-4	13.9	14.4	3	7	0	23.6	-23.9	3	1	5	-4.0	-4.7	4	11	-3	-2.7	3.2
3	11	-4	13.6	-13.2	3	8	0	-2.4	-0.3	3	2	5	-3.0	2.1	4	-10	-2	17.6	18.0
3	-10	-3	17.2	-17.5	3	9	0	12.7	-12.3	4	-3	7	10.1	-10.3	4	-9	-2	10.8	-11.0
3	-9	-3	6.4	-6.1	3	10	0	15.5	-16.2	4	-2	7	-4.4	3.3	4	-8	-2	-2.7	-3.1
3	-8	-3	22.9	22.5	3	11	0	8.6	-7.8	4	-1	7	15.3	15.0	4	-7	-2	11.0	-10.6
3	-7	-3	19.3	19.2	3	-12	1	-3.2	-0.2	4	0	7	16.1	16.4	4	-6	-2	12.4	12.5
3	-6	-3	13.9	14.2	3	-11	1	-3.7	-3.1	4	1	-7	5.1	4.7	4	-5	-2	55.2	56.5
3	-5	-3	13.5	-14.0	3	-10	1	19.2	14.3	4	2	-7	-3.6	3.1	4	-4	-2	17.6	-17.6
3	-4	-3	-2.3	-1.0	3	-9	1	35.5	37.0	4	3	-7	16.2	17.4	4	-3	-2	12.1	12.1
3	-3	-3	23.6	23.0	3	-8	1	15.3	15.9	4	4	-7	11.0	10.9	4	-2	-2	34.5	32.8
3	-2	-3	5.4	4.8	3	-7	1	6.2	8.2	4	5	-7	-3.1	-3.0	4	-1	-2	32.2	32.2
3	-1	-3	49.1	-48.4	3	-6	1	19.4	-19.4	4	6	-7	13.8	-14.3	4	0	-2	62.8	61.6
3	0	-3	2.6	2.3	3	-5	1	17.7	17.5	4	7	-7	9.1	-9.6	4	1	-2	17.2	-17.4
3	1	-3	13.4	-12.7	3	-4	1	13.2	13.3	4	8	-6	12.3	-11.4	4	2	-2	23.1	-22.4
3	2	-3	19.7	20.5	3	-3	1	35.7	-37.2	4	-5	-6	8.0	8.1	4	3	-2	0.0	1.8
3	3	-3	19.7	18.9	3	-2	1	8.8	-8.9	4	-4	-6	18.0	18.2	4	4	-2	-0.3	-1.4
3	4	-3	36.1	-35.7	3	-1	1	6.1	5.3	4	-3	-6	-2.9	1.1	4	5	-2	12.4	12.0
3	5	-3	6.6	-6.3	3	0	1	9.4	9.5	4	-2	-6	12.0	11.6	4	6	-2	5.4	-5.4
3	6	-3	0.0	0.3	3	1	1	32.4	32.2	4	-1	-6	-4.0	3.7	4	7	-2	10.5	10.8
3	7	-3	10.4	-10.7	3	2	1	43.1	-43.6	4	0	-6	25.2	25.6	4	8	-2	28.6	28.8
3	8	-3	18.5	-18.4	3	3	1	24.5	25.1	4	1	-6	31.0	31.6	4	9	-2	7.8	7.6
3	9	-3	42.6	-42.2	3	4	1	14.8	15.0	4	2	-6	19.6	-19.9	4	10	-2	9.0	-9.8
3	10	-3	-2.0	1.0	3	5	1	-2.0	-3.3	4	3	-6	-1.0	-2.5	4	11	-2	4.9	-7.4
3	11	-3	-1.5	3.0	3	6	1	12.8	-13.1	4	4	-6	8.0	-8.5	4	-11	-1	15.4	-15.3
3	-11	-2	5.3	-4.7	3	7	1	49.1	-50.1	4	5	-6	8.5	9.8	4	-10	-1	0.0	-0.1
3	-10	-2	20.6	20.3	3	8	1	12.0	-13.1	4	6	-6	7.8	8.8	4	-9	-1	5.9	5.0
3	-9	-2	-2.2	-1.0	3	9	1	10.4	10.3	4	7	-6	16.3	-16.8	4	-8	-1	-1.8	2.4
3	-8	-2	6.9	7.4	3	10	1	7.6	-7.3	4	8	-6	8.5	8.1	4	-7	-1	6.2	6.3
3	-7	-2	22.6	22.3	3	-11	2	-1.6	0.2	4	9	-6	9.9	9.4	4	-6	-1	-3.3	-3.7
3	-6	-2	-3.1	-2.4	3	-10	2	0.0	-1.1	4	8	-5	5.2	-6.0	4	-5	-1	47.3	47.8
3	-5	-2	11.2	11.0	3	-9	2	21.4	21.4	4	7	-5	15.0	14.9	4	-4	-1	31.3	31.8
3	-4	-2	41.0	-40.3	3	-8	2	13.0	13.3	4	-6	-5	-2.5	1.5	4	-3	-1	25.1	24.8
3	-3	-2	19.8	-19.0	3	-7	2	15.0	15.4	4	-5	-5	21.9	22.0	4	-2	-1	9.1	9.1
3	-2	-2	25.6	24.7	3	-6	2	23.9	-24.9	4	-4	-5	31.0	31.8	4	-1	-1	20.6	19.8
3	-1	-2	17.0	-16.5	3	-5	2	16.4	-16.4	4	-3	-5	-3.3	-4.2	4	0	-1	16.7	-15.6
3	0	-2	59.7	59.6	3	-4	2	37.5	38.8	4	-2	-5	22.1	21.8	4	1	-1	-1.2	0.4
3	1	-2	51.4	48.6	3	-3	2	15.5	-15.7	4	-1	-5	6.1	5.2	4	2	-1	8.1	7.6
3	2	-2	26.8	-25.9	3	-2	2	3.2	3.7	4	0	-5	15.4	-15.6	4	3	-1	10.6	10.5
3	3	-2	14.6	-12.7	3	-1	2	8.3	8.4	4	1	-5	8.8	8.5	4	4	-1	4.5	4.5
3	4	-2	51.4	-50.1	3	0	2	10.8	10.9	4	2	-5	13.9	-13.9	4	5	-1	12.5	12.2
3	5	-2	8.5	8.8	3	1	2	28.5	30.1	4	3	-5	29.6	29.6	4	6	-1	25.7	25.7
3	6	-2	30.2	-28.8	3	2	2	22.4	-24.0	4	4	-5	14.6	14.2	4	7	-1	14.7	15.4
3	7	-2	38.0	-38.4	3	3	2	10.5	-10.5	4	5	-5	11.1	-10.7	4	8	-1	0.0	-1.0
3	8	-2	7.6	-7.7	3	4	2	-2.3	-2.4	4	6	-5	11.7	11.6	4	9	-1	-3.1	-2.7
3	9	-2	5.2	-5.5	3	5	2	23.4	-24.5	4	7	-5	12.8	12.9	4	10	-1	10.0	-9.7
3	10	-2	4.1	3.1	3	6	2	8.5	-8.7	4	8	-5	-3.7	4.9	4	-11	0	-0.4	2.7
3	11	-2	-1.8	-2.0	3	7	2	-3.6	-2.9	4	9	-5	5.6	5.7	4	-10	0	7.1	6.2
3	-11	-1	8.4	-9.2	3	8	2	-4.4	-3.4	4	10	-5	18.3	-18.3	4	-9	0	11.0	11.5
3	-10	-1	10.0	9.7	3	9	2	-2.9	1.5	4	-9	-4	22.1	22.3	4	-8	0	-3.4	-3.2
3	-9	-1	5.6	5.9	3	-10	3	-1.3	1.8	4	-8	-4	5.9	5.2	4	-7	0	6.0	9.7
3	-8	-1	-2.5	0.6	3	-9	3	6.3	6.1	4	-7	-4	5.9	5.8	4	-6	0	23.6	24.8
3	-7	-1	14.8	15.9	3	-8	3	6.6	-7.3	4	-6	-4	14.6	14.5	4	-5	0	14.3	14.2
3	-6	-1	30.3	-30.9	3	-7	3	-1.7	1.2	4	-5	-4	23.3	23.5	4	-4	0	21.4	22.2
3	-5	-1	4.3	4.4	3	-6	3	26.6	27.2	4	-4	-4	36.7	37.0	4	-3	0	-2.1	-1.7
3	-4	-1	7.2	7.6	3	-5	3	11.5	11.5</										

H	K	L	FO	FC	H	K	L	FN	FC	H	K	L	FO	FC	H	K	L	FO	FC
4	5	0	25.0	-25.1	5	-2	-6	4.0	3.9	5	-8	-1	-0.6	-3.0	5	-2	4	5.3	6.3
4	6	0	14.9	-15.5	5	-1	-6	17.0	12.2	5	-7	-1	10.7	10.9	5	-1	4	6.2	5.6
4	7	0	4.2	4.2	5	0	-6	9.0	-8.3	5	-6	-1	21.8	22.8	5	0	4	7.2	-6.8
4	8	0	6.7	6.6	5	1	-6	15.6	15.4	5	-5	-1	16.6	-16.8	6	-2	-7	12.1	-12.9
4	9	0	6.5	5.3	5	2	-6	5.6	5.4	5	-4	-1	7.4	-8.5	6	-1	-7	0.0	-1.5
4	10	0	13.6	-13.3	5	3	-6	8.9	-9.0	5	-3	-1	7.6	7.8	6	0	-7	5.1	3.9
4	-1	1	0.0	-0.8	5	4	-6	4.8	3.9	5	-2	-1	12.6	-12.5	6	1	-7	9.9	-10.2
4	-2	1	10.7	10.6	5	5	-6	6.0	-6.1	5	-1	-1	25.6	-24.7	6	2	-7	-3.1	-3.9
4	-3	1	24.2	23.6	5	6	-6	19.3	20.1	5	0	-1	21.5	-21.2	6	3	-7	25.1	-26.3
4	-4	1	-2.1	3.6	5	7	-6	22.5	23.1	5	1	-1	-1.5	-1.3	6	4	-7	5.6	-6.8
4	-5	1	19.0	-20.0	5	8	-6	0.0	3.7	5	2	-1	58.0	57.9	6	5	-7	7.7	7.4
4	-6	1	13.9	14.4	5	-7	-5	5.4	-5.5	5	3	-1	12.2	11.9	6	-5	-6	5.0	-6.0
4	-7	1	6.9	-7.8	5	-6	-5	23.3	23.7	5	4	-1	10.6	10.0	6	-4	-6	8.2	-8.5
4	-8	1	13.1	13.0	5	-5	-5	0.0	-1.4	5	5	-1	7.5	7.7	6	-3	-6	17.6	17.8
4	-9	1	9.8	-5.8	5	-4	-5	-1.3	-2.3	5	6	-1	11.5	11.1	6	-2	-6	6.5	-5.9
4	-10	1	16.6	11.2	5	-3	-5	11.8	-11.7	5	7	-1	21.5	21.4	6	-1	-6	27.8	-27.8
4	0	1	57.8	57.8	5	-2	-5	4.9	9.2	5	8	-1	6.0	-5.6	6	0	-6	25.4	-26.3
4	1	1	22.9	25.0	5	-1	-5	16.5	16.8	5	9	-1	7.1	-7.8	6	1	-6	8.5	-9.2
4	2	1	4.1	4.6	5	0	-5	15.8	-15.4	5	10	-1	-2.3	7.8	6	2	-6	10.3	10.4
4	3	1	14.5	-14.5	5	1	-5	18.5	-18.7	5	-10	0	-4.5	5.7	6	3	-6	9.3	-9.3
4	4	1	20.5	20.3	5	2	-5	20.5	20.1	5	-9	0	5.2	-5.4	6	4	-6	11.4	-10.7
4	5	1	11.7	-12.5	5	3	-5	30.1	30.7	5	-8	0	0.7	0.6	6	5	-6	8.1	8.4
4	6	1	4.3	-4.4	5	4	-5	30.3	31.1	5	-7	0	15.7	-15.9	6	6	-6	9.2	9.4
4	7	1	6.5	7.4	5	5	-5	-3.0	-0.3	5	-6	0	9.8	9.5	6	7	-6	6.7	6.4
4	8	1	0.0	0.7	5	6	-5	7.3	-7.3	5	-5	0	8.9	-8.5	6	-6	-5	-3.2	-4.2
4	9	1	6.9	6.1	5	7	-5	17.4	17.5	5	-4	0	36.2	-36.3	6	-5	-5	-2.5	-1.2
4	-10	2	-3.5	-0.7	5	8	-5	10.2	10.4	5	-3	0	6.4	6.2	6	-4	-5	16.7	-16.7
4	-11	2	-1.6	-4.1	5	9	-5	6.5	-7.3	5	-2	0	0.0	-0.5	6	-3	-5	19.9	-19.9
4	-12	2	6.0	-5.2	5	-8	-4	-2.5	1.4	5	-1	0	13.6	12.7	6	-2	-5	14.4	-13.9
4	-13	2	-3.5	-0.7	5	-7	-4	6.5	-6.5	5	0	0	10.9	10.8	6	-1	-5	-3.8	-3.7
4	-14	2	0.0	-3.6	5	-6	-4	-2.2	-0.8	5	1	0	15.9	-15.4	6	0	-5	10.3	-10.9
4	-15	2	20.9	20.8	5	-5	-4	-7.9	-2.7	5	2	0	25.4	25.0	6	1	-5	4.7	-4.7
4	-16	2	5.4	-6.3	5	-4	-4	19.9	-19.8	5	3	0	7.4	7.4	6	2	-5	7.3	-5.7
4	-17	2	-2.2	1.0	5	-3	-4	8.7	-7.7	5	4	0	13.2	13.3	6	3	-5	9.3	9.8
4	-18	2	19.7	20.2	5	-2	-4	-2.5	1.9	5	5	0	9.3	9.8	6	4	-5	5.4	-5.4
4	-19	2	33.3	35.7	5	-1	-4	11.5	-10.6	5	6	0	8.2	-8.5	6	5	-5	-3.0	0.8
4	-20	2	37.7	39.5	5	0	-4	20.2	20.7	5	7	0	5.4	4.2	6	6	-5	0.0	0.7
4	-21	2	7.9	-7.2	5	1	-4	19.4	18.8	5	8	0	-1.6	1.5	6	7	-5	14.3	-13.1
4	-22	2	14.6	-14.2	5	2	-4	29.1	28.4	5	9	0	6.5	5.8	6	8	-5	-3.7	-3.9
4	-23	2	9.5	9.7	5	3	-4	26.2	28.3	5	-10	1	5.8	-6.2	6	9	-5	-0.2	2.2
4	-24	2	10.4	10.7	5	4	-4	12.1	-11.3	5	-9	1	16.8	-15.5	6	8	-4	0.0	-0.8
4	-25	2	-1.7	-1.1	5	5	-4	17.9	18.1	5	-8	1	0.8	-1.6	6	-7	-4	-4.4	4.3
4	-26	2	4.6	-4.5	5	6	-4	-3.4	2.0	5	-7	1	9.2	-8.6	6	-6	-4	30.9	-30.8
4	-27	2	-3.6	2.1	5	7	-4	7.4	-8.3	5	-6	1	11.1	-11.5	6	-5	-4	40.0	-39.9
4	-28	2	18.5	18.3	5	8	-4	6.8	6.2	5	-5	1	7.3	-7.0	6	-4	-4	-2.6	-1.0
4	-29	2	13.6	13.5	5	9	-4	6.9	-7.2	5	-4	1	14.2	-14.4	6	-3	-4	4.7	5.1
4	-30	2	-2.4	0.3	5	10	-4	12.9	13.1	5	-3	1	28.2	28.4	6	-2	-4	8.0	7.6
4	-31	2	7.3	-7.7	5	-9	-3	15.4	-15.0	5	-2	1	12.3	12.6	6	-1	-4	18.3	-18.6
4	-32	2	-2.2	-1.6	5	-8	-3	12.5	-12.9	5	-1	1	0.0	0.3	6	0	-4	14.4	-14.3
4	-33	2	17.3	17.3	5	-7	-3	14.2	14.0	5	0	1	12.2	-12.6	6	1	-4	29.7	29.9
4	-34	2	32.6	32.9	5	-6	-3	14.1	-13.6	5	-1	1	6.0	0.1	6	2	-4	13.6	-14.3
4	-35	2	4.1	3.1	5	-5	-3	-2.2	-1.7	5	-2	1	21.1	20.9	6	3	-4	17.7	-17.7
4	-36	2	9.3	-9.0	5	-4	-3	45.1	-45.5	5	-3	1	7.6	-7.8	6	4	-4	23.2	-23.2
4	-37	2	6.0	5.7	5	-3	-3	14.7	-13.9	5	-4	1	22.3	-22.0	6	5	-4	18.1	-15.9
4	-38	2	-0.7	1.3	5	-2	-3	65.9	65.8	5	-5	1	5.7	6.3	6	6	-4	18.2	17.0
4	-39	2	10.6	10.5	5	-1	-3	17.0	16.9	5	-6	1	21.1	20.9	6	7	-4	8.0	-8.6
4	-40	2	3.1	5.0	5	0	-3	3.2	-2.7	5	-7	1	15.7	14.3	6	8	-4	9.0	-8.7
4	-41	2	-2.0	-0.4	5	1	-3	0.0	-0.7	5	-8	1	-3.3	2.4	6	9	-4	10.0	9.8
4	-42	2	22.8	23.7	5	2	-3	4.0	4.6	5	-9	2	23.6	-23.8	6	8	-3	13.7	-13.1
4	-43	2	-2.9	-0.5	5	3	-3	48.9	-48.3	5	-8	2	12.0	-12.5	6	-8	-3	22.4	-22.1
4	-44	2	8.4	9.0	5	4	-3	31.6	-31.8	5	-7	2	10.0	10.1	6	-7	-3	0.0	-2.1
4	-45	2	7.7	8.5	5	5	-3	15.9	-15.9	5	-6	2	9.5	9.5	6	-6	-3	-2.0	-1.7
4	-46	2	6.3	6.3	5	6	-3	27.0	26.0	5	-5	2	-2.2	-1.1	6	-5	-3	25.3	-25.4
4	-47	2	17.2	16.3	5	7	-3	17.5	17.7	5	-4	2	7.7	-7.1	6	-4	-3	6.8	8.2
4	-48	2	6.5	-7.2	5	8	-3	10.4	10.5	5	-3	2	-2.0	1.1	6	-3	-3	15.7	-16.2
4	-49	2	0.0	1.0	5	9	-3	0.0	0.2	5	-2	2	7.1	6.3	6	-2	-3	4.8	5.6
4	-50	2	0.0	0.3	5	10	-3	-3.0	2.9	5	-1	2	-0.3	1.0	6	-1	-3	-1.4	0.9
4	0	2	7.4	-6.8	5	-10	-2	-0.7	1.1	5	0	2	14.2	-14.0	6	0	-3	20.1	-19.9
4	1	2	16.8	16.5	5	-9	-2	9.6	-9.8	5	1	2	5.7	-5.2	6	1	-3	-2.0	2.6
4	2	2	4.7	-4.4	5	-8	-2	26.4	-27.0	5	2	2	5.1	-5.7	6	2	-3	24.3	-23.5
4	3	2	-1.9	4.7	5	-7	-2	6.7	7.1	5	3	2	6.8	6.7	6	3	-3	33.0	-32.5
4	4	2	17.6	16.8	5	-6	-2	10.4	-10.3	5	4	2	-2.3	3.7	6	4	-3	-2.1	-0.2
4	5	2	8.7	8.4	5	-5	-2	11.7	12.1	5	5	2	-3.1	4.8	6	5	-3	7.8	-8.4
4	6	2	20.7	21.9	5	-4	-2	22.5	22.6	5	6	2	19.9	20.0	6	6	-3	5.3	5.4
4	7	2	6.3	-5.7	5	-3	-2	10.4	-10.0	5	-8	3	8.8	-3.0	6	7	-3	6.4	6.4
4	8	2	19.6	15.2	5	-2	-2	4.5	3.3	5	-7	3	0.0	0.9	6	8	-3	-2.1	-0.1
4	9	2	11.7	-11.9	5	-1	-2	12.1	-11.7	5	-6	3	-5.4	-4.4	6	9	-3	10.8	11.3
4	-10	3	7.8	6.6	5	0	-2	4.8	-4.3	5	-5	3	9.8	-9.9	6	8	-2	-3.3	0.8
4	-11	3	32.5	33.2	5	1	-2	13.2	12.9	5	-4	3	11.9	12.8	6	-8	-2	-4.0	4.1
4	-12	3	5.5	6.1	5	2	-2	8.4	-8.0	5	-3	3	-4.2	-4.4	6	-7	-2	8.3	-8.2
4	-13	3	5.7	6.2	5	3	-2	4.4	3.9	5	-2	3	7.7	-8.1	6	-6	-2	8.5	-8.3
4	-14	3	-2.2	-1.0	5	4	-2	17.8	17.7	5	-1	3	12.9	-14.2	6	-5	-2	18.4	-19.0
4	-15	3	7.7	8.1	5	5	-2	12.1	12.5	5	0	3	11.1	-10.7	6	-4	-2	12.3	12.3
4	-16	3	5.1	6.1	5	6	-2	24.3	24.1	5	1	3	23.1	23.9	6	-3	-2		

H	K	L	FO	FC
6	4	-2	6.1	-6.0
6	5	-2	28.0	28.0
6	6	-2	-1.6	-2.0
6	7	-2	9.3	-10.5
6	8	-2	8.5	-8.5
6	9	-2	-3.7	-1.6
6	-3	-1	8.8	-6.0
6	-8	-1	8.5	7.2
6	-7	-1	-0.9	-3.4
6	-6	-1	15.6	-16.0
6	-5	-1	5.6	-6.1
6	-4	-1	35.8	-36.7
6	-3	-1	8.1	-7.6
6	-2	-1	5.6	-6.1
6	-1	-1	27.3	-26.9
6	0	-1	0.0	-0.8
6	1	-1	11.8	-11.7
6	2	-1	13.3	13.0
6	3	-1	19.4	19.9
6	4	-1	21.2	-20.8
6	5	-1	-3.6	-3.0
6	6	-1	15.7	-14.6
6	7	-1	13.9	-14.0
6	8	-1	-1.4	-0.1
6	-9	0	-3.4	-2.9
6	-8	0	0.0	1.2
6	-7	0	5.5	-5.2
6	-6	0	36.4	-34.0
6	-5	0	-3.8	-2.7
6	-4	0	6.7	-9.3
6	-3	0	11.4	-10.6
6	-2	0	9.2	-9.6
6	-1	0	14.8	-14.1
6	0	0	23.6	23.1
6	1	0	4.2	4.4
6	2	0	26.0	-25.6
6	3	0	15.9	-15.8
6	4	0	12.4	-12.6
6	5	0	-1.8	2.5
6	6	0	4.9	-3.5
6	7	0	11.1	-11.1
6	-8	1	-1.1	-0.3
6	-7	1	6.9	7.3
6	-6	1	13.1	-13.0
6	-5	1	17.2	-17.4
6	-4	1	0.0	-0.3
6	-3	1	7.2	7.7
6	-2	1	-3.8	-1.9
6	-1	1	20.6	-20.0
6	0	1	16.9	-16.9
6	1	1	7.0	-6.8
6	2	1	8.4	-7.9
6	3	1	17.3	-16.2
6	4	1	-2.1	-2.4
6	5	1	-4.0	2.8
6	6	1	6.4	6.6
6	-7	2	5.7	-6.1
6	-6	2	5.1	5.5
6	-5	2	-2.7	2.0
6	-4	2	0.0	2.3
6	-3	2	13.2	-14.2
6	-2	2	31.8	-33.3
6	-1	2	10.4	-10.4
6	0	2	-3.7	-2.6
6	1	2	-2.1	-1.4
6	2	2	-3.3	-4.1
6	3	2	10.3	-10.8

H	K	L	FO	FC
6	4	2	14.3	14.0
6	-4	3	-4.3	-3.1
6	-3	3	-3.7	-6.5
6	-2	3	16.7	-14.2
6	-1	3	-4.6	-3.8
6	0	3	-2.4	-2.0
7	1	-7	-3.0	-5.0
7	2	-7	16.3	-16.8
7	3	-7	6.3	-6.5
7	-3	-6	9.6	-9.9
7	-2	-6	8.8	-8.7
7	-1	-6	10.9	-10.8
7	0	-6	13.3	-13.5
7	1	-6	7.2	-6.2
7	2	-6	5.7	-5.9
7	3	-6	7.0	7.1
7	4	-6	10.6	10.6
7	5	-6	7.4	-7.1
7	6	-6	11.6	-11.6
7	-5	-5	5.7	-5.3
7	-4	-5	10.1	9.8
7	-3	-5	9.9	-9.2
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7	-4	-4	-3.9	-3.2
7	-3	-4	-4.5	4.7
7	-2	-4	14.5	-14.9
7	-1	-4	-4.3	5.0
7	0	-4	15.6	15.6
7	1	-4	-3.4	-1.9
7	2	-4	6.2	5.5
7	3	-4	10.4	-9.8
7	4	-4	8.4	-7.5
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7	-2	-3	7.9	-8.0
7	-1	-3	0.0	2.2
7	0	-3	0.0	-0.7
7	1	-3	14.7	-14.7
7	2	-3	10.8	10.9
7	3	-3	27.1	27.4
7	4	-3	13.4	14.0
7	5	-3	7.6	-8.3
7	6	-3	25.9	-25.4
7	-1	-3	8.8	7.9
7	0	-3	-2.1	-1.0
7	1	-3	27.6	-27.4
7	2	-3	23.5	-23.5
7	3	-3	7.1	-7.4
7	4	-3	5.4	5.4
7	5	-3	10.8	10.3
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7	8	-3	5.2	3.2
7	-8	-2	13.5	13.4
7	-7	-2	6.5	6.3
7	-6	-2	6.5	-6.9

H	K	L	FO	FC
7	-5	-2	10.4	11.0
7	-4	-2	7.5	6.5
7	-3	-2	6.0	-5.7
7	-2	-2	14.8	-14.9
7	-1	-2	20.2	-20.4
7	0	-2	4.5	5.0
7	1	-2	-2.6	3.4
7	2	-2	13.4	-13.1
7	3	-2	12.9	12.9
7	4	-2	8.7	-9.0
7	5	-2	10.3	-10.1
7	6	-2	8.6	-8.8
7	7	-2	13.1	-13.1
7	-4	-1	7.4	-7.1
7	-3	-1	-2.6	2.0
7	-2	-1	5.8	-5.5
7	-1	-1	-3.2	3.2
7	0	-1	-1.6	-1.0
7	1	-1	23.7	-23.1
7	2	-1	21.3	22.0
7	3	-1	15.7	15.0
7	4	-1	-2.0	3.3
7	5	-1	4.6	-4.9
7	6	-1	27.2	-27.2
7	7	-1	5.0	4.5
7	8	-1	-1.6	1.2
7	9	-1	22.7	-22.0
7	-6	-1	14.7	-14.2
7	-5	0	-4.3	-4.1
7	-4	0	7.0	-6.7
7	-3	0	-3.0	-1.0
7	-2	0	23.2	23.5
7	-1	0	-2.5	3.1
7	0	0	-3.5	2.1
7	1	0	-3.4	1.1
7	2	0	-2.0	-0.6
7	3	0	-2.6	-1.9
7	4	0	16.0	-15.5
7	5	0	20.1	-20.0
7	6	0	-2.5	-3.8
7	7	0	-2.7	-2.5
7	8	0	15.5	15.9
7	9	0	10.2	10.3
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7	-2	1	-2.5	-4.3
7	-3	1	-3.5	-2.8
7	-4	1	5.4	5.2
7	-5	1	0.0	-1.4
7	-6	1	18.8	-18.4
7	-7	1	-1.4	-0.4
7	-8	1	-3.2	2.2
7	-9	1	7.3	-5.9
7	0	2	12.1	-12.1
7	1	2	0.0	1.3
7	2	2	15.0	14.2
7	3	2	17.5	17.9
7	4	2	4.3	9.2
7	5	2	-1.7	-1.9
7	6	2	13.5	13.3
7	7	2	8.8	6.8
7	8	2	13.4	13.8
7	9	2	7.7	7.9
7	-1	3	14.1	14.7
7	0	3	16.9	17.1
7	1	3	-2.5	-3.6
7	2	3	9.5	9.6
7	3	3	-2.3	2.9

H	K	L	FO	FC
8	4	-5	10.4	-10.2
8	5	-5	-3.0	-6.8
8	-5	-4	19.5	19.7
8	-4	-4	5.0	-4.1
8	-3	-4	7.9	7.7
8	-2	-4	13.1	12.9
8	-1	-4	12.5	12.1
8	0	-4	-3.3	2.8
8	1	-4	13.4	-12.9
8	2	-4	0.0	0.3
8	3	-4	15.8	15.5
8	4	-4	0.0	3.9
8	5	-4	-0.6	-0.5
8	6	-4	0.0	-0.1
8	-6	-3	13.6	13.7
8	-5	-3	19.3	18.9
8	-4	-3	8.4	7.5
8	-3	-3	4.5	-9.2
8	-2	-3	-3.7	-2.8
8	-1	-3	-3.9	4.3
8	0	-3	-3.6	4.5
8	1	-3	7.2	6.9
8	2	-3	6.5	5.8
8	3	-3	17.6	17.7
8	4	-3	11.8	11.2
8	5	-3	-1.4	-2.1
8	6	-3	-4.2	4.9
8	-6	-2	14.3	13.9
8	-5	-2	10.0	-10.1
8	-4	-2	0.0	0.0
8	-3	-2	0.0	3.4
8	-2	-2	20.1	20.2
8	-1	-2	11.2	10.5
8	0	-2	12.7	-13.0
8	1	-2	14.4	14.2
8	2	-2	20.1	19.6
8	3	-2	12.4	12.3
8	4	-2	-4.6	4.3
8	5	-2	17.3	-17.0
8	-5	-1	-4.3	5.0
8	-4	-1	9.1	8.5
8	-3	-1	-4.0	3.3
8	-2	-1	10.9	11.5
8	-1	-1	25.8	25.5
8	0	-1	-2.8	-2.0
8	1	-1	-2.2	-1.7
8	2	-1	-3.8	3.8
8	3	-1	5.0	-3.7
8	4	-1	-1.2	1.6
8	-4	0	5.5	6.5
8	-3	0	18.4	18.1
8	-2	0	7.7	7.8
8	-1	0	-2.2	-1.8
8	0	0	-3.4	-3.2
8	1	0	-4.0	-4.1
8	2	0	9.8	9.8
8	-1	1	0.0	0.7
8	0	1	-2.9	-3.0
8	1	1	6.7	6.5
8	-2	1	5.7	-4.7
8	-1	1	-1.3	-0.4
8	0	1	0.0	1.4
8	1	1	17.3	17.2
8	2	1	25.1	25.2
8	-1	2	10.3	9.8
8	0	2	5.2	4.7

CHAPTER 4

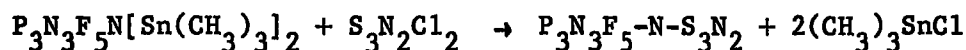
The Crystal Structure of  $P_3N_3F_5-N-S_3N_2$



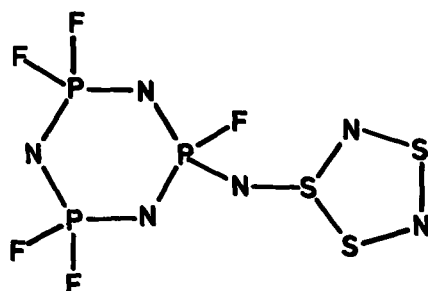
#### 4.1 Introduction.

The  $[\text{S}_3\text{N}_2]_2^{2+}$  cation, as just described, may be considered to consist of two  $\text{S}_3\text{N}_2$  rings, each containing a  $6\pi$  system, held together by a four-centre two electron interaction. From this it follows that if the cation  $\text{S}_3\text{N}_2^{2+}$  could be prepared then it would exist as a monomeric planar five-membered ring. On completion of the previous work a report was received of the preparation of various compounds containing the  $\text{S}_3\text{N}_2^{2+}$  cation (Roesky and Dielt, 1973). These were prepared by the action of halosulphuric acids on  $\text{S}_3\text{N}_2\text{Cl}_2$  which gave monosubstituted and disubstituted derivatives of the form  $\text{S}_3\text{N}_2\text{ClX}$  and  $\text{S}_3\text{N}_2\text{X}_2$  where  $\text{X} = \text{SO}_3\text{Cl}^-$ ,  $\text{SO}_3\text{F}^-$  and  $\text{SO}_3\text{CF}_3^-$ . These compounds were characterised by elemental analysis and by their infrared spectra, which showed that the  $\text{S}_3\text{N}_2\text{Cl}^+$  cation was present in the monosubstituted products and that the  $\text{S}_3\text{N}_2$  ring was retained in the disubstituted products. An attempt was made to obtain a crystalline derivative (Roesky, 1973) but this work only produced fine powders which could not be recrystallised. A related compound however,  $\text{P}_3\text{N}_3\text{F}_5\text{-N-S}_3\text{N}_2$  was prepared in crystalline form, and was held to contain the same  $\text{S}_3\text{N}_2$  ring as in the  $\text{S}_3\text{N}_2^{2+}$  derivatives from comparison of their infrared spectra. It was obviously not ionic in nature since the material was soluble in normal organic solvents such as methylene chloride and could also be sublimed.

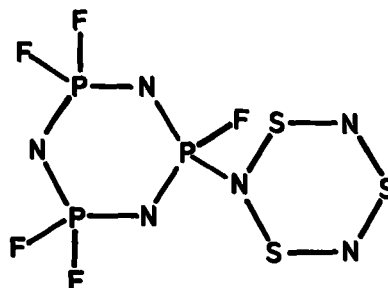
This compound was prepared by the reaction



(Roesky and Janßen, 1974). From the infrared spectrum the most likely structure was thought to be (I), although the possibility that it could be II could not be excluded.



I



II

This compound was of interest because it represented a new exocyclic group for sulphur-nitrogen ring systems.

#### 4.2 Crystal data.

The crystals were obtained by sublimation, as well formed yellow prisms, elongated along  $c$  and showing prominent  $\{100\}$  and  $\{010\}$  faces. The crystal used for data collection had dimensions  $0.5 \times 0.3 \times 0.3$  mm and was sealed in a quartz tube.

Preliminary work using precession and Weissenberg methods showed the unit cell to be orthorhombic and that the conditions limiting reflections were

$$0 \ k \ l \quad k = 2n$$

$$h \ 0 \ l \quad l = 2n$$

$$h \ k \ 0 \quad h = 2n$$

These uniquely define the space group as  $Pbca$  (No. 61). Accurate

cell dimensions were obtained from a least squares treatment of the positions of twelve high order reflections as measured on a four-circle diffractometer.

$P_3N_3F_6-N-S_3N_2$	M	=	368.13
	a	=	15.915(3)Å
	b	=	14.641(3)Å
	c	=	6.700(3)Å
	U	=	2260.2 Å <sup>3</sup>
	Z	=	8
	Dm	=	2.09g cm <sup>-3</sup> (by floatation in CH <sub>3</sub> I/C <sub>2</sub> H <sub>5</sub> I)
	Dc	=	2.16g cm <sup>-3</sup>

Absorption coefficient for MoK $\alpha$  radiation ( $\lambda = 0.7107\text{Å}$ ) =  $11.1\text{cm}^{-1}$ .

#### 4.3 Data Collection and Correction.

The intensity data were collected on a Hilger and Watts Y290 four-circle diffractometer using Zr-filtered MoK $\alpha$  radiation. A  $2\theta - \omega$  scan technique was used consisting of 80 steps of  $0.01^\circ$  at two seconds per step. The background was measured for 40 seconds at the beginning and end of each scan. Three standard reflections were measured every 40 reflections and showed no systematic changes, indicating that the crystal was stable throughout the experiment. These were used to place the intensities on a common scale. A quarter of the sphere of reflection was measured for  $0 < \theta \leq 25^\circ$ ,

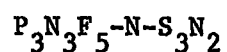
giving two equivalent sets of reflections which were averaged if the difference between them was not significant. A total of 1993 independent reflections was recorded; 1528 of these were considered observed having net counts  $> 2.5 \text{ esd's.}$  The intensities were corrected for Lorentz and polarisation effects, but no corrections were made for absorption.

#### 4.4 Solution and Refinement.

The structure was solved by symbolic addition procedures using a multiresolution program (Long, 1968). A set of normalised structure factors were calculated and signs were given to 230 of these with  $E > 1.62$ . The program initially chose three reflections which were arbitrarily given positive signs and hence defined the origin. A further four reflections were chosen, the signs of which were varied systematically so that each of the sixteen possible combinations was used together with the origin determining reflections as a starting set for the symbolic addition procedure. These reflections together with a summary of the results are shown in table 4.1.

The most self-consistent set corresponds to set 1 which has a consistency index of 0.84. Two other sets have a high consistency index, namely sets 9 and 14 each with a value of 0.79. In set 9 there is a change in sign of one member of the starting set which makes it equivalent to set 1 and in set 14 a change in sign of one of the origin determining planes makes this starting set equivalent to the first by changing the origin.

Table 4.1



The initial reflections used in the Symbolic Addition Procedure.

Origin determining reflections			$ E $	Reflections whose signs were varied			$ E $
4	3	1	2.59	10	1	1	2.56
2	6	7	2.84	12	1	1	2.87
11	0	4	3.20	8	2	7	2.90
				4	1	2	2.10

Results for Symbolic Addition Procedure.

Set No.	Signs	Changes	Cycles	No +	No -	Consistency Index
1	++++		5	130	100	0.837
2	+++ -		6	113	117	0.534
3	++ - +	*	16	113	117	0.358
4	++ - -		9	120	110	0.483
5	+ - + +		16	113	117	0.369
6	+ - + -	.	8	119	111	0.483
7	+ - - +	- - - +	16	116	114	0.353
8	+ - - -	*	16	115	115	0.369
9	- + + +	+ + + +	7	130	100	0.794
10	- + + -	+ + + -	16	104	126	0.500
11	- + - +		8	119	111	0.414
12	- + - -		16	117	113	0.506
13	- - + +	*	9	116	114	0.491
14	- - + -	*	7	106	124	0.794
15	- - - +		16	110	120	0.542
16	- - - -		8	107	123	0.414

\* A sign change occurred for one of the origin determining planes.

An E-map was calculated using the phases estimated from set 1, and revealed the correct positions of all atoms except F(2) and N(3), which were positioned incorrectly due to spurious peaks. In the E-map the heights of the peaks due to the heavier atoms ranged from 3.2 - 5.6 e. $\text{\AA}^{-3}$ , the lighter atoms from 0.9 - 1.1 e. $\text{\AA}^{-3}$ , and with a background fluctuation of  $\pm 1$  e. $\text{\AA}^{-3}$ .

All of these atoms were included in two cycles of least squares refinement using the block-diagonal approximation, at the end of which the R value was 0.26. Initially the atoms were given isotropic temperature factors of 3.0 $\text{\AA}^2$  but during the refinement the temperature factors for the atoms taken as F(2) and N(3) increased to about 10 $\text{\AA}^2$  indicating that they had been incorrectly positioned. A difference synthesis revealed two peaks of height 5.0 e. $\text{\AA}^{-3}$  and 4.5 e. $\text{\AA}^{-3}$  corresponding to the correct positions for F(2) and N(3). These were included in the subsequent refinement, during which all atoms were refined with anisotropic thermal parameters; after this R fell to 0.045. Further refinement using full matrix least squares methods saw R converge to its final value of 0.0367. The parameter shifts in the last cycle were all  $< 0.3\sigma$ . A difference synthesis calculated from the final structure factors showed no peaks greater than 0.3 e. $\text{\AA}^{-3}$  and these were associated with the heavier atom positions.

The weighting scheme used in the initial stages of refinement was the same as used previously except that  $P_1 = 20.0$  and  $P_2 = 0.1$ . This was replaced in the final stages of refinement by one based on counting statistics as described earlier. The optimum value for P was 0.06 as determined by an even distribution of  $w\Delta^2$  as a function of  $|F_o|$ . The unobserved reflections were not included in the refinement.

Table 4.2  $P_3 N_3 F_5 - N - S_3 N_2$ Least Squares Totals

$\Sigma F_o $	$\Sigma F_c $	$\Sigma \Delta $	R
46932.68	46716.14	1722.88	0.0367

Weighting Analysis

$ F_o $ Ranges	N	$\Sigma w\Delta^2/N$	R
0 - 10	257	0.53	0.152
10 - 20	477	0.45	0.057
20 - 30	257	0.42	0.033
30 - 40	177	0.44	0.029
40 - 50	111	0.32	0.024
50 - 100	194	0.30	0.022
100 - Upwards	54	0.37	0.028

Table 4.3  $P_3N_3F_5-N-S_3N_2$ 

Final Atomic Coordinates with their Estimated Standard Deviations  
( $\times 10^5$ ) and their Isotropic Temperature Factors ( $\text{\AA}^2$ )<sup>†</sup>

Atom	x/a	y/b	z/c	B
S(1)	0.08047 (7)	-0.14147 (8)	0.37507 (13)	4.67
S(2)	0.06783 (8)	-0.11637(10)	0.09886 (13)	5.05
S(3)	-0.02359 (6)	-0.04711 (7)	0.32020 (11)	3.63
P(1)	0.07479 (6)	0.11573 (7)	0.29691 (10)	3.16
P(2)	0.24404 (7)	0.08205 (8)	0.29268 (12)	4.01
P(3)	0.18279 (7)	0.21593 (8)	0.45582 (12)	4.14
F(1)	0.03595(16)	0.16244(18)	0.16970 (26)	4.97
F(2)	0.28642(19)	-0.00430(21)	0.34375 (39)	6.75
F(3)	0.30111(17)	0.09890(22)	0.16969 (32)	6.09
F(4)	0.20141(19)	0.31696(20)	0.43801 (36)	6.28
F(5)	0.18409(19)	0.21258(23)	0.61292 (27)	6.28
N(1)	0.11828(23)	-0.15593(26)	0.22052 (39)	4.66
N(2)	0.01408(22)	-0.06874(27)	0.15428 (38)	4.40
N(3)	0.00009(19)	0.05327(23)	0.35541 (35)	3.63
N(4)	0.15333(20)	0.06055(24)	0.24230 (35)	3.82
N(5)	0.25852(21)	0.15912(27)	0.40100 (39)	4.92
N(6)	0.09305(21)	0.19472(22)	0.40413 (37)	3.79

† The temperature factors from the last cycle of Isotropic Refinement.



Final values of Anisotropic thermal Parameters and their  
Estimated Standard Deviations (Both  $\text{\AA}^2 \times 10^5$ )

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
S(1)	5861 (67)	5745 (66)	6549 (75)	790 (55)	-48 (56)	702 (55)
S(2)	6099 (73)	8761 (93)	5593 (69)	-2235 (64)	-305 (56)	702 (63)
S(3)	3352 (48)	5415 (61)	5400 (59)	-145 (48)	329 (43)	-463 (43)
P(1)	3552 (48)	4525 (54)	4168 (53)	290 (44)	84 (40)	297 (41)
P(2)	3807 (53)	6004 (68)	6239 (70)	565 (56)	781 (48)	847 (49)
P(3)	5109 (60)	5695 (66)	5331 (65)	-514 (53)	-119 (50)	-693 (52)
F(1)	6366(154)	7597(181)	5603(144)	2030(130)	-1157(131)	31(136)
F(2)	7336(188)	7411(194)	13371(284)	1806(195)	-628(191)	2989(166)
F(3)	4542(144)	11903(261)	8078(189)	-300(176)	2880(138)	-162(141)
F(4)	8354(203)	5750(162)	10825(236)	-773(157)	-57(183)	-2114(147)
F(5)	8425(198)	10584(240)	5293(158)	-1492(152)	-810(149)	-621(167)
N(1)	5830(215)	5974(222)	7113(257)	-1381(190)	355(193)	1017(186)
N(2)	4971(197)	7483(248)	5535(217)	-961(188)	-983(166)	80(189)
N(3)	3769(166)	5103(195)	5489(207)	142(159)	954(143)	121(147)
N(4)	4047(164)	5414(192)	5463(194)	-806(163)	1089(150)	0(153)
N(5)	4169(184)	7585(251)	6719(230)	-484(195)	429(176)	-239(180)
N(6)	4312(173)	5048(200)	6233(218)	-1092(166)	508(164)	250(151)

The final least squares totals and weighting analysis are given in table 4.2. The final atomic coordinates and anisotropic thermal parameters are given in tables 4.3 and 4.4. The sulphur and phosphorus atoms were corrected for anomalous dispersion; these correction factors were taken from International Tables Vol. III as were the scattering factors for all atom except fluorine which were those calculated by Freeman (1959). The final calculated and observed structure factors are given in table 4.10.

#### 4.5 The Structure and Bonding in $P_3N_3F_5-N-S_3N_2$ .

The molecule consists of a six-membered phosphonitrilic ring bonded through a bridging nitrogen to a five-membered  $S_3N_2$  ring, as shown in figure 4.1, with an angle of  $57.0^\circ$  between the mean planes of these rings. The bond distances and angles are given in tables 4.5 and 4.7. The molecule may be discussed in terms of the phosphonitrilic ring and the  $N-S_3N_2$  fragment.

##### 4.5.a Structure and Bonding in $-N-S_3N_2$ .

This part of the molecule is directly analogous to  $S_3N_2Cl^+$  in which formally S-Cl is replaced by S=N-. The bonding across the bridging nitrogen involves substantial multiple bonding since the S-N and P-N distances are considerably shorter than the corresponding single bond. The S(3) - N(3) bond distance of  $1.555\text{\AA}$  is very short and approaches the length of an S-N double bond, for example  $1.54\text{\AA}$  in  $S_4N_4F_4$  (Weigers and Vos, 1963) or  $1.550\text{\AA}$  in  $R-S-N=S=N-S-R$ , where  $R = p-C_6H_4Cl$  (Olsen and Barrick, 1973). The P(1) - N(3) distance of  $1.603\text{\AA}$  is also short compared to the P-N single bond distance of  $1.77\text{\AA}$

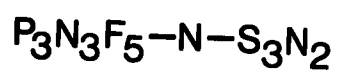
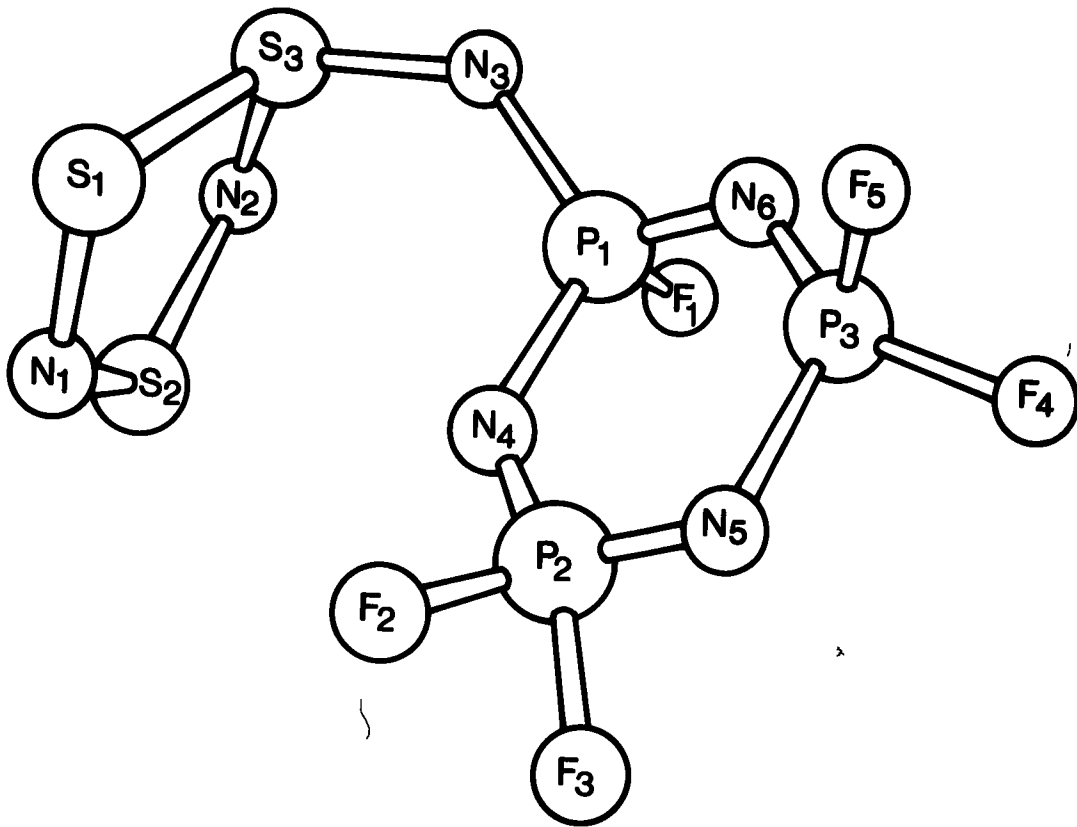
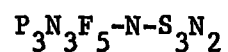


Figure 4.1

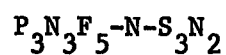
Table 4.5



Final Bond Distances ( $\text{\AA}$ ) and their Estimated Standard  
Deviations ( $\text{\AA} \times 10^3$ ).

S(1) - S(3)	2.221(2)
S(1) - N(1)	1.629(4)
S(2) - N(1)	1.540(4)
S(2) - N(2)	1.572(4)
S(3) - N(2)	1.647(4)
S(3) - N(3)	1.555(4)
P(1) - N(3)	1.603(3)
P(1) - N(4)	1.579(3)
P(1) - N(6)	1.582(4)
P(2) - N(4)	1.555(3)
P(2) - N(5)	1.559(4)
P(3) - N(5)	1.557(4)
P(3) - N(6)	1.544(4)
P(1) - F(1)	1.540(3)
P(2) - F(2)	1.516(3)
P(2) - F(3)	1.519(3)
P(3) - F(4)	1.518(3)
P(3) - F(5)	1.525(3)

Table 4.6



Some Mean Planes

	$-0.6182X - 0.7844Y - 0.0512Z - 0.6296 = 0$					
Atom	S(1)	S(2)	S(3)	N(1)	N(2)	N(3) <sup>†</sup>
P	0.018	-0.009	-0.016	-0.111	0.222	-1.419
$\sigma(\text{P})$	0.001	0.001	0.001	0.004	0.004	0.003
	$-0.4978X - 0.8635Y - 0.0810Z - 0.8569 = 0$					
Atom	S(1)	S(2)	S(3) <sup>†</sup>	N(1)	N(2)	N(3) <sup>†</sup>
P	-0.0003	-0.0006	-0.326	0.005	0.002	-1.810
$\sigma(\text{P})$	0.0012	0.0014	0.001	0.004	0.004	0.003
	$0.1098X + 0.6564Y - 0.7464Z + 0.9056 = 0$					
Atom	P(1)	P(2)	P(3)	N(4)	N(5)	N(6)
P	-0.001	0.002	0.000	0.001	-0.017	0.014
$\sigma(\text{P})$	0.001	0.001	0.001	0.004	0.004	0.004
	$0.1157X + 0.6577Y - 0.7443Z + 0.8755 = 0$					
Atom	P(1) <sup>†</sup>	P(2)	P(3)	N(4)	N(5)	N(6)
P	-0.016	0.002	0.000	-0.009	-0.012	0.004
$\sigma(\text{P})$	0.001	0.001	0.001	0.003	0.004	0.003

Where P and  $\sigma(\text{P})$  represent the distance and its e.s.d. of an atom from the mean plane

X, Y and Z refer to orthogonal coordinates in Å whose directions lie along a, b and c.

† this atom was not included in calculation of the mean plane.

Final Bond Angles (degrees) with their Estimated Standard  
Deviations (deg. x 10<sup>2</sup>)

S(3) - S(1) - N(1)	97.78(15)
N(1) - S(2) - N(2)	109.66(21)
S(1) - S(3) - N(2)	92.65(14)
S(1) - S(3) - N(3)	110.78(14)
N(2) - S(3) - N(3)	111.97(19)
N(3) - P(1) - N(4)	114.40(18)
N(3) - P(1) - N(6)	108.69(18)
N(4) - P(1) - N(6)	116.69(18)
N(3) - P(1) - F(1)	103.86(16)
N(4) - P(1) - F(1)	106.00(17)
N(6) - P(1) - F(1)	106.01(17)
N(4) - P(2) - N(5)	119.68(20)
N(4) - P(2) - F(2)	110.27(19)
N(4) - P(2) - F(3)	109.90(18)
N(5) - P(2) - F(2)	108.52(20)
N(5) - P(2) - F(3)	108.87(19)
F(2) - P(2) - F(3)	97.26(18)
N(5) - P(3) - N(6)	119.77(20)
N(5) - P(3) - F(4)	109.31(19)
N(5) - P(3) - F(5)	108.27(19)
N(6) - P(3) - F(4)	109.84(19)
N(6) - P(3) - F(5)	109.30(19)
F(4) - P(3) - F(5)	98.18(18)
S(1) - N(1) - S(2)	117.64(24)
S(2) - N(2) - S(3)	119.69(24)
S(3) - N(3) - P(1)	129.86(22)
P(1) - N(4) - P(2)	121.65(22)
P(2) - N(5) - P(3)	120.16(24)
P(1) - N(6) - P(3)	122.01(22)

in  $\text{NH}_3\text{PO}_3^-$  (Cruickshank, 1964a) and approaches the P(1) - N(4) and P(1) - N(6) ring distances of  $1.579\text{\AA}$  and  $1.582\text{\AA}$ . As with S-N bonds, the P-N single bond distance varies with the electronegativity of its ligands and also with the hybridisation, so that the shortness will in part be due to the fluorine and nitrogen atoms attached to P(1). In addition the angle at N(3) is  $129.9^\circ$ , which indicates essentially  $sp^2$  hybridisation at this nitrogen. The increase in this angle may be a steric requirement since its decrease would result in short contacts between the two parts of the molecule, (table 4.8.) The shortness of these bonds and the size of the angle at nitrogen suggest that there is substantial multiple bonding in both bridge bonds.

The  $\text{S}_3\text{N}_2$  ring is not planar; S(3) which carries the exocyclic nitrogen lies  $0.33\text{\AA}$  above the mean plane of the remaining ring atoms. For these atoms the maximum deviation from their mean plane is  $0.005\text{\AA}$  as given in table 4.6. The S-N bond lengths within the ring are all shorter than the normal S-N single bond distance of  $1.73\text{\AA}$  as seen in  $\text{S}_7\text{NH}$  (Weiss and Neubert, 1965) and indicate substantial multiple bonding around the ring. The S(2) - N(1) bond distance of  $1.540\text{\AA}$  is particularly short and is the length normally associated with S-N double bonds eg.  $1.54\text{\AA}$  in  $\text{S}_4\text{N}_4\text{F}_4$ . The S(1) - S(3) distance of  $2.221\text{\AA}$  is similar to that of  $2.066\text{\AA}$  in  $\text{S}_4\text{N}_3^+$  or  $2.136\text{\AA}$  in  $\text{S}_3\text{N}_2\text{Cl}^+$ , although as noted in section 3.5.b, the length of S-S bonds depends markedly on the hybridisation; so that it is not possible to estimate bond orders from bond lengths alone.

4.5.b A Comparison of the Structures of  $(S_3N_2)_2^{2+}$ ,  $N-S_3N_2$ , and  $S_3N_2Cl^+$ .

The bonding in  $N-S_3N_2$  may be discussed by comparison with the analogous  $S_3N_2Cl^+$  ion, but the structure of  $[S_3N_2]_2^{2+}$  has just been described in chapter 3, and it is meaningful to correlate the structures of all three. The dimensions of these three compounds are shown in figure 4.2. This task is not simple since it is impossible to describe the bonding in any one of these compounds without resorting to molecular orbital calculations, but it is possible to make several qualitative observations.

The dimensions of these three rings are all very similar, since the maximum difference between corresponding bond lengths in any of these rings is less than  $0.09\text{\AA}$ . Likewise the bond angles in the rings are very similar, particularly those at nitrogen which are all close to  $120^\circ$ . Angles of  $120^\circ$  or greater at nitrogen are a characteristic feature of  $\pi$ -bonded sulphur-nitrogen compounds since nitrogen requires  $sp^2$  hybridisation in order to participate effectively in the  $\pi$ -system, whereas for sulphur the  $\pi$ -bonding is less dependent on angle because of the larger number of orbitals available.

Calculations have shown that  $S_3N_2Cl^+$  contains a pseudo  $6\pi$  system (Adams et al., 1971) where the term pseudo refers to the lack of planarity of the  $S_3N_2$  ring. In view of the similarities between these three ring compounds it is reasonable to conclude that  $[S_3N_2]_2^{2+}$  and  $N-S_3N_2$  contain  $6\pi$  systems. These calculations also suggested that the majority of the positive charge in  $S_3N_2Cl^+$ , i.e.  $+0.76e$ , resides on the apical sulphur, whereas they suggest that there is only a charge of  $+0.12e$  on the sulphur attached to chlorine and  $+0.24e$  on the remaining sulphur. By comparison the charge distribution in the



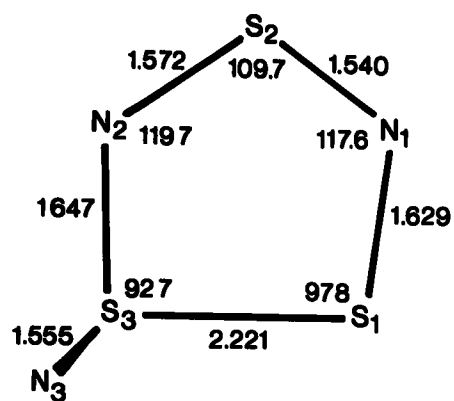
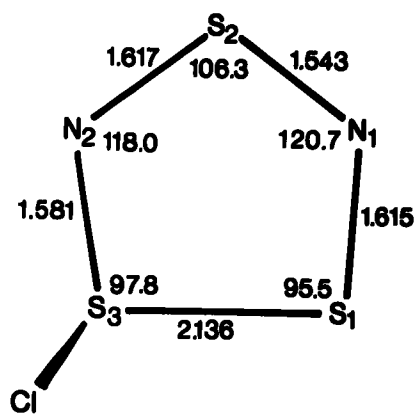
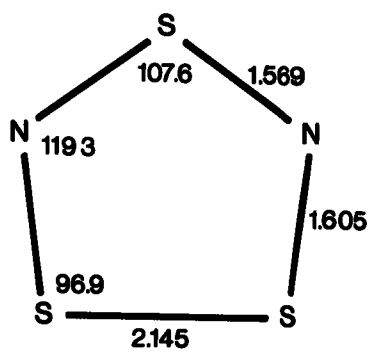
 $N-S_3N_2$  $S_3N_2Cl^+$  $[S_3N_2]^{2+}$ 

Figure 4.2

$S_3N_2$  rings of  $[S_3N_2]_2^{2+}$  is expected to be more even. This is shown by the smaller variation in the mean S-N distances of 1.569 - 1.605 Å as compared to 1.543 - 1.617 Å in  $S_3N_2Cl^+$ . In comparing these compounds it is convenient to consider the effects produced by attaching a chlorine or nitrogen atom to the  $S_3N_2$  ring in  $[S_3N_2]_2^{2+}$ .

It is reasonable to suggest that the S-Cl bond in  $S_3N_2Cl^+$  is essentially a single bond so that since most of the positive charge does not reside on S(3), this sulphur must be involved in the multiple bonding to S(1) and N(2). Compared to  $[S_3N_2]_2^{2+}$ , the attachment of a chlorine atom produces a decrease in the S(3) - N(2) bond distance which is presumably due to the contraction of the orbitals on S(3) by the electronegative chlorine atom. This change does not appear to affect the S-S bond distance significantly. Conversely because N(2) is more involved in the  $\pi$ -bonding with S(3) there is an increase in the S(2) - N(2) distance to 1.617 Å and a decrease in the S(2) - N(1) distance to 1.543 Å compared to the mean of 1.569 Å in  $[S_3N_2]_2^{2+}$ .

The attachment of a nitrogen atom to the  $S_3N_2$  ring formally removes the positive charge, and results in a larger variation in the S-N bond lengths i.e. 1.540 - 1.647 Å. The length of the S(3) - N(3) bond external to the ring shows that there is considerable multiple bonding in this bond, and so S(3) is not able to participate as effectively in the  $\pi$ -bonding of the  $S_3N_2$  ring. This accounts for the increase in the S(3) - N(2) bond from 1.605 Å in  $[S_3N_2]_2^{2+}$  to 1.647 Å and the increase in the S-S distance from 2.145 Å to 2.221 Å. From the foregoing discussion it would be expected that removal of the positive charge would result in an increase in all the S-N distances in the ring, because the sulphur atoms

will carry less positive charge and hence the orbitals should be less contracted. However both S(2) - N(1) and S(2) - N(2) are still very short i.e. 1.540Å and 1.572Å compared to 1.569Å in  $[S_3N_2]_2^{2+}$ , and suggest that the bonding across N(1) - S(2) - N(2) is approaching that of a sulphur diimide. Strong  $\pi$ -bonding is possible in this part of the ring because S(2) is attached to two nitrogen atoms which contract its orbitals. Conversely the orbitals on S(1) are contracted by only one nitrogen and more affected by the loss of the positive charge, resulting in an increase in the S(1) - N(1) distance to 1.629Å. Further confirmation that S(3) is less involved in the  $\pi$ -bonding in the  $S_3N_2$  ring is shown by S(3) being further from the mean plane of the other ring atoms than S(3) in  $S_3N_2Cl^+$  i.e. 0.33Å as compared to 0.24 Å, (Shearer, 1972).

#### 4.5.c The Structure and Bonding in $P_3N_3F_5^-$

This part of the molecule as shown in figure 4.4 is a derivative of  $P_3N_3F_6$  in which one fluorine has been replaced by a nitrogen. The most interesting aspects of this part are the changes in the structure caused by this substitution. The parent molecule,  $P_3N_3F_6$  shows 3mm symmetry within experimental error and its dimensions are shown in figure 4.3.

Substitution of a fluorine by nitrogen causes a loss of the planarity in the  $P_3N_3$  ring. The mean planes given in table 4.6 show that the atoms in the  $P_3N_3$  ring deviate from their mean plane by as much as 0.017Å. Removal of P(1) from the calculation shows that the remaining ring atoms are coplanar to within 0.012Å.

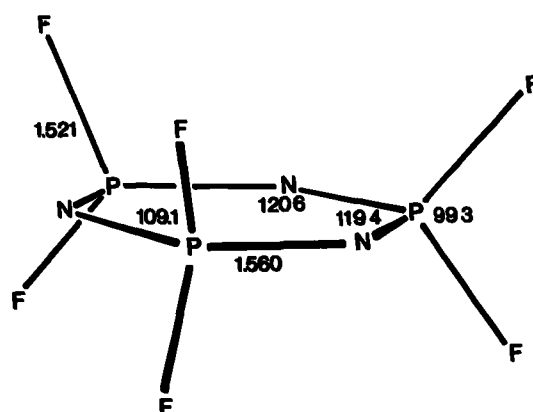


Figure 4.3

The bond distances may be considered in two parts, those involving P(1) and those which do not. The P-N distances not involving P(1) are all the same within experimental error, i.e. P(2) - N(4) 1.555(4)Å, P(2) - N(5) 1.559(4)Å, P(3) - N(5) 1.557(4)Å and P(3) - N(6) 1.544(4)Å, and the mean value of 1.553(2)Å does not differ significantly from that of 1.560(6)Å found in  $\text{P}_3\text{N}_3\text{F}_6$  (Dougill, 1963). The P-N distances involving P(1) are substantially longer i.e. P(1) - N(4) 1.579(4)Å and P(1) - N(6) 1.582(4)Å. A similar effect is seen in the P-F distances. Except for P(1) - F(1) they are the same within experimental error and their mean of 1.520(2)Å does not differ significantly from the P-F distance of 1.521(5)Å seen in  $\text{P}_3\text{N}_3\text{F}_6$ ; conversely P(1) - F(1) has a bond distance of 1.540(3)Å and is significantly longer. This effect is caused by the smaller electronegativity of nitrogen as compared to fluorine, resulting in less orbital contraction and longer bonds.

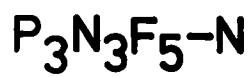
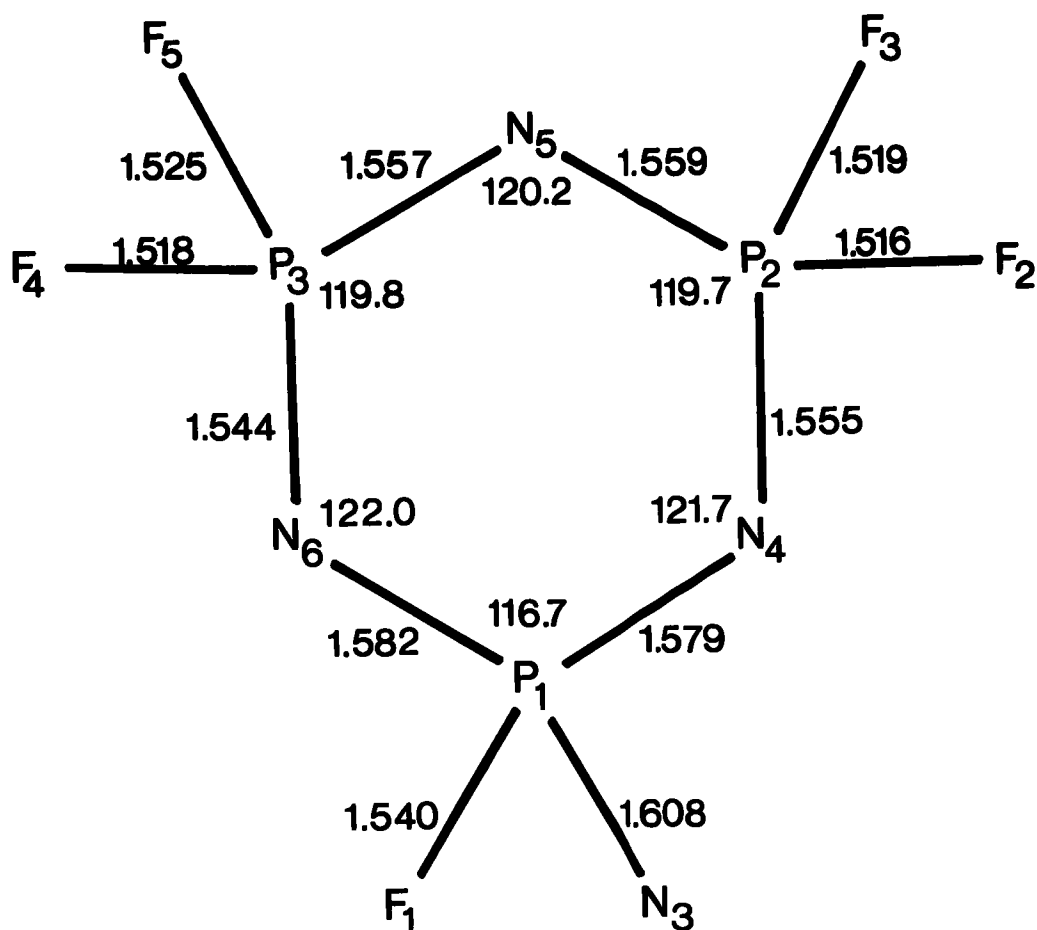


Figure 4.4

The theories of the bonding in phosphonitrilic compounds have been reviewed extensively (Craig and Paddock, 1971). It is impossible to describe the bonding in phosphonitrilic derivatives without invoking d-orbital participation, since the alternative ionic model which does not require d-orbital participation cannot explain the geometry observed for these compounds. For example the ionic model is not able to explain the angles at nitrogen in these compounds being close to or larger than  $120^\circ$ . The nature of the delocalisation however has been the subject of considerable controversy.

It has been argued that because of the equalisation of bond lengths within the ring and the planarity or near planarity of some of the phosphonitrilic compounds, such as  $P_3N_3F_6$ , the  $\pi$ -bonding should be viewed in terms of molecular orbitals which encompass the entire ring as in organic aromatic compounds (Craig et al, 1961). An alternative interpretation considers that the  $\pi$ -system should be viewed in terms of P-N-P islands of delocalisation because  $\pi$  molecular orbitals involving d orbitals must have a node at phosphorus. (Dewar, Lucken and Whitehead, 1960). These two theories have been compared (Craig and Mitchell, 1965) and it has been shown that the two theories are capable of explaining most structural features but that cyclic delocalisation is necessary to explain the observed ionisation potentials. It is not easy to estimate the extent of d orbital participation from bond lengths alone because of the variation in the P-N distance with hybridisation. However it has been estimated that  $\approx 60\%$  of the shortening of these bonds can be ascribed to  $\pi$ -bonding (Craig and Paddock, 1971).

The most important prerequisite for d-orbital participation in any phosphorus compound is orbital contraction, so that the shortest

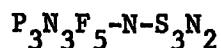
bond lengths are found when phosphorus is bound to highly electronegative ligands such as fluorine. Thus substitution of a fluorine atom by a less electronegative element or group produces an increase in the associated P-N distances. This is best illustrated by the series:  $P_3N_3F_6$ ,  $P_3N_3Cl_6$  and  $P_3N_3Ph_6$  which have P-N bond lengths of 1.560Å, 1.583Å and 1.597Å (Craig and Paddock, 1971). In  $P_3N_3F_4Ph_2$  the geminal replacement of two fluorine atoms by phenyl groups increases the adjacent P-N distances to 1.618Å (Allen et al., 1969) and as expected this effect is far greater than the replacement of one fluorine atom by a nitrogen atom.

The decrease in  $\pi$ -bonding in the ring with substitution of a less electronegative atom is also reflected in a reduction in the ring angle at that phosphorus. The angle at P(1) is 116.7° as compared to 119.7° at the unsubstituted phosphorus atoms. The angles at the nitrogen atoms adjacent to P(1) are both larger than that at N(5), i.e. P(1) - N(4) - P(2) and P(1) - N(6) - P(3) have values of 121.7° and 122.0° as compared to the value of 120.2° for P(2) - N(5) - P(3). The coordination at P(2) and P(3) is very similar to that seen in  $P_3N_3F_6$ , the average N-P-F angle of 109.2° being close to the value of 109.1° in  $P_3N_3F_6$ . The attachment of the bridging nitrogen to P(1) is not symmetrical since the angle N(3) - P(1) - N(4) of 114.4° is substantially greater than N(3) - P(1) - N(6) of 108.7°. This distortion increases the separation between N(4) in the phosphonitrilic ring and the atoms in the  $S_3N_2$  ring (table 4.8). The average N(3) - P - N angle of 111.6° external to the ring is larger than the N-P-F angles at P(2) and P(3) as a consequence of some multiple bonding in the P(1) - N(3) bond.

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There are many similarities between the  $\pi$ -bonding in sulphur-nitrogen and phosphorus-nitrogen ring compounds. In both cases contraction of the orbitals is necessary for effective delocalisation. In phosphorus compounds, this is provided by highly electronegative ligands giving rise to  $(PNX_2)_n$  species, whereas in sulphur-nitrogen chemistry it is provided both by electronegative ligands, giving rise to  $(SNX)_n$  and  $(SNOX)_n$  type compounds and also by the presence of positive charges as in  $S_4N_3^+$ ,  $S_3N_2Cl^+$  or  $S_5N_5^+$ .

Table 4.8



Intramolecular Contacts between N(4) and the  $S_3N_2$  ring Å.

S(2) - N(4)	3.239
S(3) - N(4)	3.313
N(1) - N(4)	3.225
N(2) - N(4)	3.377

4.6 Intermolecular Contacts and Packing.

In view of the large number of short contacts seen in  $[S_3N_2]_2^{2+}(ClS_2O_6^-)_2$  described earlier, it is of interest to see if short contacts occur with this molecule. The van der Waals radii for the atoms in this structure are  $S = 1.80\text{Å}$ ,  $P = 1.80\text{Å}$ ,  $F = 1.47\text{Å}$  and  $N = 1.55\text{Å}$  (Bondi, 1964).

Any secondary bonding present will be between sulphur and nitrogen or fluorine, since it is known that in these compounds the sulphur atoms carry a slight positive charge and the nitrogen and



fluorine atoms a slight negative charge. The only S---N contacts less than 3.35Å are those of 3.185Å for S(1)---N(3<sup>I</sup>), and 3.170Å for S(3)---N(3<sup>I</sup>) whereas the only S---F contact less than 3.27Å is that of 3.157Å for S(2)---F(1<sup>II</sup>), as given in table 4.9.

Table 4.9  $P_3N_3F_5-N-S_3N_2$

Some Intermolecular Contacts < 3.35Å

S(1) - N(3 <sup>I</sup> )	3.185
S(2) - F(1 <sup>II</sup> )	3.157
S(3) - N(3 <sup>I</sup> )	3.170
F(1) - F(5 <sup>III</sup> )	3.034
F(2) - F(4 <sup>IV</sup> )	2.779
F(3) - F(4 <sup>III</sup> )	3.014
F(4) - F(5 <sup>III</sup> )	3.195

The superscripts refer to the following equivalent positions with reference to the molecule at x, y, z

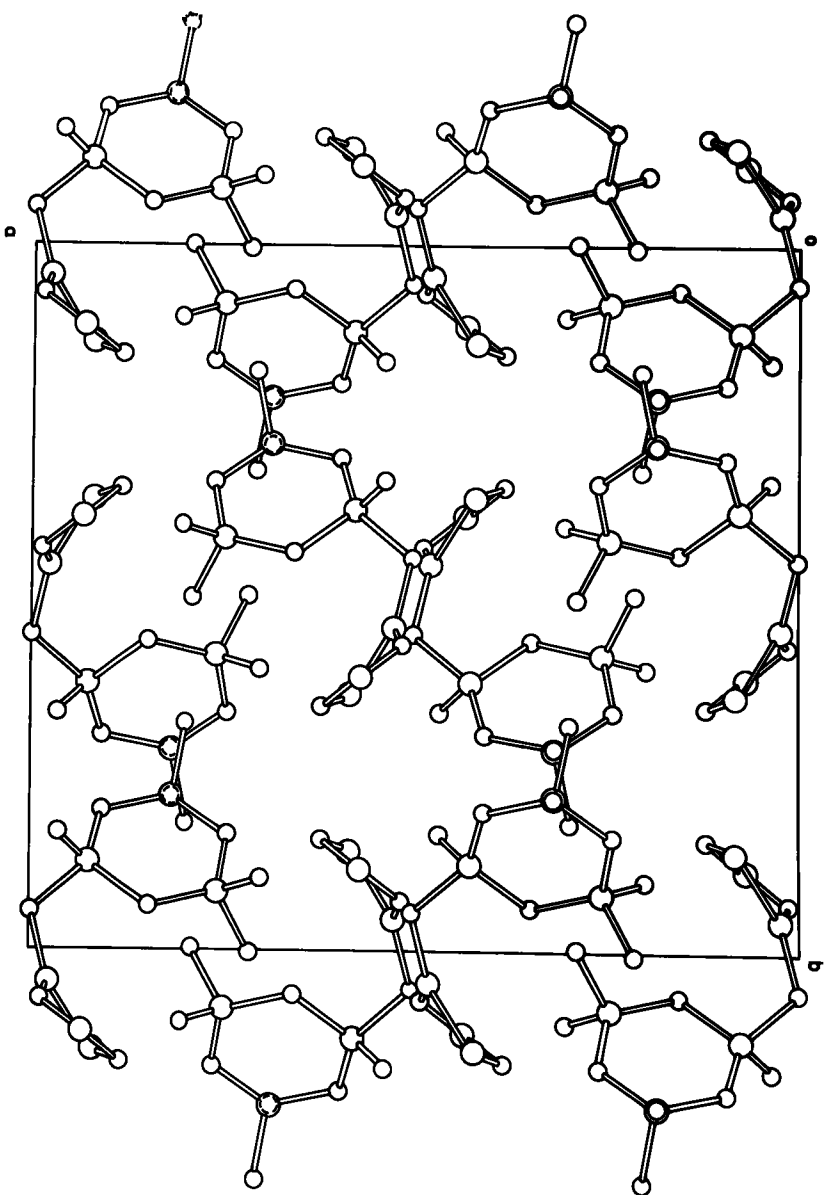
I	$\bar{x}, \bar{y}, 1-z$	III	$x, \frac{1}{2}y, -\frac{1}{2}z$
II	$\bar{x}, \bar{y}, \bar{z}$	IV	$\frac{1}{2}x, -\frac{1}{2}y, z$

There are no short contacts involving phosphorus because of its fourfold coordination.

In contrast to S---F and S---N contacts, interactions between nitrogen and fluorine are not expected to lower the potential energy of the packing. Consequently, there are no N---F contacts less than

3.02Å and there is only one F---F distance less than 2.94Å namely F(2)---F(4<sup>IV</sup>) of length 2.779Å thus it is clear that there are no very strong intermolecular contacts involved in the packing of these molecules. This might have been expected because the compound may be sublimed.

A projection on the [001] plane of the contents of the unit cell is shown in figure 4.5.



$P_3N_5-N-S_3N_2$

projection on the  $[001]$  plane

Figure 4.5

Table 4.10  $P_3N_3F_5-N-S_3N_2$

Final Calculated and Observed Structure Factors

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	0	0	39.2	40.2	6	11	0	-5.8	4.6	11	4	1	-3.8	-1.8	6	10	1	23.8	-24.2
4	0	0	211.2	208.0	8	11	0	40.4	42.7	12	4	1	41.7	-41.9	7	10	1	64.4	63.0
4	0	0	93.6	-93.1	10	11	0	39.9	39.3	13	4	1	13.0	-14.4	8	10	1	34.8	33.9
8	0	0	121.6	-126.3	12	11	0	7.4	-9.8	14	4	1	19.3	-21.2	9	10	1	29.8	-30.1
10	0	0	50.6	50.3	14	11	0	-6.7	4.9	15	4	1	24.6	25.0	10	10	1	35.7	-34.8
12	0	0	105.5	107.4	0	12	0	51.5	-43.4	16	4	1	38.9	-38.8	11	10	1	-6.2	5.0
14	0	0	8.5	4.3	2	12	0	74.7	-75.1	17	4	1	-4.5	5.5	12	10	1	-5.2	6.4
16	0	0	38.3	37.8	4	12	0	32.4	31.2	18	4	1	7.3	-6.1	13	10	1	0.0	-3.9
18	0	0	64.9	-65.0	6	12	0	19.2	-19.8	1	5	1	57.5	-59.0	14	10	1	20.8	-19.8
2	1	0	122.2	-121.5	8	12	0	57.3	56.3	2	5	1	80.5	84.4	15	10	1	10.2	-7.6
4	1	0	156.0	159.5	10	12	0	25.8	-28.1	3	5	1	12.7	13.8	1	11	1	48.9	49.7
6	1	0	133.4	-130.5	12	12	0	16.7	-15.6	4	5	1	43.3	45.9	2	11	1	31.0	31.6
8	1	0	75.9	-76.3	2	13	0	12.8	12.2	5	5	1	19.8	17.6	3	11	1	17.5	-15.5
10	1	0	10.6	10.0	4	13	0	35.8	-35.8	6	5	1	47.1	47.1	4	11	1	16.9	-16.5
12	1	0	69.5	-69.7	6	13	0	10.5	11.1	7	5	1	18.8	-18.9	5	11	1	35.4	34.9
14	1	0	15.8	-18.3	8	13	0	29.2	28.5	8	5	1	52.4	-52.9	6	11	1	8.4	-7.8
16	1	0	7.3	5.9	10	13	0	-5.9	6.3	9	5	1	55.4	55.6	7	11	1	13.2	-13.7
18	1	0	13.2	-12.5	12	13	0	23.2	24.2	10	5	1	34.9	-36.4	8	11	1	37.1	-37.9
0	2	0	40.1	40.3	0	14	0	21.8	21.2	11	5	1	42.1	-41.3	9	11	1	7.1	-3.2
2	2	0	133.1	135.1	2	14	0	38.0	-38.5	12	5	1	60.4	-62.4	10	11	1	42.1	-40.8
4	2	0	193.4	192.9	4	14	0	-1.1	-2.9	13	5	1	13.2	13.7	11	11	1	25.9	24.4
6	2	0	17.7	12.0	6	14	0	7.0	7.2	14	5	1	21.0	21.9	12	11	1	17.6	-17.2
8	2	0	141.7	136.7	8	14	0	-5.8	5.9	15	5	1	-6.1	2.9	13	11	1	0.0	-0.5
10	2	0	35.9	-35.5	10	14	0	-3.8	3.4	16	5	1	13.6	13.8	14	11	1	15.6	-15.9
12	2	0	-3.1	3.0	2	15	0	20.8	21.1	17	5	1	14.3	-15.5	0	12	1	32.8	-31.8
14	2	0	30.9	32.4	4	15	0	44.9	41.7	18	5	1	21.0	21.5	1	12	1	14.0	-12.2
16	2	0	21.6	-20.6	6	15	0	-2.8	2.1	1	6	1	33.9	35.3	2	12	1	39.2	-40.5
18	2	0	11.7	-10.8	8	15	0	-5.3	-4.4	0	6	1	60.1	63.9	3	12	1	53.6	54.2
2	3	0	117.2	121.6	0	16	0	7.2	5.3	2	6	1	15.8	17.1	4	12	1	12.7	13.6
4	3	0	126.1	-128.3	2	16	0	22.7	20.1	3	6	1	-2.0	-2.3	5	12	1	26.2	25.4
6	3	0	32.3	32.2	4	16	0	-4.8	-4.1	4	6	1	89.0	88.1	6	12	1	29.1	28.6
8	3	0	89.0	-86.2	6	16	0	10.6	-8.9	5	6	1	50.4	-49.1	7	12	1	23.7	-22.2
10	3	0	113.7	-115.8	2	17	0	12.8	10.2	6	6	1	23.1	24.5	8	12	1	16.1	14.7
12	3	0	29.8	29.0	4	17	0	7.8	7.9	7	6	1	55.9	56.1	9	12	1	14.9	-14.3
14	3	0	72.1	-74.8	1	1	1	49.7	-49.2	8	6	1	6.4	-6.2	10	12	1	14.3	-14.2
16	3	0	13.3	-13.9	2	1	1	149.6	-141.2	9	6	1	25.1	-25.7	11	12	1	19.1	-19.6
18	3	0	13.2	-15.0	3	1	1	13.6	-13.8	10	6	1	-4.9	5.4	12	12	1	9.4	-10.0
0	4	0	232.9	-251.1	4	1	1	166.6	-167.6	11	6	1	35.7	37.0	13	12	1	6.9	-3.5
2	4	0	137.7	-144.8	5	1	1	-1.5	-2.0	12	6	1	16.7	-17.9	1	13	1	-3.8	5.5
4	4	0	47.3	46.3	6	1	1	111.9	103.8	13	6	1	50.1	51.2	2	13	1	-5.9	7.2
6	4	0	254.6	259.1	7	1	1	25.5	-25.1	14	6	1	7.6	-7.9	3	13	1	17.5	17.2
8	4	0	52.5	51.4	8	1	1	58.5	59.4	15	6	1	-4.0	-6.2	4	13	1	17.7	17.9
10	4	0	48.0	49.8	9	1	1	9.6	-9.7	16	6	1	12.4	-12.8	5	13	1	-1.1	2.1
12	4	0	67.7	-69.3	10	1	1	114.3	112.5	17	6	1	-5.3	4.8	6	13	1	-4.6	-3.6
14	4	0	54.7	-55.2	11	1	1	46.7	-46.9	1	7	1	42.9	42.7	7	13	1	13.2	13.3
16	4	0	30.2	-31.5	12	1	1	95.3	98.5	2	7	1	61.3	-61.8	8	13	1	25.1	-25.1
18	4	0	24.6	24.4	13	1	1	-4.1	-2.2	3	7	1	63.1	-66.0	9	13	1	15.1	15.0
2	5	0	158.8	-162.8	14	1	1	-4.5	-6.2	4	7	1	120.9	-121.5	10	13	1	36.4	-36.2
4	5	0	30.1	-26.2	15	1	1	-3.9	7.7	5	7	1	94.9	97.7	11	13	1	0.0	-2.0
6	5	0	34.8	-35.6	16	1	1	11.3	12.5	6	7	1	23.7	-23.5	12	13	1	17.1	-15.8
8	5	0	22.0	-21.1	17	1	1	12.8	11.9	7	7	1	0.0	-1.5	0	14	1	13.0	-13.5
10	5	0	24.8	-24.2	18	1	1	12.5	-14.2	8	7	1	14.9	-14.6	1	14	1	-3.4	3.0
12	5	0	18.1	-16.8	0	2	1	87.3	-88.0	9	7	1	10.9	-9.8	2	14	1	-5.8	6.9
14	5	0	52.8	-54.0	1	2	1	72.9	74.3	10	7	1	21.3	19.0	3	14	1	24.8	-25.1
16	5	0	-5.1	-7.4	2	2	1	167.5	170.7	11	7	1	11.9	12.2	4	14	1	39.0	-39.3
18	5	0	29.8	-30.6	3	2	1	20.5	21.8	12	7	1	27.2	-27.8	5	14	1	12.4	-11.5
0	6	0	0.0	-11.1	4	2	1	94.8	-91.4	13	7	1	29.6	-30.1	6	14	1	-3.5	-4.6
2	6	0	10.0	11.8	5	2	1	49.0	47.6	14	7	1	-5.5	-1.4	7	14	1	9.5	-10.0
4	6	0	53.7	-53.9	6	2	1	49.3	49.1	15	7	1	9.3	-9.1	8	14	1	13.1	-13.5
6	6	0	40.4	-37.6	7	2	1	23.0	-20.7	16	7	1	35.4	-35.1	9	14	1	-0.9	4.0
8	6	0	35.5	-30.4	8	2	1	15.6	-15.2	17	7	1	19.0	17.7	10	14	1	12.9	12.8
10	6	0	34.0	35.4	9	2	1	10.9	12.6	0	8	1	114.4	119.0	11	14	1	-1.9	-4.1
12	6	0	56.9	-56.5	10	2	1	52.8	51.7	1	8	1	74.6	-78.2	1	15	1	10.7	-10.2
14	6	0	8.6	7.6	11	2	1	50.6	-51.7	2	8	1	23.3	-22.7	2	15	1	10.5	-9.4
16	6	0	28.7	-29.0	12	2	1	41.7	-43.0	3	8	1	35.3	-33.9	3	15	1	0.0	1.9
2	7	0	68.4	-68.1	13	2	1	18.6	18.9	4	8	1	7.0	8.4	4	15	1	-4.2	-3.3
4	7	0	0.0	2.1	14	2	1	8.9	9.8	5	8	1	-2.0	-1.3	5	15	1	12.6	11.7
6	7	0	94.5	-96.3	15	2	1	19.9	-21.0	6	8	1	57.3	-57.4	6	15	1	0.0	1.2
8	7	0	39.7	-39.1	16	2	1	25.4	-24.6	7	8	1	30.0	-31.3	7	15	1	7.2	8.6
10	7	0	47.1	-45.5	17	2	1	20.5	19.5	8	8	1	-5.5	4.7	8	15	1	-5.9	3.4
12	7	0	42.3	-43.7	18	2	1	14.5	14.3	9	8	1	59.3	61.5	9	15	1	-1.8	-0.5
14	7	0	-5.9	-5.8	1	3	1	12.5	11.8	10	8	1	0.0	-0.4	0	16	1	-4.0	2.3
16	7	0	14.2	-14.9	2	3	1	186.8	193.0	11	8	1	31.0	31.2	1	16	1	0.0	0.1
0	8	0	42.4	-39.8	3	3	1	109.5	-110.7	12	8	1	21.7	22.7	2	16	1	13.0	12.3
2	8	0	28.3	29.4	4	3	1	223.0	223.4	13	8	1	12.5	-11.6	3	16	1	20.6	-21.2
4	8	0	94.2	-96.5	5	3	1	43.9	-41.9	14	8	1	11.9	-10.4	4	16	1	21.9	-20.5
6	8	0	125.9	-127.4	6	3	1	73.3	73.3	15	8	1	14.5	13.2	5	16	1	14.6	-14.5
8	8	0	101.5	-105.5	7	3	1	47.6	-46.9	16	8	1	7.3	7.4	6	16	1	9.9	-11.1
10	8	0	8.2	-6.6	8	3	1	19.3	-18.7	1	9	1	5.6	2.6	7	16	1	-4.1	0.8
12	8	0	13.7	12.5	9	3	1	10.8	-12.5	2	9	1	14.7	-14.8	1	17	1	8.4	6.4
14	8	0	52.7	53.1	10	3	1	-1.6	-2.5	3	9	1	74.3	75.9	2	17	1	-6.2	-5.2
16	8	0	11.1	11.0	11	3	1	60.8											

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
10	0	2	28.3	28.9	8	6	2	28.6	29.0	11	12	2	-4.8	5.7	2	4	3	32.0	-32.8
11	1	1	46.9	48.9	9	6	2	70.2	-70.5	12	12	2	-5.6	-1.5	3	4	3	41.9	-40.9
12	2	2	32.3	-47.6	10	6	2	23.2	-25.1	13	12	2	7.1	9.7	4	4	3	32.0	-28.7
13	3	3	35.8	-54.0	11	6	2	10.8	8.4	1	13	2	13.5	12.2	5	4	3	31.8	-92.4
14	4	4	184.1	170.7	12	6	2	37.5	38.3	2	13	2	0.0	1.6	6	4	3	61.2	-60.0
15	5	5	-3.1	3.4	13	6	2	19.1	-19.1	3	13	2	-4.8	-1.6	7	4	3	31.8	-29.8
16	6	6	9.2	9.1	14	6	2	0.0	-2.6	4	13	2	11.6	-11.1	8	4	3	33.2	32.5
17	7	7	46.7	-46.7	15	6	2	25.1	25.1	5	13	2	10.5	-10.9	9	4	3	51.0	-52.1
18	8	8	21.8	19.6	16	6	2	11.5	11.2	6	13	2	0.0	6.5	10	4	3	40.3	-40.9
19	9	9	9.2	8.4	17	6	2	-2.6	1.2	7	13	2	14.8	-15.5	11	4	3	9.7	10.2
20	1	2	18.1	19.4	1	7	2	86.4	-98.3	8	13	2	-6.3	-6.2	12	4	3	42.6	42.0
21	1	2	26.2	27.1	2	7	2	44.3	-62.2	9	13	2	-2.9	2.9	13	4	3	48.2	-47.8
22	1	2	61.3	-60.4	3	7	2	47.1	-45.8	10	13	2	10.9	-12.3	14	4	3	21.4	-20.9
23	1	2	77.7	-73.3	4	7	2	37.3	-36.7	11	13	2	0.0	0.8	15	4	3	-3.2	0.3
24	1	2	38.5	38.8	5	7	2	0.0	-1.3	12	13	2	0.0	0.8	16	4	3	17.5	16.9
25	1	2	30.5	30.6	6	7	2	12.7	12.0	0	14	2	14.7	13.4	17	4	3	21.6	-22.6
26	1	2	19.7	16.9	7	7	2	43.2	43.7	1	14	2	21.1	20.7	1	5	3	49.6	-50.6
27	1	2	14.9	15.4	8	7	2	68.7	69.6	2	14	2	16.5	15.8	2	5	3	-3.4	3.0
28	1	2	7.5	6.2	9	7	2	43.1	43.9	3	14	2	11.5	10.5	3	5	3	53.1	54.1
29	1	2	262.0	-273.4	10	7	2	92.4	92.4	4	14	2	-5.7	-5.1	4	5	3	-4.6	4.1
30	1	2	7.3	-6.7	11	7	2	13.7	13.4	5	14	2	19.9	19.8	5	5	3	27.0	-27.8
31	2	2	96.8	95.5	12	7	2	33.5	33.0	6	14	2	8.8	9.0	6	5	3	28.1	27.6
32	2	2	77.7	-73.9	13	7	2	-6.3	-5.9	7	14	2	-5.2	5.2	7	5	3	73.9	74.6
33	2	2	83.5	-79.1	14	7	2	9.4	9.8	8	14	2	23.4	-22.8	8	5	3	0.0	-2.0
34	2	2	7.0	-7.2	15	7	2	-1.0	-6.1	9	14	2	-5.9	-2.7	9	5	3	-3.1	2.0
35	2	2	64.4	-60.4	16	7	2	9.5	-8.4	10	14	2	-5.6	7.2	10	5	3	-1.5	6.0
36	2	2	18.2	-19.0	17	7	2	-6.0	6.8	1	15	2	19.8	-19.5	11	5	3	19.9	-15.8
37	2	2	19.5	20.5	0	8	2	11.0	10.7	2	15	2	31.3	-29.1	12	5	3	8.1	-8.6
38	2	2	17.2	16.7	1	8	2	-5.3	-2.6	3	15	2	0.0	-2.8	13	5	3	9.2	-9.4
39	2	2	13.4	-13.0	2	8	2	19.2	19.4	4	15	2	14.1	-14.1	14	5	3	17.4	-19.2
40	2	2	18.0	-17.6	3	8	2	24.4	24.8	5	15	2	24.3	25.4	15	5	3	12.5	-10.4
41	2	2	29.7	-26.6	4	8	2	39.8	39.4	6	15	2	11.1	-8.8	16	5	3	-4.6	6.0
42	2	2	25.6	-26.4	5	8	2	7.5	7.1	7	15	2	28.2	27.2	17	5	3	-8.7	-3.5
43	2	2	25.8	25.0	6	8	2	34.2	34.1	8	15	2	11.0	-9.2	0	6	3	118.4	-120.5
44	2	2	13.9	-13.3	7	8	2	12.2	13.1	9	15	2	10.3	9.0	1	6	3	7.5	7.7
45	2	2	-4.7	-6.4	8	8	2	56.4	57.6	0	16	2	10.3	-11.0	2	6	3	107.4	-106.2
46	2	2	10.7	-11.6	9	8	2	-6.1	-5.6	1	16	2	-4.3	0.3	3	6	3	0.0	3.5
47	2	2	19.6	19.7	10	8	2	34.7	-35.4	2	16	2	0.0	-0.3	4	6	3	29.4	26.3
48	1	3	66.3	65.4	11	8	2	11.6	11.1	3	16	2	-6.8	8.1	5	6	3	20.5	-19.6
49	1	3	193.4	196.5	12	8	2	6.7	4.3	4	16	2	8.3	5.8	6	6	3	75.9	75.7
50	1	3	9.6	7.5	13	8	2	9.0	9.9	5	16	2	0.0	1.5	7	6	3	24.8	-24.1
51	3	3	27.1	28.6	14	8	2	23.6	-21.9	6	16	2	10.8	-9.5	8	6	3	74.7	75.8
52	3	3	38.3	31.8	15	8	2	26.5	27.0	1	17	2	-6.8	4.0	9	6	3	42.3	-43.2
53	3	3	78.6	77.8	16	8	2	-6.1	-7.4	2	17	2	0.0	2.6	10	6	3	18.8	-19.7
54	3	3	46.9	-47.3	1	9	2	62.4	-61.3	1	1	3	107.7	110.0	11	6	3	54.5	-55.2
55	3	3	14.1	12.8	2	9	2	22.0	22.9	2	1	3	-1.9	-1.7	12	6	3	43.9	-44.6
56	3	3	0.0	-3.1	3	9	2	6.2	-5.2	3	1	3	56.0	54.2	13	6	3	24.1	-24.6
57	3	3	23.9	-24.4	4	9	2	-5.6	-3.7	4	1	3	114.4	-107.5	14	6	3	17.8	-16.8
58	3	3	8.2	-0.7	5	9	2	-5.5	-3.5	5	1	3	11.9	11.7	15	6	3	18.6	-20.9
59	3	3	9.7	-8.9	6	9	2	30.5	31.3	6	1	3	19.3	-17.9	16	6	3	13.5	-13.9
60	3	3	37.0	38.2	7	9	2	29.4	28.6	7	1	3	24.4	-22.3	17	6	3	-5.8	5.5
61	3	3	40.6	41.5	8	9	2	0.0	-2.2	8	1	3	7.0	-5.4	11	1	7	11.1	-10.2
62	3	3	39.3	42.1	9	9	2	16.3	-15.8	9	1	3	9.3	9.2	2	7	3	9.5	-10.4
63	3	3	10.7	10.2	10	9	2	12.8	-13.5	10	1	3	38.3	37.1	3	7	3	21.2	-21.3
64	3	3	25.2	24.9	11	9	2	19.3	-19.8	11	1	3	38.4	36.9	4	7	3	23.7	-26.5
65	3	3	31.5	31.7	12	9	2	19.6	21.2	12	1	3	24.4	-24.9	5	7	3	55.8	-56.7
66	0	4	126.1	126.8	13	9	2	-5.1	-4.6	13	1	3	24.7	25.3	6	7	3	9.1	-8.0
67	1	4	10.7	11.6	14	9	2	-6.4	-9.3	14	1	3	9.3	10.4	7	7	3	14.0	-14.2
68	1	4	30.3	-33.4	15	9	2	11.4	10.0	15	1	3	-4.6	1.8	8	7	3	7.4	7.5
69	1	4	35.9	-36.4	0	10	2	44.7	44.8	16	1	3	12.7	-12.1	9	7	3	40.1	-39.2
70	1	4	28.9	-28.0	1	10	2	12.5	12.5	17	1	3	13.7	-16.0	10	7	3	7.6	5.2
71	1	4	28.1	-28.7	2	10	2	28.4	29.2	18	1	3	-3.2	1.5	11	7	3	42.9	42.8
72	1	4	26.8	-27.2	3	10	2	10.3	-9.5	0	2	3	198.5	196.0	12	7	3	36.0	36.7
73	1	4	60.2	59.7	4	10	2	-5.1	-4.9	1	2	3	30.4	-31.2	13	7	3	9.4	11.2
74	1	4	31.8	-32.2	5	10	2	11.7	11.5	2	2	3	42.8	42.2	14	7	3	11.7	-12.7
75	1	4	11.5	-11.4	6	10	2	49.8	50.2	3	2	3	-4.7	3.1	15	7	3	12.3	12.1
76	1	4	-3.8	3.5	7	10	2	22.4	21.3	4	2	3	14.9	-12.0	16	7	3	0.0	-4.2
77	1	4	36.4	37.5	8	10	2	-2.7	2.6	5	2	3	58.3	-58.1	0	8	3	45.3	-43.6
78	1	4	32.7	33.2	9	10	2	35.8	35.7	6	2	3	106.7	-105.2	1	8	3	6.5	6.2
79	1	4	45.1	-46.1	10	10	2	14.2	14.6	7	2	3	71.0	66.0	2	8	3	6.2	6.4
80	1	4	8.1	-7.1	11	10	2	33.4	34.1	8	2	3	102.3	-97.7	3	8	3	20.3	20.4
81	1	4	23.5	-23.0	12	10	2	13.7	-14.5	9	2	3	38.8	-39.0	4	8	3	36.6	-38.0
82	1	4	25.8	25.9	13	10	2	15.4	15.1	10	2	3	32.0	-33.1	5	8	3	35.9	55.6
83	1	4	20.4	-21.0	14	10	2	8.2	-9.6	11	2	3	48.0	46.2	6	8	3	42.6	43.7
84	1	4	12.1	-12.3	15	10	2	-3.9	2.8	12	2	3	59.5	58.5	7	8	3	39.8	-60.4
85	1	5	30.6	28.2	1	11	2	55.6	53.4	13	2	3	18.5	-17.7	8	8	3	40.4	-40.6
86	1	5	25.6	22.6	2	11	2	8.0	8.6	14	2	3	46.4	47.9	9	8	3	-5.1	-3.8
87	1	5	27.0	23.8	3	11	2	-3.8	1.6	15	2	3	0.0	0.5	10	8	3	30.1	31.3
88	1	5	18.2	-17.9	4	11	2	56.9	57.5	16	2	3	18.3	18.5	11	8	3	54.7	-56.2
89	1	5	8.6	5.8	5	11	2	28.7	-30.5	17	2	3	23.6	-23.9	12	8	3	-8.2	-6.5
90	1	5	16.9	-15.7	6	11	2	13.2	-13.6	18	2	3	16.2	-16.2	13	8	3	9.2	-8.2
91	1	5	9.8	-9.5	7														

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	10	3	27.6	28.9	7	1	4	-1.7	4.2	4	7	4	53.9	54.5	6	14	4	17.0	15.8
2	10	3	44.9	47.1	8	1	4	44.0	43.4	5	7	4	30.2	30.7	7	14	4	-3.3	1.7
3	10	3	40.4	-63.1	9	1	4	32.5	-31.2	6	7	4	25.5	26.1	8	14	4	8.5	8.5
4	10	3	32.6	-33.7	10	1	4	55.3	54.1	7	7	4	24.7	-24.7	9	14	4	24.8	-24.8
5	10	3	15.2	-16.1	11	1	4	15.9	16.4	8	7	4	21.1	-21.7	1	15	4	-2.4	-1.6
6	10	3	53.7	-53.2	12	1	4	39.2	39.5	9	7	4	-2.1	0.6	2	15	4	-4.0	1.4
7	10	3	24.8	-24.1	13	1	4	40.0	-37.7	10	7	4	14.6	-14.6	3	15	4	15.0	-12.4
8	10	3	23.0	-24.0	14	1	4	10.8	-10.1	11	7	4	10.7	9.9	4	15	4	8.9	6.4
9	10	3	-3.0	4.8	15	1	4	13.0	-13.8	12	7	4	0.0	-4.3	5	15	4	12.2	-11.6
10	10	3	-4.0	3.2	16	1	4	11.7	-12.9	13	7	4	8.2	-6.7	6	15	4	0.0	-3.4
11	10	3	-6.2	-4.1	17	1	4	0.0	-4.9	14	7	4	-6.2	4.0	7	15	4	9.8	-10.5
12	10	3	10.6	10.1	0	2	4	9.9	9.5	15	7	4	-3.6	-3.1	8	16	4	8.0	-6.9
13	10	3	15.3	15.1	1	2	4	116.5	-117.0	16	7	4	11.8	11.1	1	16	4	-5.0	-7.7
14	10	3	26.4	27.0	2	2	4	40.0	-36.4	0	8	4	39.0	-36.7	2	16	4	0.0	-1.6
1	11	3	45.3	-46.4	3	2	4	49.7	49.3	1	8	4	42.6	-43.8	3	16	4	9.7	-9.0
2	11	3	25.0	24.7	4	2	4	51.1	-45.9	2	8	4	30.5	30.3	1	1	5	75.3	-75.0
3	11	3	47.6	-49.4	5	2	4	12.7	-12.0	3	8	4	47.6	-48.4	2	1	5	46.7	-44.5
4	11	3	0.0	-1.2	6	2	4	50.1	-48.0	4	8	4	20.0	20.3	3	1	5	39.7	-38.5
5	11	3	-3.7	-3.2	7	2	4	23.6	22.9	5	8	4	40.3	-40.7	4	1	5	53.0	50.0
6	11	3	31.3	31.8	8	2	4	11.8	-11.6	6	8	4	14.9	37.8	5	1	5	21.1	-20.7
7	11	3	-5.9	-7.5	9	2	4	45.6	44.8	7	8	4	35.2	-34.5	6	1	5	41.2	-39.8
8	11	3	6.7	-7.0	10	2	4	37.0	-37.1	8	8	4	25.6	26.0	7	1	5	51.5	52.5
9	11	3	14.6	-15.3	11	2	4	35.3	34.6	9	8	4	33.3	33.8	8	1	5	21.1	-21.1
10	11	3	-2.3	-4.1	12	2	4	16.2	16.8	10	8	4	20.9	21.7	9	1	5	19.4	19.2
11	11	3	0.0	-5.4	13	2	4	-3.5	-1.5	11	8	4	7.8	-8.0	10	1	5	36.9	-36.2
12	11	3	7.4	5.5	14	2	4	7.0	-7.1	12	8	4	-4.8	-1.7	11	1	5	-3.8	6.6
13	11	3	7.3	-8.7	15	2	4	33.9	32.3	13	8	4	-5.0	2.6	12	1	5	16.2	-16.6
0	12	3	18.4	18.7	16	2	4	-6.1	-6.8	14	8	4	0.0	-4.4	13	1	5	21.2	-22.2
1	12	3	14.9	-16.6	17	2	4	-6.3	-2.8	15	8	4	26.9	-27.0	14	1	5	15.5	-16.2
2	12	3	-1.8	-1.9	1	3	4	27.7	-26.3	1	9	4	-3.2	-2.1	15	1	5	0.0	-3.5
3	12	3	31.5	-30.5	2	3	4	102.8	-102.5	2	9	4	32.4	-32.3	16	1	5	10.9	-10.6
4	12	3	10.0	12.0	3	3	4	88.0	88.3	3	9	4	35.0	35.1	17	1	5	0.0	-4.4
5	12	3	9.1	-10.1	4	3	4	35.2	-35.4	4	9	4	47.4	-45.1	0	2	5	48.0	-45.7
6	12	3	-5.2	4.1	5	3	4	30.3	-29.4	5	9	4	20.6	21.1	1	2	5	29.2	29.4
7	12	3	0.0	-1.2	6	3	4	19.3	-19.9	6	9	4	-1.4	-0.6	2	2	5	10.0	-16.9
8	12	3	13.5	-12.7	7	3	4	58.2	59.2	7	9	4	20.5	20.4	3	2	5	19.4	18.6
9	12	3	28.3	28.4	8	3	4	53.6	52.9	8	9	4	24.3	24.9	4	2	5	16.1	16.7
10	12	3	-2.1	0.9	9	3	4	9.1	-7.1	9	9	4	-4.1	2.5	5	2	5	38.8	39.9
11	12	3	21.4	21.3	10	3	4	44.5	45.6	10	9	4	34.7	34.1	6	2	5	10.1	10.9
12	12	3	-6.6	-3.7	11	3	4	38.3	-36.5	11	9	4	16.6	-15.5	7	2	5	53.0	-51.9
1	13	3	40.4	-41.4	12	3	4	44.3	46.9	12	9	4	0.0	1.8	8	2	5	7.8	6.6
2	13	3	0.0	-0.5	13	3	4	15.5	-16.5	13	9	4	-6.2	-3.1	9	2	5	6.2	5.5
3	13	3	13.2	-13.1	14	3	4	11.0	-10.2	14	9	4	8.4	-7.0	10	2	5	9.3	8.5
4	13	3	0.0	2.5	15	3	4	13.2	-14.0	0	10	4	31.9	32.5	11	2	5	23.8	-22.5
5	13	3	16.0	-17.8	16	3	4	8.4	-9.4	1	10	4	15.3	-17.1	12	2	5	42.7	-42.4
6	13	3	0.0	-4.2	17	3	4	22.0	-21.2	2	10	4	32.4	32.0	13	2	5	30.6	28.6
7	13	3	-4.7	-1.0	0	4	4	57.7	57.5	3	10	4	35.5	-33.9	14	2	5	-4.1	3.4
8	13	3	-1.3	1.5	1	4	4	26.9	29.5	4	10	4	25.4	25.9	15	2	5	14.2	15.3
9	13	3	-2.9	-1.0	2	4	4	53.1	53.0	5	10	4	56.7	-57.4	16	2	5	-3.8	3.8
10	13	3	22.2	20.5	3	4	4	79.7	79.0	6	10	4	13.0	-12.4	1	3	5	37.7	-35.6
11	13	3	-3.7	-6.0	4	4	4	13.0	-13.5	7	10	4	-3.0	-0.9	2	3	5	25.9	-26.4
0	14	3	16.0	-15.8	5	4	4	65.0	63.3	8	10	4	0.0	-2.4	3	3	5	18.7	-19.8
1	14	3	-2.5	4.6	6	4	4	46.0	-44.3	9	10	4	36.4	-37.6	4	3	5	60.0	-57.5
2	14	3	-3.8	-3.8	7	4	4	-4.4	2.2	10	10	4	0.0	1.6	5	3	5	-0.8	-4.4
3	14	3	32.1	30.1	8	4	4	51.4	-50.8	11	10	4	-5.1	5.8	6	3	5	46.5	-45.8
4	14	3	17.5	16.9	9	4	4	22.7	-23.5	12	10	4	21.1	21.9	7	3	5	43.3	-41.0
5	14	3	16.7	16.7	10	4	4	7.1	-4.9	13	10	4	12.3	-12.6	8	3	5	0.0	-2.1
6	14	3	-6.0	5.3	11	4	4	59.1	-57.4	14	10	4	-1.5	1.3	9	3	5	25.2	-26.2
7	14	3	25.9	24.3	12	4	4	14.7	14.7	1	11	4	9.8	-9.4	10	3	5	24.7	-23.2
8	14	3	18.5	16.8	13	4	4	23.1	22.6	2	11	4	13.6	-13.2	11	3	5	-5.7	-5.3
9	14	3	-4.8	-5.6	14	4	4	10.0	11.3	3	11	4	18.9	-19.0	12	3	5	7.3	9.4
10	14	3	0.0	1.6	15	4	4	7.3	9.0	4	11	4	19.4	-20.0	13	3	5	23.5	24.5
1	15	3	-4.8	1.2	16	4	4	-1.4	1.6	5	11	4	18.1	18.5	14	3	5	22.8	-21.9
2	15	3	7.6	-8.4	17	4	4	30.5	30.7	6	11	4	12.5	-13.3	15	3	5	25.2	27.0
3	15	3	0.0	0.2	1	5	4	29.0	31.9	7	11	4	8.6	9.4	16	3	5	16.1	-16.8
4	15	3	12.8	-13.0	2	5	4	30.5	31.4	8	11	4	6.6	-3.7	0	4	5	24.5	-23.5
5	15	3	8.1	-11.2	3	5	4	-1.5	-2.4	9	11	4	8.6	10.5	1	4	5	49.4	48.9
6	15	3	-5.0	2.1	4	5	4	80.2	80.1	10	11	4	8.9	8.9	2	4	5	34.4	-35.4
7	15	3	0.0	-2.7	5	5	4	10.1	-10.2	11	11	4	-4.5	-0.4	3	4	5	23.0	-23.6
8	15	3	11.0	10.1	6	5	4	34.6	34.3	12	11	4	-3.8	-6.7	4	4	5	34.3	-35.3
9	16	3	0.0	0.3	7	5	4	14.3	15.7	13	11	4	10.0	-10.7	5	4	5	75.9	76.8
0	16	3	-4.4	5.8	8	5	4	37.0	-36.4	0	12	4	17.3	17.8	6	4	5	-5.7	-4.1
1	16	3	-4.9	-5.3	9	5	4	7.7	-9.2	1	12	4	21.4	-20.7	7	4	5	10.4	-10.9
2	16	3	26.9	25.0	10	5	4	34.7	-34.2	2	12	4	14.2	14.4	8	4	5	51.6	-50.4
3	16	3	11.9	11.6	11	5	4	15.5	14.9	3	12	4	34.9	36.7	9	4	5	59.8	57.8
4	16	3	13.9	11.9	12	5	4	7.0	-5.1	4	12	4	-3.9	0.7	10	4	5	29.6	30.9
0	0	4	201.4	-197.8	13	5	4	9.5	-8.3	5	12	4	-5.1	-5.2	11	4	5	-1.1	-4.0
1	0	4	46.7	45.8	14	5	4	14.7	15.5	6	12	4	14.8	-15.3	12	4	5	18.1	18.0
2	0	4	118.5	-115.7	15	5	4	-4.2	-6.1	7	12	4	11.3	-10.2	13	4	5	45.4	44.5
3	0	4	16.0	-16.1	16	5	4	24.4	24.8	8	12	4	11.2	11.1	14	4	5	-5.1	3.8
4	0	4	75.0	-68.4	0	6	4	69.7	-69.2	9	12	4	30.3	-29.1	15	4	5	8.0	-1.3
5	0	4	86.9	-83.2	1	6	4	57.8	56.5	10	12								

6	9	9	2	1	10	9	8	7	6	5	4	3	2	1	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136	137	138	139	140	141	142	143	144	145	146	147	148	149	150	151	152	153	154	155	156	157	158	159	160	161	162	163	164	165	166	167	168	169	170	171	172	173	174	175	176	177	178	179	180	181	182	183	184	185	186	187	188	189	190	191	192	193	194	195	196	197	198	199	200	201	202	203	204	205	206	207	208	209	210	211	212	213	214	215	216	217	218	219	220	221	222	223	224	225	226	227	228	229	230	231	232	233	234	235	236	237	238	239	240	241	242	243	244	245	246	247	248	249	250	251	252	253	254	255	256	257	258	259	260	261	262	263	264	265	266	267	268	269	270	271	272	273	274	275	276	277	278	279	280	281	282	283	284	285	286	287	288	289	290	291	292	293	294	295	296	297	298	299	300	301	302	303	304	305	306	307	308	309	310	311	312	313	314	315	316	317	318	319	320	321	322	323	324	325	326	327	328	329	330	331	332	333	334	335	336	337	338	339	340	341	342	343	344	345	346	347	348	349	350	351	352	353	354	355	356	357	358	359	360	361	362	363	364	365	366	367	368	369	370	371	372	373	374	375	376	377	378	379	380	381	382	383	384	385	386	387	388	389	390	391	392	393	394	395	396	397	398	399	400	401	402	403	404	405	406	407	408	409	410	411	412	413	414	415	416	417	418	419	420	421	422	423	424	425	426	427	428	429	430	431	432	433	434	435	436	437	438	439	440	441	442	443	444	445	446	447	448	449	450	451	452	453	454	455	456	457	458	459	460	461	462	463	464	465	466	467	468	469	470	471	472	473	474	475	476	477	478	479	480	481	482	483	484	485	486	487	488	489	490	491	492	493	494	495	496	497	498	499	500	501	502	503	504	505	506	507	508	509	510	511	512	513	514	515	516	517	518	519	520	521	522	523	524	525	526	527	528	529	530	531	532	533	534	535	536	537	538	539	540	541	542	543	544	545	546	547	548	549	550	551	552	553	554	555	556	557	558	559	560	561	562	563	564	565	566	567	568	569	570	571	572	573	574	575	576	577	578	579	580	581	582	583	584	585	586	587	588	589	590	591	592	593	594	595	596	597	598	599	600	601	602	603	604	605	606	607	608	609	610	611	612	613	614	615	616	617	618	619	620	621	622	623	624	625	626	627	628	629	630	631	632	633	634	635	636	637	638	639	640	641	642	643	644	645	646	647	648	649	650	651	652	653	654	655	656	657	658	659	660	661	662	663	664	665	666	667	668	669	670	671	672	673	674	675	676	677	678	679	680	681	682	683	684	685	686	687	688	689	690	691	692	693	694	695	696	697	698	699	700	701	702	703	704	705	706	707	708	709	710	711	712	713	714	715	716	717	718	719	720	721	722	723	724	725	726	727	728	729	730	731	732	733	734	735	736	737	738	739	740	741	742	743	744	745	746	747	748	749	750	751	752	753	754	755	756	757	758	759	760	761	762	763	764	765	766	767	768	769	770	771	772	773	774	775	776	777	778	779	780	781	782	783	784	785	786	787	788	789	790	791	792	793	794	795	796	797	798	799	800	801	802	803	804	805	806	807	808	809	810	811	812	813	814	815	816	817	818	819	820	821	822	823	824	825	826	827	828	829	830	831	832	833	834	835	836	837	838	839	840	841	842	843	844	845	846	847	848	849	850	851	852	853	854	855	856	857	858	859	860	861	862	863	864	865	866	867	868	869	870	871	872	873	874	875	876	877	878	879	880	881	882	883	884	885	886	887	888	889	890	891	892	893	894	895	896	897	898	899	900	901	902	903	904	905	906	907	908	909	910	911	912	913	914	915	916	917	918	919	920	921	922	923	924	925	926	927	928	929	930	931	932	933	934	935	936	937	938	939	940	941	942	943	944	945	946	947	948	949	950	951	952	953	954	955	956	957	958	959	960	961	962	963	964	965	966	967	968	969	970	971	972	973	974	975	976	977	978	979	980	981	982	983	984	985	986	987	988	989	990	991	992	993	994	995	996	997	998	999	1000	1001	1002	1003	1004	1005	1006	1007	1008	1009	1010	1011	1012	1013	1014	1015	1016	1017	1018	1019	1020	1021	1022	1023	1024	1025	1026	1027	1028	1029	1030	1031	1032	1033	1034	1035	1036	1037	1038	1039	1040	1041	1042	1043	1044	1045	1046	1047	1048	1049	1050	1051	1052	1053	1054	1055	1056	1057	1058	1059	1060	1061	1062	1063	1064	1065	1066	1067	1068	1069	1070	1071	1072	1073	1074	1075	1076	1077	1078	1079	1080	1081	1082	1083	1084	1085	1086	1087	1088	1089	1090	1091	1092	1093	1094	1095	1096	1097	1098	1099	1100	1101	1102	1103	1104	1105	1106	1107	1108	1109	1110	1111	1112	1113	1114	1115	1116	1117	1118	1119	1120	1121	1122	1123	1124	1125	1126	1127	1128	1129	1130	1131	1132	1133	1134	1135	1136	1137	1138	1139	1140	1141	1142	1143	1144	1145	1146	1147	1148	1149	1150	1151	1152	1153	1154	1155	1156	1157	1158	1159	1160	1161	1162	1163	1164	1165	1166	1167	1168	1169	1170	1171	1172	1173	1174	1175	1176	1177	1178	1179	1180	1181	1182	1183	1184	1185	1186	1187	1188	1189	1190	1191	1192	1193	1194	1195	1196	1197	1198	1199	1200	1201	1202	1203	1204	1205	1206	1207	1208	1209	1210	1211	1212	1213	1214	1215	1216	1217	1218	1219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H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC
2	7	7	24.8	23.9	4	2	8	17.2	-16.8	7	10	8	21.2	20.1	3	9	9	8.7	-9.1
3	7	7	10.9	11.2	5	2	8	-4.9	5.5	8	10	8	11.9	13.2	4	9	9	29.9	30.3
4	7	7	21.5	-21.2	6	2	8	17.2	16.3	1	11	8	14.8	-15.4	5	9	9	8.3	6.7
5	7	7	-5.8	4.7	7	2	8	16.1	-16.7	2	11	8	8.7	9.1	6	9	9	9.4	9.1
6	7	7	8.8	7.6	8	2	8	10.0	-8.7	3	11	8	14.7	-15.0	0	10	9	-3.8	-4.2
7	7	7	-3.4	5.7	9	2	8	0.0	4.6	4	11	8	-2.1	2.8	1	10	9	9.2	-10.9
8	7	7	16.3	-17.6	10	2	8	-5.2	5.5	5	11	8	19.3	19.3	2	10	9	11.4	10.4
9	7	7	8.1	-7.8	11	2	8	-3.8	-1.6	6	11	8	0.0	1.4	3	10	9	15.2	14.0
10	7	7	38.7	-38.2	12	2	8	0.0	-0.8	0	12	8	-6.3	3.6	4	10	9	13.6	-12.8
11	7	7	0.0	-4.6	13	2	8	12.0	-12.5	1	12	8	13.2	2.8	0	0	10	34.3	34.4
12	7	7	-2.4	-1.0	1	3	8	37.8	-37.1	2	12	8	10.2	9.3	1	0	10	16.8	16.8
0	8	7	30.3	51.8	2	3	8	17.6	17.2	3	12	8	19.0	18.5	2	0	10	16.1	16.1
1	8	7	24.1	21.9	3	3	8	10.9	11.8	1	1	9	7.0	7.0	3	0	10	18.1	18.0
2	8	7	24.3	-28.1	4	3	8	54.9	55.3	2	1	9	7.8	6.4	4	0	10	0.0	0.5
3	8	7	17.1	-18.2	5	3	8	7.5	7.3	3	1	9	8.9	5.2	5	0	10	32.8	32.8
4	8	7	17.9	19.4	6	3	8	16.9	16.3	4	1	9	19.0	19.1	6	0	10	63.6	-62.2
5	8	7	17.7	16.5	7	3	8	40.7	39.7	5	1	9	14.2	14.3	7	0	10	12.9	13.1
6	8	7	19.6	19.8	8	3	8	8.7	-7.3	6	1	9	0.0	0.7	8	0	10	8.2	-7.8
7	8	7	-3.1	-1.7	9	3	8	28.4	27.6	7	1	9	17.3	17.0	9	0	10	-4.1	1.2
8	8	7	14.0	-13.7	10	3	8	0.0	2.3	8	1	9	23.7	-24.9	1	1	10	0.0	3.2
9	8	7	7.0	-4.5	11	3	8	0.0	-4.3	9	1	9	0.0	-0.7	2	1	10	-6.0	9.1
10	8	7	0.0	1.1	12	3	8	-4.7	-3.6	10	1	9	18.4	-16.4	3	1	10	10.3	9.6
11	8	7	15.7	-14.5	13	3	8	8.3	-9.1	11	1	9	-3.4	-1.0	4	1	10	16.1	-15.6
12	8	7	8.5	7.2	0	4	8	8.3	-7.0	0	2	9	22.8	23.1	5	1	10	11.7	9.8
1	9	7	22.0	22.7	1	4	8	32.8	34.2	1	2	9	28.1	29.2	6	1	10	7.0	7.5
2	9	7	20.3	-21.9	2	4	8	11.5	-12.4	2	2	9	6.4	-4.5	7	1	10	9.7	9.3
3	9	7	9.8	-10.3	3	4	8	26.0	-26.3	3	2	9	-4.1	4.6	8	1	10	13.5	12.0
4	9	7	18.4	18.5	4	4	8	7.7	3.9	4	2	9	6.8	-2.1	9	1	10	-3.0	1.2
5	9	7	-5.5	-4.5	5	4	8	9.3	6.7	5	2	9	30.6	31.4	0	2	10	12.0	10.8
6	9	7	8.4	-8.8	6	4	8	0.0	-6.5	6	2	9	44.6	-44.1	1	2	10	0.0	5.5
7	9	7	11.4	-11.0	7	4	8	-1.7	4.6	7	2	9	7.5	-7.3	2	2	10	9.6	-9.7
8	9	7	22.0	-21.2	8	4	8	-4.1	5.9	8	2	9	-1.7	-0.2	3	2	10	0.0	1.1
9	9	7	0.0	-2.4	9	4	8	11.4	-9.9	9	2	9	-3.6	-2.1	4	2	10	-3.9	2.3
10	9	7	0.0	1.5	10	4	8	-4.6	-5.2	10	2	9	0.0	-3.1	5	2	10	12.8	10.7
11	9	7	14.8	15.2	11	4	8	-6.3	-5.7	11	2	9	12.6	-12.6	6	2	10	-3.0	-3.0
0	10	7	44.3	-43.6	12	4	8	-3.8	4.1	1	3	9	20.6	21.5	7	2	10	-3.9	4.1
1	10	7	-4.3	-5.2	1	5	8	34.7	38.7	2	3	9	6.5	-7.7	8	2	10	10.9	-11.5
2	10	7	-2.6	-2.6	2	5	8	30.3	-30.9	3	3	9	20.9	20.3	9	2	10	11.2	9.4
3	10	7	28.7	-28.7	3	5	8	-3.2	-2.2	4	3	9	22.8	-23.5	1	3	10	6.9	6.3
4	10	7	18.3	17.4	4	5	8	24.1	-24.6	5	3	9	0.0	-1.4	2	3	10	-2.0	-2.4
5	10	7	0.0	4.1	5	5	8	-5.8	-5.5	6	3	9	-6.3	-3.6	3	3	10	14.6	15.1
6	10	7	7.8	7.6	6	5	8	7.1	7.8	7	3	9	0.0	0.3	4	3	10	7.0	6.2
7	10	7	15.6	-15.1	7	5	8	-6.1	-6.2	8	3	9	-2.6	-7.0	5	3	10	11.5	11.0
8	10	7	34.5	32.0	8	5	8	28.6	27.4	9	3	9	0.0	-0.2	6	3	10	9.4	-8.8
9	10	7	29.4	28.0	9	5	8	14.5	-13.3	10	3	9	-4.4	-3.3	7	3	10	8.0	7.7
10	10	7	8.1	-9.9	10	5	8	35.1	33.3	11	3	9	-5.8	4.5	8	3	10	6.9	7.0
1	11	7	-3.0	3.6	11	5	8	13.1	12.8	0	4	9	13.5	-14.4	0	4	10	44.0	-46.2
2	11	7	-4.5	-3.0	12	5	8	23.6	24.4	1	4	9	6.7	7.7	1	4	10	8.2	-8.6
3	11	7	-6.2	5.5	0	6	8	28.7	31.3	2	4	9	32.0	-35.3	2	4	10	7.6	-5.7
4	11	7	33.6	-33.4	1	6	8	10.8	11.0	3	4	9	15.2	-16.0	3	4	10	11.1	-9.3
5	11	7	7.3	-8.0	2	6	8	-3.0	-3.9	4	4	9	-5.0	2.4	4	4	10	-5.2	4.2
6	11	7	7.2	-7.7	3	6	8	19.1	-18.3	5	4	9	-4.4	0.8	5	4	10	10.0	-9.2
7	11	7	-2.9	1.8	4	6	8	-1.6	4.0	6	4	9	7.3	-7.1	6	4	10	28.2	27.5
8	11	7	10.9	-12.1	5	6	8	9.3	8.4	7	4	9	11.7	-10.2	7	4	10	-5.5	6.2
9	11	7	13.2	11.0	6	6	8	26.5	-27.1	8	4	9	-5.6	-3.3	8	4	10	19.9	20.1
0	12	7	0.0	-2.3	7	6	8	22.1	-22.0	9	4	9	14.5	-15.1	1	5	10	15.6	15.0
1	12	7	-4.9	5.6	8	6	8	9.1	-6.3	10	4	9	-5.1	-3.3	2	5	10	-3.5	9.3
2	12	7	-6.6	-8.1	9	6	8	0.0	2.8	11	4	9	15.8	-15.2	3	5	10	9.2	10.6
3	12	7	10.6	-10.1	10	6	8	7.4	-3.8	1	5	9	-3.3	1.8	4	5	10	9.9	-8.9
4	12	7	9.3	-8.1	11	6	8	-1.9	-2.2	2	5	9	24.2	-24.4	5	5	10	8.2	6.6
5	12	7	-5.1	-5.3	1	7	8	16.8	16.7	3	5	9	0.0	0.4	6	5	10	-4.6	-6.3
6	12	7	0.0	-1.5	2	7	8	7.4	-8.0	4	5	9	15.6	-16.3	7	5	10	0.0	-2.4
7	12	7	-1.7	3.5	3	7	8	6.6	7.1	5	5	9	-1.9	-0.8	0	6	10	9.9	-10.5
8	12	7	11.6	-11.3	4	7	8	8.7	-6.7	6	5	9	17.5	-17.3	1	6	10	10.2	-8.5
9	12	7	9.9	-8.4	5	7	8	17.5	-16.6	7	5	9	-1.7	1.4	2	6	10	-4.3	2.4
0	13	7	-3.1	-1.9	6	7	8	13.8	15.0	8	5	9	9.0	9.1	3	6	10	7.3	6.5
1	13	7	0.0	-2.7	7	7	8	24.8	-23.7	9	5	9	7.6	1.1	4	6	10	-2.7	-4.2
2	13	7	24.2	-24.5	8	7	8	19.2	19.2	10	5	9	20.3	18.2	5	6	10	-3.0	-2.7
3	13	7	41.5	-42.2	9	7	8	12.9	-12.6	0	6	9	42.2	-42.8	6	6	10	21.8	20.2
4	13	7	-2.7	-2.3	10	7	8	28.7	29.1	1	6	9	16.4	-13.1	1	7	10	15.9	15.7
5	13	7	-3.7	-0.3	11	7	8	-6.2	1.5	2	6	9	9.6	-11.2	2	7	10	0.0	1.9
6	13	7	12.7	12.7	0	8	8	13.2	13.9	3	6	9	12.8	-15.7	3	7	10	12.9	13.0
7	13	7	42.5	-43.7	1	8	8	6.9	7.5	4	6	9	-4.5	-3.4	4	7	10	-4.8	-3.0
8	13	7	54.6	-52.1	2	8	8	11.4	9.7	5	6	9	13.2	-12.3	5	7	10	9.5	9.8
9	13	7	11.9	-11.4	3	8	8	-6.0	-5.7	6	6	9	0.0	-4.0	0	8	10	23.1	24.4
0	14	7	37.4	37.4	4	8	8	16.4	17.4	7	6	9	22.2	-21.4	1	8	10	0.0	1.4
1	14	7	0.0	0.9	5	8	8	12.5	13.8	8	6	9	9.4	11.1	2	8	10	18.4	18.6
2	14	7	26.9	-27.5	6	8	8	-3.9	-4.0	9	6	9	10.0	-1.5	3	8	10	7.3	6.9
3	14	7	-3.9	1.0	7	8	8	-9.1	-6.2	1	7	9	11.8	-12.2	1	1	11	-2.7	-0.8
4	14	7	7.4	7.7	8	8	8	7.6	3.8	2	7	9	-3.1	7.4	2	1	11	14.2	-16.6
5	14	7	-6.4	6.9	9	8	8	10.9	10.6	3	7	9	-5.6	0.8	3	1	11	-4.6	-5.6
6	14	7	15.3	-14.3	10	8	8	-1.4	0.1	4	7	9	12.1	-12.1	4	1	11	20.1	-19.4
7	14	7	32.5	-32.7	1	9	8	11.6	-13.2	5	7	9	-6.6	-7.8	5	1	11	7.4	-8.5

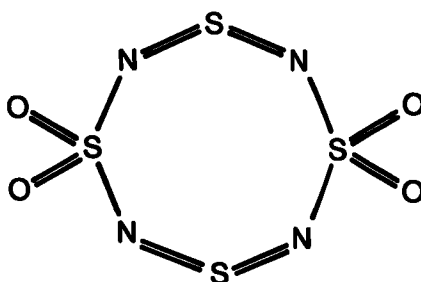
CHAPTER 5

The Crystal Structure of  $S_5N_5^+S_3N_3O_4^-$

### 5.1 Introduction.

$S_4N_4$  has been known since 1835 (Gregory, 1835) and constitutes the most well known and studied sulphur-nitrogen compound. As mentioned in section 2.2 it is a very reactive compound and is the starting point for the preparation of many other cyclic sulphur-nitrogen species. Many compounds have been prepared in which the  $S_4N_4$  ring is retained; the simplest of these are derivatives such as  $S_4N_4F_4$ , described earlier or  $S_4N_4H_4$  which contains a puckered  $S_4N_4$  ring and shows  $4m$  symmetry (Sabine and Cox, 1967).  $S_4N_4$  also forms a wide range of adducts with Lewis acids such as  $SbCl_5$ , which coordinates to a nitrogen in the ring to give  $SbCl_5 \cdot S_4N_4$ .

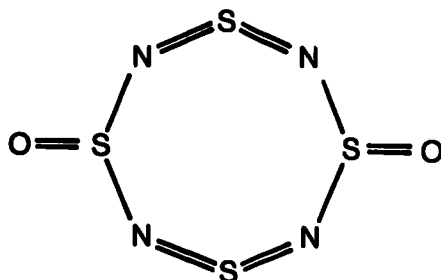
In contrast, the first oxide of  $S_4N_4$  has only been prepared quite recently (Roesky and Petersen, 1972), and corresponds to  $S_4N_4O_4$ . This has been assigned the structure shown below from infrared and mass spectral studies.



In the course of further investigation of inorganic ring systems, Roesky and Grosse Böwing (1973) succeeded in isolating two compounds which they formulated as  $S_4N_4O_2$ . Both compounds were

prepared by the reaction between  $\text{Me}_3\text{Si-N=S=N-SiMe}_3$  and  $\text{FSO}_2\text{-N=S=O}$  in methylene chloride. The reaction proceeded readily at room temperature, and when the reaction was complete the solvent and volatile products were removed in vacuo. The residues were redissolved in methylene chloride and after several days violet-black crystals of compound I were deposited. When a small amount of solvent was removed yellow crystals of compound II were produced. Cryoscopic molecular weight measurements and elemental analysis yielded results in good agreement with the formulation of both compounds as  $\text{S}_4\text{N}_4\text{O}_2$ .

Compound I was thought to be



and its crystal structure is described in this chapter. The crystal structure of compound II is discussed in chapter 7.

## 5.2 Crystal Data.

The crystals were obtained as violet-black prisms, elongated along a with prominent  $\{011\}$  faces. The crystal used for data

collection had dimensions 0.6 x 0.2 x 0.2mm and was sealed in a quartz tube.

Precession photographs showed the unit cell to be monoclinic with space group  $P2_1/c$ . Accurate cell dimensions were obtained from a least squares treatment of the positions of twelve high order reflections as measured on a four-circle diffractometer.

$S_8N_8O_4$	M	=	432.53	
	a	=	8.874(1)Å	$\alpha = 90^\circ$
	b	=	11.299(2)Å	$\beta = 97.27^\circ$
	c	=	13.112(2)Å	$\gamma = 90^\circ$
	U	=	1314.7Å <sup>3</sup>	
	Z	=	4	
	Dm	=	2.14g cm <sup>-3</sup>	(by floatation in CH <sub>3</sub> I/C <sub>2</sub> H <sub>5</sub> I)
	Dc	=	2.185g cm <sup>-3</sup>	

Absorption coefficient for MoK $\alpha$  radiation ( $\lambda = 0.7107\text{\AA}$ ) = 13.3cm<sup>-1</sup>.

### 5.3 Data Collection and Correction.

The intensity data were collected on a Hilger and Watts Y290 four-circle diffractometer (described before) using Zr-filtered MoK $\alpha$  radiation. A  $2\theta - \omega$  scan was used consisting of 80 steps of  $0.01^\circ$  with a counting time of 2 seconds per step. The background was measured for 40 seconds at the beginning and end of each scan. Three standard reflections were measured every 40 reflections, and showed no systematic changes indicating that the crystal was stable throughout the experiment. The standard reflections were used to place the reflections on a common scale.

Half the sphere of reflection was recorded for  $0 < \theta \leq 26^\circ$ . This yielded two sets of equivalent reflections which on averaging gave a total of 2563 independent reflections, and of these 1915 were taken as observed having net counts  $> 3$  e.s.d's.

The intensities were corrected for Lorentz and polarisation effects but not for absorption.

#### 5.4 Solution and Refinement.

The structure was solved by the symbolic addition procedure using a multiresolution program (Long, 1968). A set of normalised structure factors were calculated and 214 of these with  $E \geq 1.7$  were phased. Seven reflections were chosen by the program (Table 5.1); the first three were arbitrarily given positive signs and hence determined the origin. The phases of the remainder were varied to form, together with the origin determining reflections, 16 starting sets for the reiterative application of Sayre's relationship. The results are shown in table 5.1.

The most self-consistent phases were obtained from starting set 15 which has a consistency index of 0.97. The only other set with a high consistency index is set 13 however this shows a sign change in the starting set that leaves it equivalent to set 15.

An E-map was computed using the phases estimated from set 15 which revealed the positions of all the sulphur atoms and most of the lighter atoms. The structure was very different from that expected and did not contain the  $S_4N_4O_2$  molecules originally proposed, so that only the positions of the sulphur atoms were included in the first stages of refinement. The sulphur atoms were refined with isotropic temperature factors of  $3.0\text{\AA}^2$  using least squares methods

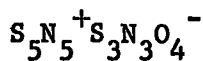
with the block-diagonal approximation and after two cycles this resulted in an R value of 0.37. An electron density map was calculated based on the phases obtained from the sulphur atoms and this revealed positions for all the lighter atoms except for one nitrogen. Because the anion was new it was not certain which atoms were oxygen so that all the lighter atoms were included as nitrogen. Further refinement and the calculation of difference syntheses revealed the remaining nitrogen atom and indicated which atoms were oxygen (R = 0.081). All atoms were then given anisotropic thermal parameters and with further refinement, using full matrix least squares methods, R converged on its final value of 0.0300. During the last cycle all the parameter shifts were  $< 0.2\sigma$ . A difference synthesis calculated from the final structure factors showed no peaks  $> 0.3e.\text{\AA}^{-3}$ .

The initial weighting scheme used was the same as that described earlier except that  $P_1 = 20$  and  $P_2 = 0.15$ . This was replaced in the final stages of refinement by one based on counting statistics as described in section 3.4 and took the form

$$\sqrt{w} = 2.N/(F_o.[T + B.G + (PN)^2]^{1/2})$$

The optimum value of P as determined by a uniform distribution of  $w\Delta^2$  over the whole range of  $F_o$ , was 0.05. The unobserved reflections were not included in the refinement. The final least squares totals and weighting analysis are given in table 5.2. The final structure factors are shown in table 5.9. The sulphur atoms were corrected

Table 5.1



The reflections used in the starting sets.

<u>Origin determining reflections</u>			E	<u>Reflections whose signs were varied</u>			E
6	2	$\bar{7}$	3.48	4	2	$\bar{9}$	3.45
3	3	10	3.16	4	5	4	2.98
2	3	9	3.14	7	6	$\bar{6}$	2.87
				0	3	3	2.84

Results for Symbolic Addition Procedure

Set No	Signs	Changes	Cycles	No +	No -	Consistency Index
1	++++		10	124	90	0.766
2	+++ -		11	107	107	0.580
3	++ - +		9	110	104	0.568
4	++ - -		12	110	104	0.529
5	+ - + +		11	113	101	0.518
6	+ - + -		11	111	103	0.690
7	+ - - +	+ - + +	10	103	111	0.601
8	+ - - -		9	105	109	0.720
9	- + + +		10	119	95	0.633
10	- + + -	- + - +	15	100	114	0.723
11	- + - +		10	119	95	0.667
12	- + - -		9	110	104	0.757
13	- - + +	- - - +	12	111	103	0.941
14	- - + -		11	105	109	0.548
15	- - - +		7	111	103	0.972
16	- - - -		16	109	105	0.599



Table 5.2  $S_5N_5^+S_3N_3O_4^-$ Final Least Squares Totals

$\Sigma F_o $	$\Sigma F_c $	$\Sigma \Delta $	R
48031.63	48009.02	1442.51	0.0300

Weighting Analysis

$ F_o $ Ranges	N	$\Sigma w\Delta^2/N$	R
0 - 7	84	0.39	0.160
7 - 9	169	0.27	0.102
9 - 15	516	0.29	0.051
15 - 20	282	0.32	0.030
20 - 45	636	0.32	0.021
45 - 70	143	0.27	0.018
70 Upwards	85	0.57	0.028

Table 5.3  $S_5N_5^+S_3N_3O_4^-$ 

Final Atomic Coordinates with their Estimated Standard Deviations ( $\times 10^5$ )  
and their Isotropic Temperature Factor  $^\dagger$  ( $\text{\AA}^2$ )

Atom	x/a	y/b	z/c	B
S(1)	0.71855 (11)	0.00867 ( 8)	0.07288 ( 7)	3.82
S(2)	0.48780 (10)	0.15440 ( 8)	0.17082 ( 7)	3.70
S(3)	0.61041 (10)	0.33077 ( 8)	0.31946 ( 7)	3.47
S(4)	0.93756 (10)	0.30549 ( 8)	0.33504 ( 7)	3.38
S(5)	0.99551 (10)	0.12928 ( 8)	0.18528 ( 7)	3.57
S(6)	0.30339 ( 8)	0.35385 ( 7)	-0.07419 ( 6)	2.95
S(7)	0.20910 ( 8)	0.42751 ( 7)	0.10532 ( 6)	2.66
S(8)	0.24056 (10)	0.59349 ( 7)	-0.04941 ( 6)	3.26
O(1)	0.24664 (29)	0.28272 (24)	-0.16087 (19)	4.26
O(2)	0.45972 (25)	0.33688 (25)	-0.03526 (20)	4.16
O(3)	0.07676 (27)	0.41551 (24)	0.15577 (18)	4.01
O(4)	0.35186 (26)	0.41959 (23)	0.16846 (17)	3.76
N(1)	0.57104 (34)	0.06471 (26)	0.10682 (22)	4.06
N(2)	0.60484 (30)	0.22946 (25)	0.23939 (20)	3.31
N(3)	0.78213 (33)	0.35791 (24)	0.36117 (21)	3.55
N(4)	0.90270 (30)	0.21067 (24)	0.24873 (20)	3.29
N(5)	0.88328 (34)	0.05109 (26)	0.11102 (22)	3.96
N(6)	0.19020 (28)	0.34203 (23)	0.00840 (20)	2.96
N(7)	0.20125 (29)	0.56562 (23)	0.05822 (19)	3.01
N(8)	0.28947 (30)	0.49364 (26)	-0.11704 (20)	3.19

$^\dagger$  The temperature factors obtained from the last cycle of isotropic refinement.

Table 5.4  $S_5N_5^+S_3N_3O_4^-$ 

Final Anisotropic Thermal Parameters and their Estimated Standard  
Deviations (Both  $\text{\AA}^2 \times 10^5$ )

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
S(1)	6948(61)	4157(48)	3968(45)	-750(38)	221(41)	-356(43)
S(2)	3929(44)	5250(54)	5236(51)	-475(42)	3(37)	-609(39)
S(3)	4510(46)	4392(46)	4830(48)	-811(39)	1128(37)	386(37)
S(4)	4229(46)	4239(47)	4602(47)	-385(37)	325(37)	-611(36)
S(5)	4269(45)	4675(50)	5042(50)	-469(39)	827(38)	552(38)
S(6)	3193(39)	4695(48)	3793(41)	-901(36)	634(31)	-91(35)
S(7)	3259(38)	4250(44)	3034(37)	246(32)	586(29)	-31(33)
S(8)	4576(47)	4138(47)	3966(44)	611(35)	307(36)	-158(36)
O(1)	6066(160)	6520(167)	4736(144)	2423(125)	406(126)	-143(131)
O(2)	3221(120)	7562(181)	6226(157)	-923(139)	823(111)	799(120)
O(3)	4703(136)	7166(176)	4695(133)	298(127)	2192(111)	-623(125)
O(4)	4480(131)	6410(160)	4295(130)	520(117)	-648(107)	447(117)
N(1)	6309(189)	4354(162)	4294(155)	-11(133)	188(139)	-754(144)
N(2)	4310(154)	4263(158)	4158(154)	75(122)	248(126)	104(122)
N(3)	5491(171)	3909(156)	4078(149)	-640(120)	829(128)	-274(131)
N(4)	4359(151)	3874(145)	4187(152)	217(118)	986(123)	119(120)
N(5)	6207(190)	4569(165)	4361(160)	-211(132)	472(138)	526(143)
N(6)	3736(139)	3928(147)	4118(142)	-297(117)	830(113)	-607(117)
N(7)	4201(144)	3846(142)	3761(141)	-132(117)	360(114)	368(120)
N(8)	4444(151)	5713(179)	3520(143)	273(127)	1051(120)	-755(133)

for anomalous dispersion. These correction factors as well as the scattering factors for all atoms were taken from International tables Vol III. The final atomic coordinates and anisotropic thermal parameters are given in tables 5.3 and 5.4 respectively.

### 5.5 Results and Discussion.

The structure consists of  $S_5N_5^+$  cations and  $S_3N_3O_4^-$  anions, and does not contain molecules of  $S_4N_4O_2$  as was originally suggested. It is of interest that the average molecular weight and atomic composition for these two ions does correspond to  $S_4N_4O_2$ . The bond distances and angles for these ions are shown in tables 5.5 and 5.6 respectively.

#### 5.5a The Structure of the $S_5N_5^+$ cation.

This is the second determination of the structure of this cation. As seen in figure 5.1, it consists of a ten-membered ring with alternating sulphur and nitrogen atoms. The ring is roughly planar with the maximum deviation from the mean plane being  $0.06\text{\AA}$  as shown on figure 5.2 and in table 5.7. The deviations are systematic and

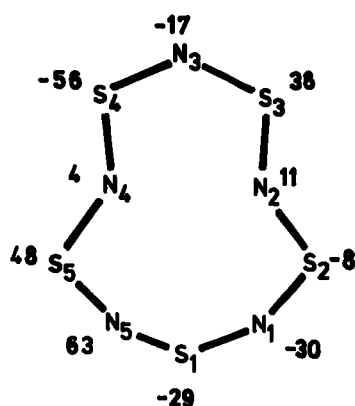


Figure 5.2

Deviations of the atoms from their mean plane ( $\text{\AA} \times 10^3$ )

indicate that the  $S_5N_5$  ring is slightly buckled along the line S(4) to N(1). This buckling is greater than that found in medium sized aromatic hydrocarbons, such as pyrene  $C_{16}H_{10}$  which shows deviations of up to  $0.02\text{\AA}$  from its mean plane (Hazell, Larsen and Lehmann, 1972) and suggests that the heterocyclic ring is more flexible than its organic counterparts. This might be expected because  $\pi$  bonding involving d orbitals is less sensitive to deviations from planarity than that involving only p orbitals. The bond lengths on either side of the ring are the same within experimental error, for example the length of  $1.568(3)\text{\AA}$  for S(1)-N(1) does not differ significantly from that of  $1.559(3)\text{\AA}$  for S(1)-N(5). Likewise the corresponding angles are equal within experimental error except for S(2)-N(2)-S(3) and S(4)-N(4)-S(5) which have values of  $139.8(2)^\circ$  and  $136.8(2)^\circ$  respectively. Thus the shape of the ion approaches mm symmetry. A similar divergence in the angles in the  $S_5N_5$  ring is found in the  $S_5N_5^+$  ion described in chapter 6 and will be discussed there.

The bond distances which vary from  $1.540$ - $1.582\text{\AA}$  are characteristic of multiple bonds in aromatic sulphur-nitrogen compounds, and may be compared with the range of  $1.548$ - $1.566\text{\AA}$  seen in  $S_4N_3^+$  (Kruss and Zeigler, 1972b). The bond angles at nitrogen which vary from  $133^\circ$  to  $151^\circ$  are also characteristic of these compounds and are similar to the angles of  $138^\circ$  and  $148^\circ$  found in  $S_4N_3^+$ . As mentioned in section 2.5 theoretical calculations have shown that the  $S_5N_5^+$  cation found originally in  $S_5N_5^+AlCl_4^-$  is a  $14\pi$  electron inorganic aromatic species. In view of the bond distances and angles found in the present determination it is reasonable to assume that this also contains a  $14\pi$  electron system.

The  $S_5N_5^+$  ion reported here differs markedly from the heart-shaped cation first reported in  $S_5N_5^+AlCl_4^-$  (Hazell and Hazell, 1972) which is shown in figure 5.3. However closer examination shows that the sulphur atoms in both structures have approximately the same distribution and that the main difference is in the position of two nitrogen atoms. There is also a far greater variation in the S-N bond distances and angles at nitrogen in  $S_5N_5^+AlCl_4^-$  than in the present structure, i.e. 1.465-1.590Å and 129-177°. In view of these differences another derivative of  $S_5N_5^+$  has been studied and is described in the following chapter, so that further discussion on these ions is deferred until then.

#### 5.5b The Structure and Bonding in the $S_3N_3O_4^-$ anion.

This is the first time that this anion has been observed although the preparation of  $HS_3N_3O_4$  has been reported (Roesky and Kutzt, 1974). As seen in figure 5.4 it consists of an  $S_3N_3$  ring with two terminal oxygen atoms on two of the sulphur atoms. The bond distances on either side of the ring are the same within experimental error. In the case of S(6)-N(6) and S(7)-N(6) of length 1.573(3)Å and 1.588(3)Å it is necessary to allow for the dependence of their lengths on the common position of N(6). Likewise corresponding angles on either side of the ring are the same within experimental error at the 0.1% level, so that the molecule shows m symmetry within experimental error.

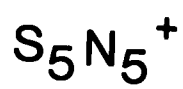
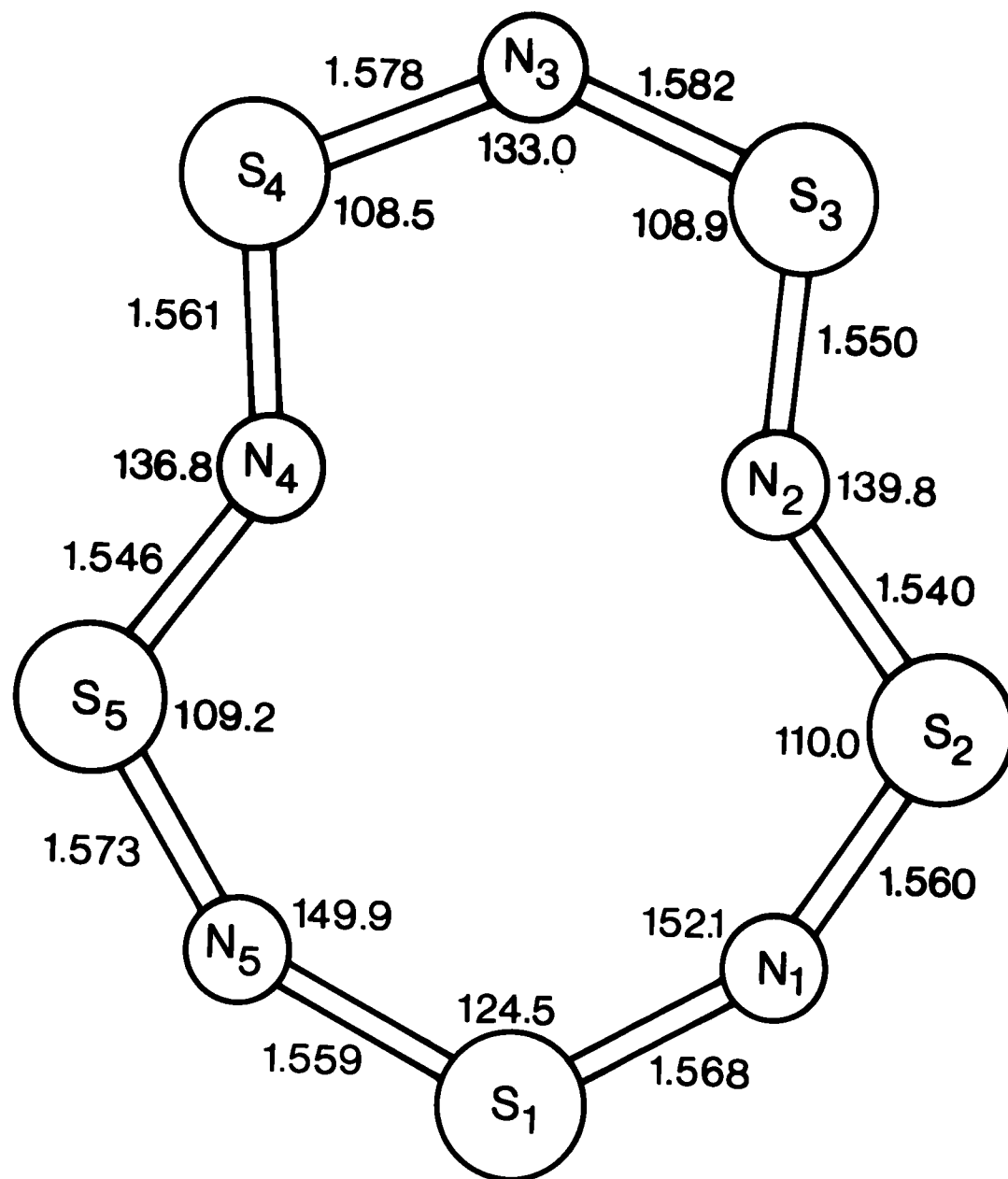


Figure 5.1

The  $S_5N_5^+$  Cation found in  $S_5N_5^+S_3N_3O_4^-$

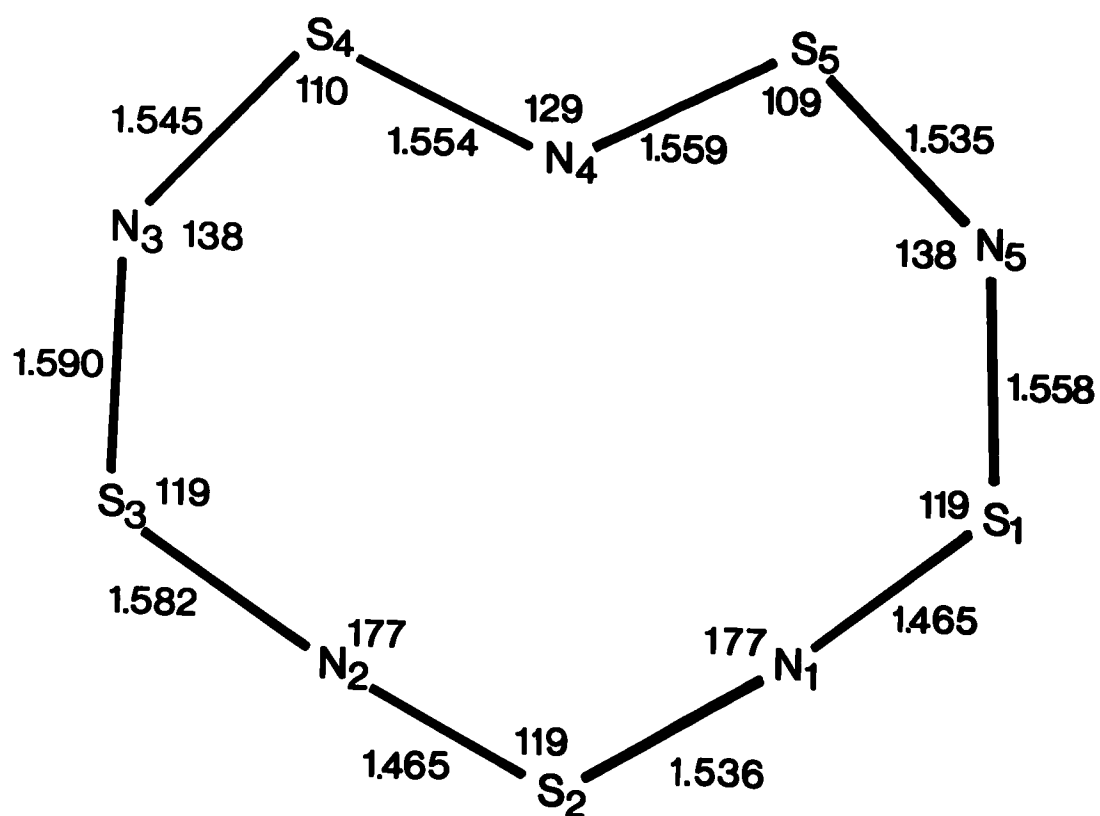


Figure 5.3

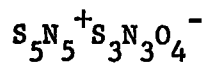
The  $S_5N_5^+$  Cation found in  $S_5N_5^+AlCl_4^-$



Table 5.5  $S_5N_5^+S_3N_3O_4^-$ Final Bond Distances ( $\text{\AA}$ ) with their Estimated Standard Deviations( $\text{\AA} \times 10^3$ )

S(1) - N(1)	1.568 (3)
S(1) - N(5)	1.559 (3)
S(2) - N(1)	1.560 (3)
S(2) - N(2)	1.540 (3)
S(3) - N(2)	1.550 (3)
S(3) - N(3)	1.582 (3)
S(4) - N(3)	1.578 (3)
S(4) - N(4)	1.561 (3)
S(5) - N(4)	1.546 (3)
S(5) - N(5)	1.573 (3)
S(6) - O(1)	1.431 (3)
S(6) - O(2)	1.429 (3)
S(6) - N(6)	1.573 (3)
S(6) - N(8)	1.676 (3)
S(7) - O(3)	1.425 (3)
S(7) - O(4)	1.426 (2)
S(7) - N(6)	1.588 (3)
S(7) - N(7)	1.677 (3)
S(8) - N(7)	1.529 (3)
S(8) - N(8)	1.532 (3)

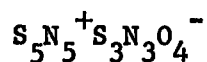
Table 5.6



Final Bond Angles (degrees) and their Estimated Standard  
Deviations (deg. x 10<sup>2</sup>)

N(1) - S(1) - N(5)	124.53(17)
N(1) - S(2) - N(2)	109.99(16)
N(2) - S(3) - N(3)	108.91(15)
N(3) - S(4) - N(4)	108.47(15)
N(4) - S(5) - N(5)	109.20(16)
S(1) - N(1) - S(2)	152.11(22)
S(2) - N(2) - S(3)	139.81(20)
S(3) - N(3) - S(4)	133.00(19)
S(4) - N(4) - S(5)	136.77(19)
S(1) - N(5) - S(5)	149.92(21)
O(1) - S(6) - O(2)	115.88(16)
N(6) - S(6) - O(1)	107.94(15)
N(6) - S(6) - O(2)	114.71(15)
N(8) - S(6) - O(1)	105.05(15)
N(8) - S(6) - O(2)	105.86(15)
N(6) - S(6) - N(8)	106.53(14)
O(3) - S(7) - O(4)	116.62(15)
N(6) - S(7) - O(3)	107.69(14)
N(6) - S(7) - O(4)	115.00(14)
N(7) - S(7) - O(3)	105.15(14)
N(7) - S(7) - O(4)	105.36(14)
N(6) - S(7) - N(7)	106.03(14)
N(7) - S(8) - N(8)	119.82(15)
S(6) - N(6) - S(7)	119.16(17)
S(7) - N(7) - S(8)	121.88(17)
S(6) - N(8) - S(8)	120.97(18)

Table 5.7

Some mean planes

$$0.0863X + 0.6869Y - 0.7217Z + 0.0486 = 0$$

Atom	S(1)	S(2)	S(3)	S(4)	S(5)
P	-0.0286	-0.0076	0.0386	-0.0556	0.0484
$\sigma(P)$	0.0009	0.0009	0.0009	0.0009	0.0009

Atom	N(1)	N(2)	N(3)	N(4)	N(5)
P	-0.0300	0.0111	-0.0168	0.0043	0.0633
$\sigma(P)$	0.0029	0.0028	0.0027	0.0027	0.0029

$$-0.9095X - 0.1548Y - 0.3858Z + 2.8057 = 0$$

Atom	S(6)	S(7)	S(8)	N(6) <sup>†</sup>	N(7)	N(8)
P	-0.0011	0.0011	-0.0002	0.6431	-0.0119	0.0171
$\sigma(P)$	0.0007	0.0007	0.0009	0.0025	0.0026	0.0025

Where P and  $\sigma(P)$  are the distance and its e.s.d. of an atom from the mean plane.

X, Y, and Z are orthogonal coordinates in Å oriented in the direction of a, b and c\* respectively.

† this atom was not included in the calculation of the mean plane.

The  $S_3N_3$  ring is not planar; however for five of the atoms the maximum deviation from their mean plane is  $0.017\text{\AA}$ , whereas the remaining nitrogen atom, N(6) lies  $0.64\text{\AA}$  away from this plane as shown in table 5.7. This is caused by the approximately tetrahedral coordination at S(6) and S(7), and by the other angles in the ring being close to  $120^\circ$ .

The bonding in this molecule may be considered in two sections; the  $SO_2-N-SO_2$  part and the N-S-N part. This may be done because the bonds lengths of S(6)-N(8) and S(7)-N(7) of  $1.676\text{\AA}$  and  $1.677\text{\AA}$  approach those expected for single S-N bonds (cf.  $1.73\text{\AA}$  in  $S_7NH$ ). Some shortening is expected because of the contraction of the orbitals on S(6) and S(7) due to the terminal oxygen atoms and also because of the  $sp^2$  hybridisation at N(7) and N(8).

The negative charge on this anion resides on the  $SO_2-N-SO_2$  part and is situated mostly on the oxygen atoms rather than on N(6). This is shown by the S-O distances being equal within experimental error and also by the length of the S-N bonds involving the bridging nitrogen atom N(6). The mean S-N distance of  $1.581\text{\AA}$  is considerably shorter than the normal single bond distance of  $1.73\text{\AA}$  and, together with the angle at N(6) of  $119.2^\circ$ , indicates that there is substantial multiple bonding in this region. This implies that the negative charge does not reside on N(6). The magnitude of the angle S(6)-N(6)-S(7) may in part be due to the steric requirements of the ring since a reduction in this angle would result in a decrease in the angles at S(8), N(7) and N(8) whereas angles of approximately  $120^\circ$  are normally found in sulphur diimides. The mean S-O distance of

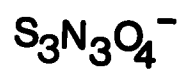
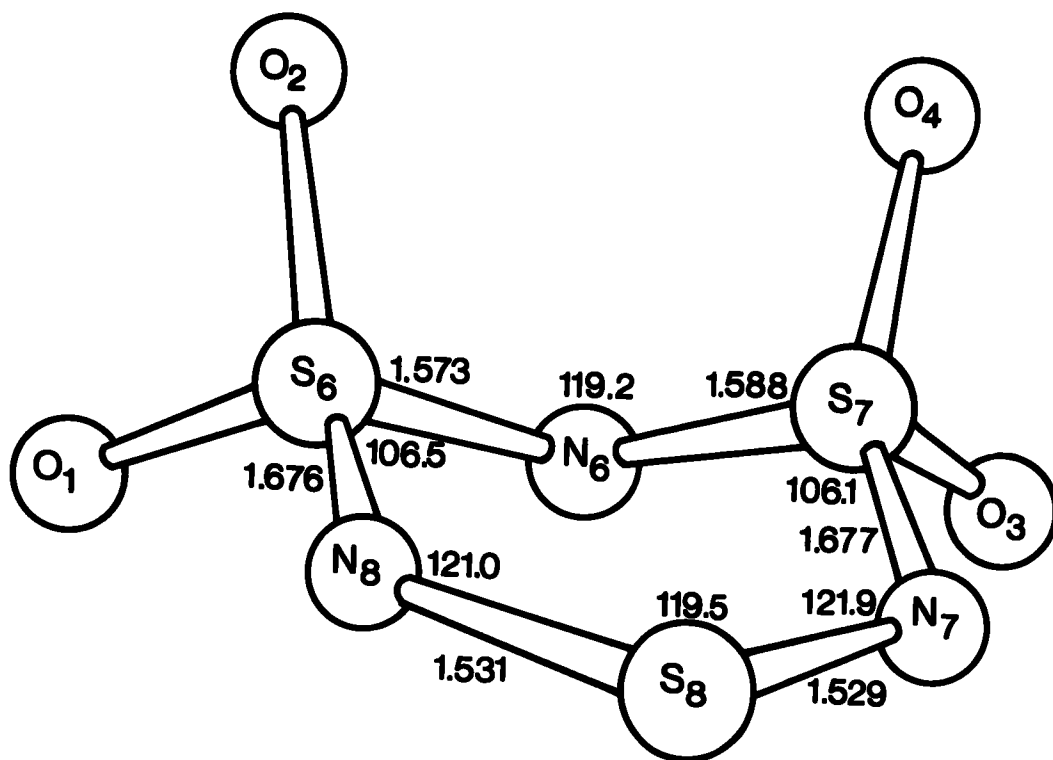
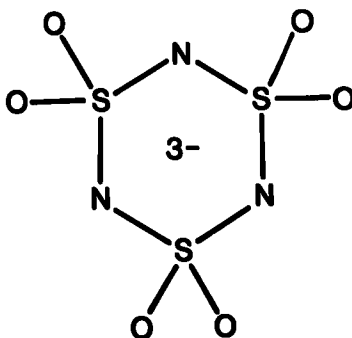


Figure 5.4

1.428 is close to that expected for a double bond eg.  $1.43\text{\AA}$  in  $\text{SO}_3$  (McDonald and Cruickshank, 1967) and as expected indicates substantial multiple bonding in these bonds.

As mentioned earlier the coordination about S(6) and S(7) is approximately tetrahedral. The mean value of  $116.3^\circ$  for the angle between the terminal oxygen atoms is significantly larger than the tetrahedral angle and may be attributed to the effects of multiple bonding. The S-O bonds will contain more s character than those not involved in multiple bonding so that the angle between these bonds will be larger than  $109^\circ 28'$ . Conversely the angles between the S-O multiple bonds and single bonds will be smaller which is seen in the values of  $105.1^\circ$  for N(8)-S(6)-O(1) and  $105.9^\circ$  for N(8)-S(6)-O(2), and similarly in the corresponding angles at S(7).

This part of the molecule may be compared with the  $(\text{NSO}_2)_3^{3-}$  anion (Dalgaard, Hazell and Hazell, 1974) shown below



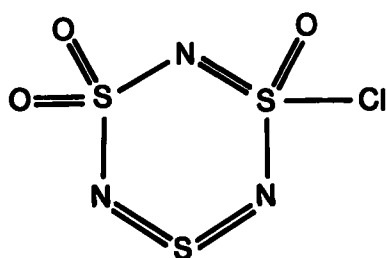
The S-N distances in this anion are all the same within experimental error and their mean value of  $1.636\text{\AA}$  is longer than that of  $1.581\text{\AA}$  seen in  $\text{S}_3\text{N}_3\text{O}_4^-$ . Likewise the mean S-O distance of  $1.446\text{\AA}$  is longer than that of  $1.428\text{\AA}$  in  $\text{S}_3\text{N}_3\text{O}_4^-$ . These differences may be accounted for by the presence of a full negative charge per  $\text{SO}_2$  group in  $(\text{NSO}_2)_3^{3-}$  as compared to formally half in  $\text{S}_3\text{N}_3\text{O}_4^-$ .

The remainder of the ring consists of a sulphur diimide fragment connected by two single bonds to the  $\text{SO}_2\text{-N-SO}_2$  part. The S-N bonds within the diimide group are very short, i.e. S(8)-N(7)  $1.529\text{\AA}$  and S(8)-N(8)  $1.532\text{\AA}$ , with a mean of  $1.531\text{\AA}$ , and are close to the length of  $1.54\text{\AA}$  normally ascribed to S-N double bonds, eg.  $1.54\text{\AA}$  in  $\text{S}_4\text{N}_4\text{F}_4$  (Wieggers and Vos, 1963). This is supported by the angle of  $119.8^\circ$  at S(8) and the mean of  $121.4^\circ$  for the angles at N(7) and N(8) which all indicate  $sp^2$  hybridisation. This diimide fragment is similar to that seen in  $\text{R-S-N=S=N-S-R}$ , where  $\text{R} = \text{p-C}_6\text{H}_4\text{Cl}$  (Olsen and Barrick, 1973) in which the mean S=N bond distance was found to be  $1.550(12)\text{\AA}$  with an N=S=N angle of  $124^\circ$ .

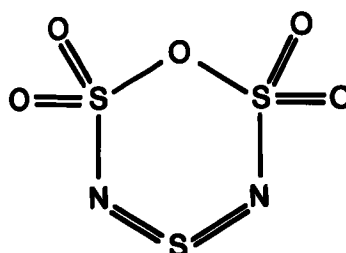
The structure of  $\text{HS}_3\text{N}_3\text{O}_4$  has not been studied crystallographically but spectroscopic studies suggested that the hydrogen is located on the nitrogen atom between the  $\text{SO}_2$  groups (Roesky and Kuhtz, 1974). Thus it is expected that in this compound the S-O bonds will be shorter and the S-N bonds to the N-H group will be longer with a smaller angle at this nitrogen atom than is seen in  $\text{S}_3\text{N}_3\text{O}_4^-$ .

There are two other analogues of  $\text{S}_3\text{N}_3\text{O}_4^-$  neither of which has

been studied crystallographically, namely  $S_3N_3O_3Cl$  (Roesky, 1971) and  $S_3N_2O_5$  (Goehring et al., 1954).  $S_3N_3O_3Cl$  has been assigned the structure III from spectroscopic evidence and is expected to contain an asymmetric  $SO_2-N-SOCl$  bridge.



III



IV

$S_3N_2O_5$  has been assigned the structure IV from spectroscopic and chemical evidence and in this compound the oxygen bridge is expected to be symmetric with a bridge angle less than  $120^\circ$ .

### 5.6 Molecular Packing.

The structure involves the packing together of positive and negative ions and it is of interest to see whether examples of secondary bonding may be found similar to those seen in  $[S_3N_2]_2^{2+}$   $(ClS_2O_6^-)_2$  described earlier. As noted before the intermolecular interactions which are most likely to give a decrease in the potential energy of the structure will involve sulphur atoms with either oxygen or nitrogen atoms; Whereas S---S, N---N, O---O or O---N interactions

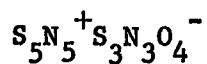


are expected to be destabilising. Thus it is not surprising that there are no contacts less than the appropriate van der Waals distance for these last four types of interaction. Conversely there are a significant number of S---O and S---N contacts less than their respective van der Waals distances of  $3.32\text{\AA}$  and  $3.35\text{\AA}$ , as shown in table 5.8.

Two of the shortest contacts are found between S(8) in the sulphur diimide fragment and O(2) at  $1-x, 1-y, -z$  and O(3) at  $-x, 1-y, -z$  with distances of  $2.860\text{\AA}$  and  $2.982\text{\AA}$  respectively. The oxygen atoms lie  $2.84\text{\AA}$  and  $2.51\text{\AA}$  away from the mean plane of S(6), S(7), S(8), N(7) and N(8) and are almost directly below and above S(8). This interaction may involve the overlap of a lone pair on each of the oxygen atoms with unfilled  $\pi$  orbitals on the sulphur atom. The shortest contacts involving the  $S_5N_5^+$  cation are associated with S(4) and S(5) to O(1) situated at  $1+x, \frac{1}{2}-y, \frac{1}{2}+z$  with distances of  $2.912\text{\AA}$  and  $2.981\text{\AA}$  so that the oxygen atom bridges these two sulphur atoms. The oxygen atom lies  $0.54\text{\AA}$  away from the plane of the ring and is similar to the interaction seen in  $[S_3N_2]_2^{2+}$  (section 3.6) but is probably not as strong. This may be interpreted as the overlap of a vacant orbital on each of the two sulphur atoms with the lone pairs on the oxygen atom. The other contacts between the ions are less specific in their orientation and may be primarily ionic in nature. It may be concluded that secondary bonding is an important feature in ionic sulphur-nitrogen compounds.

A projection on the [100] plane of the contents of the unit cell is shown in figure 5.5.

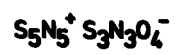
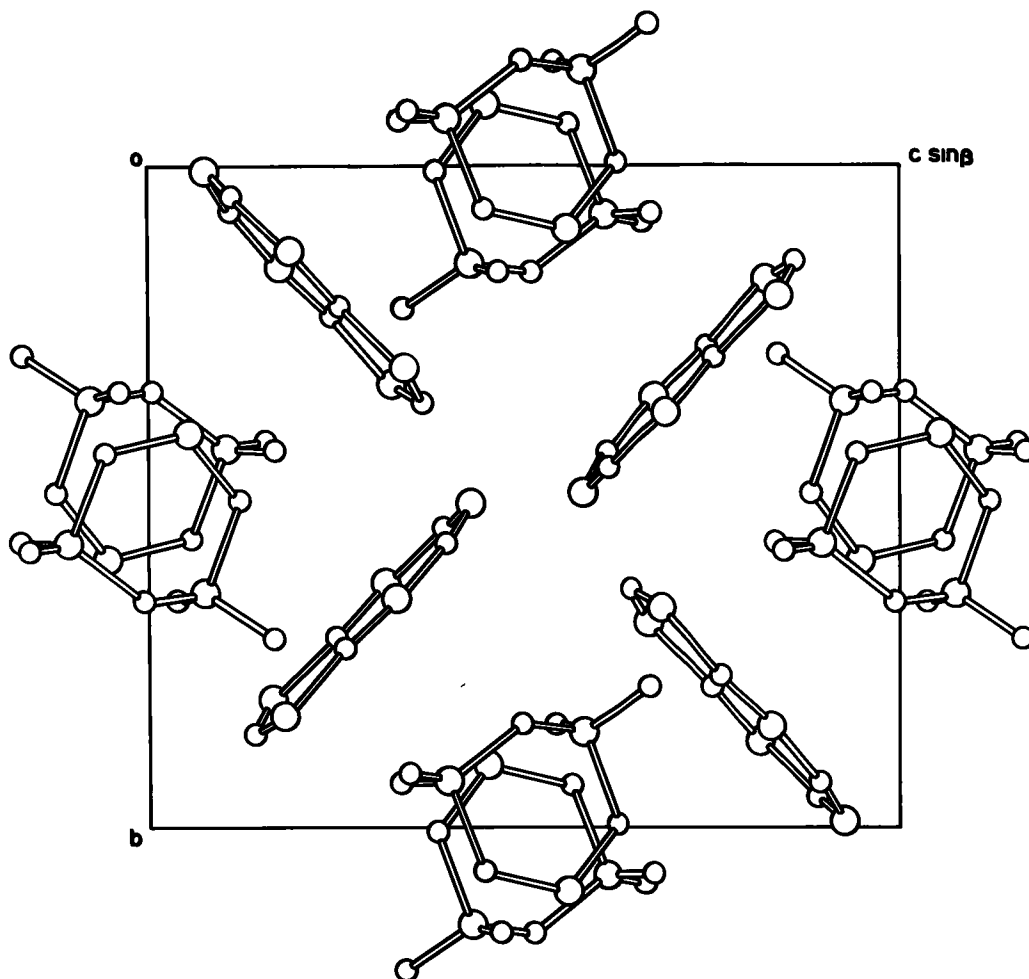
Table 5.8



S---O and S---N Intermolecular Contacts  $< 3.5\text{\AA}$

Atom A	Atom B	Equivalent Posn. of B	Cell	A-B $\text{\AA}$
S(1)	O(1)	2	(1, 0, 0)	3.490
S(1)	N(1)	2	(1, 0, 0)	3.363
S(2)	O(1)	4	(0, 0, 0)	3.339
S(3)	O(2)	4	(0, 0, 0)	3.107
S(3)	N(1)	3	(1, 0, 0)	3.303
S(4)	O(1)	4	(1, 0, 0)	2.912
S(4)	O(3)	1	(1, 0, 0)	3.055
S(4)	N(5)	3	(2, 0, 0)	3.232
S(4)	N(6)	4	(1, 0, 0)	3.418
S(4)	N(7)	3	(1, -1, 0)	3.356
S(5)	O(1)	4	(1, 0, 0)	2.981
S(5)	O(3)	1	(0, 0, 0)	3.347
S(5)	O(3)	3	(1, -1, 0)	3.306
S(8)	O(2)	2	(1, 1, 0)	2.860
S(8)	O(3)	2	(0, 1, 0)	2.982

Equivalent Position	1	x, y, z
	2	-x, -y, -z
	3	-x, $\frac{1}{2}y$ , $\frac{1}{2}z$
	4	x, $\frac{1}{2}y$ , $\frac{1}{2}z$



projection on the [100] plane

Figure 5.5

Table 5.9  $S_5N_5^+S_3N_3O_4^-$

Final Calculated and Observed Structure Factors

M	K	L	FD	FC	M	K	L	FD	FC	M	K	L	FD	FC	M	K	L	FD	FC
0	0	2	14.9	-15.6	0	6	10	-4.3	5.6	1	1	-16	14.0	13.3	1	4	-15	-5.8	-4.6
0	0	4	143.6	-149.6	0	6	11	-4.3	-4.4	1	1	-15	-4.5	-1.4	1	4	-14	6.7	-8.3
0	0	6	39.4	39.8	0	6	12	32.4	32.7	1	1	-14	27.9	-26.6	1	4	-13	9.9	-10.0
0	0	8	92.9	-92.1	0	6	13	19.8	18.3	1	1	-13	20.8	-21.0	1	4	-12	-5.0	2.3
0	0	10	23.0	-23.1	0	6	14	14.6	14.0	1	1	-12	-5.8	3.5	1	4	-11	-4.8	-4.2
0	0	12	32.3	52.1	0	7	1	45.8	45.2	1	1	-11	8.7	-8.6	1	4	-10	12.1	-11.7
0	0	14	29.9	-30.2	0	7	2	46.4	45.7	1	1	-10	21.9	-22.2	1	4	-9	64.4	65.4
0	0	16	13.5	12.9	0	7	3	59.0	-58.3	1	1	-9	19.9	20.3	1	4	-8	-2.7	-1.4
0	1	1	71.6	-67.8	0	7	4	28.4	-28.1	1	1	-8	24.6	-23.9	1	4	-7	48.1	48.0
0	1	2	21.6	21.0	0	7	5	15.2	15.4	1	1	-7	43.4	42.9	1	4	-6	43.4	42.3
0	1	3	104.7	-106.4	0	7	6	37.1	-37.8	1	1	-6	36.1	37.5	1	4	-5	70.9	-69.0
0	1	4	5.0	4.7	0	7	7	9.6	-9.7	1	1	-5	14.4	15.3	1	4	-4	32.8	30.9
0	1	5	44.0	45.9	0	7	8	27.2	27.0	1	1	-4	64.4	63.9	1	4	-3	19.8	-14.7
0	1	6	-1.4	-0.4	0	7	9	30.5	-31.5	1	1	-3	36.2	-35.0	1	4	-2	54.4	-51.3
0	1	7	0.0	-2.5	0	7	10	17.2	-16.8	1	1	-2	58.8	-58.3	1	4	-1	24.3	-22.9
0	1	8	22.9	22.8	0	7	11	14.2	12.9	1	1	-1	39.5	-37.6	1	4	0	-1.6	9.0
0	1	9	14.3	-14.1	0	7	12	-4.8	4.9	1	1	0	11.2	11.9	1	4	1	58.2	-37.4
0	1	10	26.0	-26.5	0	7	13	13.0	-12.6	1	1	1	16.2	14.7	1	4	2	71.9	67.5
0	1	11	31.4	31.6	0	8	0	21.2	-20.4	1	1	2	57.8	-56.2	1	4	3	41.9	-39.0
0	1	12	18.6	-19.3	0	8	1	27.0	-27.8	1	1	3	42.8	42.4	1	4	4	47.8	-45.7
0	1	13	9.2	9.0	0	8	2	8.3	8.1	1	1	4	-4.8	-4.5	1	4	5	45.5	-44.2
0	1	14	8.6	7.3	0	8	3	67.6	-69.1	1	1	5	15.9	15.0	1	4	6	28.1	-26.8
0	1	15	7.8	7.3	0	8	4	21.1	20.9	1	1	6	30.9	-28.5	1	4	7	19.3	-18.9
0	1	16	14.7	13.8	0	8	5	14.0	-13.8	1	1	7	50.7	-49.2	1	4	8	10.2	-10.3
0	2	0	6.9	8.3	0	8	6	22.1	-21.8	1	1	8	11.8	12.3	1	4	9	42.8	43.8
0	2	1	6.9	-7.2	0	8	7	22.3	-22.5	1	1	9	21.3	-21.3	1	4	10	10.4	-10.2
0	2	2	132.6	137.8	0	8	8	17.0	-16.1	1	1	10	27.9	-28.2	1	4	11	30.5	30.5
0	2	3	6.5	9.7	0	8	9	12.6	13.4	1	1	11	-5.6	4.8	1	4	12	13.7	14.2
0	2	4	84.0	-80.8	0	8	10	0.0	0.7	1	1	12	30.5	-30.2	1	4	13	15.0	-14.5
0	2	5	61.3	-58.1	0	8	11	16.2	16.3	1	1	13	12.8	11.7	1	4	14	-3.5	4.8
0	2	6	97.2	-97.3	0	8	12	0.0	-1.0	1	1	14	-5.0	4.1	1	4	15	16.8	-16.5
0	2	7	11.2	10.2	0	8	13	-6.4	4.8	1	1	15	7.0	8.6	1	5	-15	11.5	-11.7
0	2	8	0.0	1.6	0	9	1	9.6	9.9	1	2	-16	-6.0	-3.9	1	5	-14	28.5	27.8
0	2	9	36.4	36.4	0	9	2	8.7	6.8	1	2	-15	18.2	-18.3	1	5	-13	27.5	27.5
0	2	10	30.0	28.1	0	9	3	33.6	35.0	1	2	-14	-3.6	3.0	1	5	-12	0.0	1.9
0	2	11	15.1	14.3	0	9	4	55.2	56.5	1	2	-13	11.1	11.2	1	5	-11	7.5	7.1
0	2	12	26.6	-28.0	0	9	5	17.9	-18.3	1	2	-12	-4.2	-1.5	1	5	-10	-4.3	-5.7
0	2	13	-2.0	1.0	0	9	6	14.0	-15.0	1	2	-11	61.6	62.3	1	5	-9	0.0	0.7
0	2	14	6.5	6.0	0	9	7	25.3	-25.0	1	2	-10	18.1	17.9	1	5	-8	13.1	-12.9
0	2	15	-5.4	-5.9	0	9	8	21.4	-22.2	1	2	-9	9.9	-9.8	1	5	-7	21.5	21.3
0	3	1	38.2	36.8	0	9	9	11.4	10.4	1	2	-8	-4.6	-4.7	1	5	-6	91.1	-91.0
0	3	2	170.0	-181.4	0	9	10	16.6	19.0	1	2	-7	26.0	24.9	1	5	-5	114.4	-114.3
0	3	3	196.8	213.3	0	9	11	0.0	0.7	1	2	-6	10.6	-11.6	1	5	-4	40.0	37.8
0	3	4	43.8	42.3	0	9	12	-2.1	-4.9	1	2	-5	15.8	-16.6	1	5	-3	10.5	-11.1
0	3	5	92.1	-94.0	0	10	0	-5.9	-5.1	1	2	-4	25.7	-24.4	1	5	-2	51.1	49.0
0	3	6	15.6	13.8	0	10	1	54.4	-54.2	1	2	-3	174.3	-184.9	1	5	-1	48.8	46.5
0	3	7	62.6	-61.3	0	10	2	-5.9	4.2	1	2	-2	31.8	-31.2	1	5	0	22.5	21.3
0	3	8	30.1	-29.8	0	10	3	9.1	-8.6	1	2	-1	95.7	95.2	1	5	1	20.0	-19.5
0	3	9	25.6	24.9	0	10	4	-5.8	5.6	1	2	0	14.1	13.8	1	5	2	77.1	74.8
0	3	10	16.2	16.8	0	10	5	7.4	7.0	1	2	1	124.8	127.6	1	5	3	16.2	17.6
0	3	11	23.4	-23.3	0	10	6	-1.9	-4.9	1	2	2	39.9	39.1	1	5	4	54.4	51.9
0	3	12	26.0	-26.1	0	10	7	10.5	-10.6	1	2	3	39.6	-38.5	1	5	5	71.2	69.4
0	3	13	28.0	28.0	0	10	8	-3.9	-3.5	1	2	4	42.9	40.1	1	5	6	10.5	-10.6
0	3	14	0.0	-0.3	0	10	9	17.3	17.8	1	2	5	27.9	-28.0	1	5	7	22.8	22.0
0	3	15	24.2	23.9	0	10	10	18.2	-17.6	1	2	6	9.6	10.3	1	5	8	30.0	-29.1
0	4	0	116.5	-121.4	0	10	11	-6.4	5.4	1	2	7	16.8	15.4	1	5	9	-3.9	0.5
0	4	1	32.2	31.9	0	11	1	-4.0	-3.6	1	2	8	-4.9	-5.5	1	5	10	20.7	-20.4
0	4	2	8.4	-7.8	0	11	2	11.4	11.1	1	2	9	39.9	40.3	1	5	11	28.3	-28.1
0	4	3	11.7	15.3	0	11	3	0.0	2.3	1	2	10	7.7	-7.9	1	5	12	12.4	12.9
0	4	4	0.0	10.8	0	11	4	18.1	-17.9	1	2	11	23.1	23.5	1	5	13	16.9	-17.1
0	4	5	40.6	40.1	0	11	5	6.5	-7.4	1	2	12	13.7	-12.6	1	5	14	13.6	12.6
0	4	6	72.2	-69.1	0	11	6	29.9	-29.8	1	2	13	18.1	18.0	1	6	-14	-4.1	-2.5
0	4	7	10.4	-10.1	0	11	7	-6.3	-7.0	1	2	14	12.4	-11.3	1	6	-13	16.1	-15.5
0	4	8	56.3	55.8	0	11	8	-2.1	2.8	1	2	15	-5.4	7.4	1	6	-12	0.0	-2.9
0	4	9	10.5	10.3	0	11	9	6.7	-7.6	1	3	-15	7.3	-8.1	1	6	-11	-4.9	-4.6
0	4	10	6.9	-6.9	0	12	0	28.6	28.3	1	3	-14	13.9	13.2	1	6	-10	14.8	15.5
0	4	11	-5.4	-5.7	0	12	1	21.7	22.6	1	3	-13	-5.0	-4.0	1	6	-9	9.2	8.6
0	4	12	0.0	0.1	0	12	2	19.7	19.8	1	3	-12	20.3	-21.5	1	6	-8	67.5	69.0
0	4	13	-2.7	3.0	0	12	3	-4.1	2.6	1	3	-11	43.1	43.7	1	6	-7	11.3	-11.4
0	4	14	14.2	14.0	0	12	4	7.2	-6.6	1	3	-10	40.1	-40.3	1	6	-6	12.4	13.8
0	4	15	-4.9	-4.0	0	12	5	0.0	0.6	1	3	-9	50.3	50.9	1	6	-5	25.0	25.5
0	5	1	94.1	95.3	0	12	6	7.2	-7.2	1	3	-8	31.0	-30.2	1	6	-4	34.3	-35.9
0	5	2	85.1	-83.3	0	12	7	20.8	20.4	1	3	-7	18.8	-18.2	1	6	-3	15.0	-15.7
0	5	3	25.4	-25.8	0	12	8	10.6	-10.3	1	3	-6	10.8	10.0	1	6	-2	41.8	-40.9
0	5	4	65.2	-65.5	0	13	1	15.9	-15.4	1	3	-5	6.8	6.8	1	6	-1	9.5	-8.2
0	5	5	16.7	-16.1	0	13	2	-5.6	-1.7	1	3	-4	8.8	-6.7	1	6	0	54.8	-54.5
0	5	6	17.8	17.6	0	13	3	0.0	3.0	1	3	-3	123.9	-126.3	1	6	1	42.7	42.9
0	5	7	27.1	-27.5	0	13	4	25.4	-25.5	1	3	-2	109.5	109.3	1	6	2	31.0	31.2
0	5	8	34.2	35.4	0	13	5	-4.7	4.9	1	3	-1	127.0	-133.3	1	6	3	34.9	-39.9
0	5	9	47.9	-48.3	1	0	-16	15.8	-15.8	1	3	0	5.3	-7.4	1	6	4	65.5	65.0
0	5	10	-1.1	-0.3	1	0	-14	11.5	10.9	1	3	1	68.7	69.1	1	6	5	22.6	-21.9
0	5	11	-3.3	2.9	1	0	-12	39.1	39.4	1	3	2	18.1	15.2	1	6	6		

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
1	7	-8	16.1	-13.7	1	11	-8	-2.9	-1.3	2	2	-13	14.2	14.6	2	5	-10	39.1	39.9
1	7	-7	52.6	-53.9	1	11	-7	19.7	19.4	2	2	-12	-2.2	2.4	2	5	-9	-5.5	-9.3
1	7	-6	13.9	14.0	1	11	-6	12.8	-13.0	2	2	-11	25.3	26.7	2	5	-8	7.7	7.5
1	7	-5	31.7	-32.5	1	11	-5	0.0	2.6	2	2	-10	-4.7	-2.0	2	5	-7	55.2	56.0
1	7	-4	8.7	-7.6	1	11	-4	8.9	-8.5	2	2	-9	35.7	36.3	2	5	-6	34.2	33.9
1	7	-3	37.0	37.1	1	11	-3	6.4	-6.9	2	2	-8	11.6	11.4	2	5	-5	25.4	26.6
1	7	-2	46.4	-46.5	1	11	-2	10.9	10.3	2	2	-7	79.6	78.7	2	5	-4	25.7	28.9
1	7	-1	50.8	50.1	1	11	-1	8.2	-8.0	2	2	-6	25.6	25.0	2	5	-3	36.3	-39.0
1	7	0	10.2	9.0	1	11	0	24.4	24.7	2	2	-5	21.0	-21.4	2	5	-2	83.3	-87.0
1	7	1	34.0	-33.2	1	11	1	8.3	-8.3	2	2	-4	38.1	38.1	2	5	-1	54.1	-52.8
1	7	2	8.3	-9.4	1	11	2	19.2	19.6	2	2	-3	6.6	6.1	2	5	0	14.6	-13.5
1	7	3	-1.1	-3.0	1	11	3	19.6	19.0	2	2	-2	0.0	-2.3	2	5	1	61.0	-68.5
1	7	4	48.5	-48.9	1	11	4	-3.7	1.4	2	2	-1	66.0	65.5	2	5	2	52.8	51.2
1	7	5	6.2	-7.3	1	11	5	-2.7	-1.8	2	2	0	128.9	-134.5	2	5	3	71.0	-78.0
1	7	6	8.7	9.3	1	11	6	14.5	-12.2	2	2	1	102.2	-103.2	2	5	4	0.0	1.4
1	7	7	17.0	19.0	1	11	7	-6.3	-6.3	2	2	2	42.4	-42.5	2	5	5	32.1	32.4
1	7	8	7.5	6.0	1	11	8	0.0	2.0	2	2	3	27.3	-26.8	2	5	6	37.6	37.4
1	7	9	21.3	21.5	1	11	9	11.5	-10.1	2	2	4	0.0	2.8	2	5	7	64.0	64.3
1	7	10	0.0	-4.3	1	12	-8	11.4	11.3	2	2	5	-2.4	1.5	2	5	8	14.3	-15.5
1	7	11	19.7	-20.5	1	12	-7	-4.0	-4.3	2	2	6	34.5	32.8	2	5	9	8.5	9.0
1	7	12	10.4	11.5	1	12	-6	23.6	-23.6	2	2	7	11.4	11.7	2	5	10	24.8	-25.4
1	7	13	17.2	-16.7	1	12	-5	14.0	13.4	2	2	8	41.2	41.0	2	5	11	10.1	8.5
1	8	-13	0.0	1.0	1	12	-4	14.3	-14.3	2	2	9	16.2	15.9	2	5	12	-1.9	1.4
1	8	-12	9.6	-9.8	1	12	-3	-2.9	-0.2	2	2	10	11.8	11.9	2	5	13	16.4	11.4
1	8	-11	-1.5	-1.0	1	12	-2	18.9	19.4	2	2	11	31.2	-32.2	2	5	14	-5.8	-6.2
1	8	-10	30.7	31.7	1	12	-1	14.4	-14.2	2	2	12	16.3	-15.7	2	6	-14	29.0	-28.4
1	8	-9	25.0	-24.5	1	12	0	31.5	-31.6	2	2	13	12.2	-12.3	2	6	-13	-4.0	-0.1
1	8	-8	-2.5	0.7	1	12	1	16.9	-17.0	2	2	14	14.8	14.7	2	6	-12	25.5	-25.0
1	8	-7	29.4	-29.9	1	12	2	15.4	15.2	2	2	15	13.3	14.5	2	6	-11	19.3	19.6
1	8	-6	13.7	13.0	1	12	3	-5.9	-4.3	2	3	-15	0.0	-2.6	2	6	-10	12.9	12.2
1	8	-5	14.4	-15.0	1	12	4	22.6	22.7	2	3	-14	12.2	11.7	2	6	-9	-4.4	-3.3
1	8	-4	11.0	-13.0	1	12	5	-6.0	6.6	2	3	-13	19.1	-19.5	2	6	-8	11.7	-11.9
1	8	-3	24.7	23.8	1	12	6	7.1	-6.9	2	3	-12	-4.6	-2.6	2	6	-7	64.9	-65.8
1	8	-2	64.6	-66.0	1	12	7	-6.7	7.4	2	3	-11	52.5	-54.1	2	6	-6	45.5	43.2
1	8	-1	49.3	49.6	1	13	-5	7.4	-8.2	2	3	-10	31.6	-32.0	2	6	-5	22.6	22.9
1	8	0	6.9	-6.0	1	13	-4	0.0	-2.7	2	3	-9	38.3	37.9	2	6	-4	31.1	30.9
1	8	1	42.1	42.9	1	13	-3	19.3	14.4	2	3	-8	10.8	-9.2	2	6	-3	7.0	-6.4
1	8	2	46.4	46.9	1	13	-2	9.7	9.3	2	3	-7	60.2	61.1	2	6	-2	17.3	-17.3
1	8	3	36.6	37.4	1	13	-1	17.4	-17.0	2	3	-6	7.5	-6.7	2	6	-1	43.2	-41.9
1	8	4	28.3	29.4	1	13	0	16.3	17.0	2	3	-5	13.4	-13.2	2	6	0	39.7	39.6
1	8	5	9.5	9.0	1	13	1	7.7	-4.8	2	3	-4	45.3	-46.3	2	6	1	65.2	65.4
1	8	6	17.6	18.7	1	13	2	9.1	9.1	2	3	-3	73.9	76.1	2	6	2	10.4	-10.4
1	8	7	23.4	-23.6	1	13	3	23.1	23.6	2	3	-2	12.4	10.4	2	6	3	17.6	-17.2
1	8	8	23.1	-23.3	1	13	4	0.0	-0.1	2	3	-1	54.1	-54.9	2	6	4	36.1	-34.7
1	8	9	17.9	-17.5	1	13	5	8.4	-9.4	2	3	0	0.0	2.1	2	6	5	43.7	-42.4
1	8	10	8.4	-7.9	2	0	-14	-3.8	0.7	2	3	1	111.0	-119.5	2	6	6	31.9	31.7
1	8	11	14.0	-14.2	2	0	-14	14.4	-14.4	2	3	2	5.3	-2.2	2	6	7	59.1	60.3
1	8	12	0.0	-4.2	2	0	-12	0.0	-3.2	2	3	3	57.2	58.8	2	6	8	20.9	-21.5
1	9	-12	-4.4	3.7	2	0	-10	11.4	11.1	2	3	4	76.2	77.2	2	6	9	-1.6	-3.5
1	9	-11	35.4	34.8	2	0	-8	25.1	-25.1	2	3	5	79.4	-77.9	2	6	10	6.5	-6.0
1	9	-10	-6.0	4.6	2	0	-6	121.6	123.6	2	3	6	-4.0	-1.8	2	6	11	-6.3	-7.3
1	9	-9	7.2	7.8	2	0	-4	128.1	130.6	2	3	7	7.1	7.4	2	6	12	-4.9	6.7
1	9	-8	22.6	22.6	2	0	-2	112.8	-121.1	2	3	8	22.8	-22.7	2	6	13	0.0	3.0
1	9	-7	-3.5	-2.4	2	0	0	79.1	-78.2	2	3	9	86.9	88.3	2	7	-13	-1.8	-3.4
1	9	-6	10.7	10.3	2	0	2	231.0	-259.1	2	3	10	11.0	11.7	2	7	-12	0.0	-6.7
1	9	-5	11.3	11.2	2	0	4	53.2	-52.6	2	3	11	26.3	-26.8	2	7	-11	24.8	24.7
1	9	-4	28.8	-28.7	2	0	6	141.6	143.5	2	3	12	-3.2	-1.8	2	7	-10	-2.2	-1.9
1	9	-3	20.5	-19.2	2	0	8	12.3	11.8	2	3	13	26.8	-27.3	2	7	-9	-1.9	4.6
1	9	-2	0.0	-0.9	2	0	10	5.9	1.6	2	3	14	0.0	-0.6	2	7	-8	14.4	15.0
1	9	-1	-5.5	4.5	2	0	12	33.4	34.1	2	3	15	-2.3	-1.7	2	7	-7	20.6	-19.6
1	9	0	11.3	-11.0	2	0	14	36.3	-35.3	2	4	-15	9.9	-9.0	2	7	-6	7.7	-8.0
1	9	1	18.6	17.8	2	1	-16	-5.8	7.2	2	4	-14	-3.7	4.9	2	7	-5	51.0	52.0
1	9	2	33.0	-32.6	2	1	-15	10.4	-9.2	2	4	-13	6.6	-4.6	2	7	-4	24.3	24.1
1	9	3	47.0	-48.8	2	1	-14	12.9	11.6	2	4	-12	7.1	-8.8	2	7	-3	9.6	-9.5
1	9	4	6.8	-5.3	2	1	-13	35.4	-35.7	2	4	-11	13.2	14.1	2	7	-2	7.9	-7.9
1	9	5	27.5	27.7	2	1	-12	0.0	-0.4	2	4	-10	21.7	-21.6	2	7	-1	50.4	-50.3
1	9	6	-5.3	-3.7	2	1	-11	6.5	5.9	2	4	-9	0.0	-1.4	2	7	0	-3.6	2.7
1	9	7	12.8	12.6	2	1	-10	56.8	-57.6	2	4	-8	33.3	33.8	2	7	1	16.7	-16.9
1	9	8	13.3	13.5	2	1	-9	0.0	-1.0	2	4	-7	30.7	-30.9	2	7	2	-5.2	6.5
1	9	9	25.5	-25.0	2	1	-8	15.9	-15.4	2	4	-6	28.9	-28.8	2	7	3	20.2	-20.9
1	9	10	23.5	23.4	2	1	-7	-3.2	1.4	2	4	-5	21.5	-20.6	2	7	4	31.1	-31.7
1	9	11	-6.0	-4.1	2	1	-6	24.8	-23.0	2	4	-4	7.0	-5.2	2	7	5	32.9	32.3
1	10	-11	10.4	-10.3	2	1	-5	-4.5	5.5	2	4	-3	35.1	35.7	2	7	6	11.3	-11.2
1	10	-10	11.6	-12.4	2	1	-4	81.7	-79.7	2	4	-2	59.4	59.2	2	7	7	30.2	31.0
1	10	-9	15.1	-15.1	2	1	-3	97.4	-98.9	2	4	-1	36.8	37.5	2	7	8	10.9	11.7
1	10	-8	16.7	-16.5	2	1	-2	77.5	76.7	2	4	0	45.4	-44.1	2	7	9	10.8	-10.4
1	10	-7	9.8	-9.2	2	1	-1	76.8	77.2	2	4	1	23.5	-22.6	2	7	10	16.5	-15.7
1	10	-6	-2.7	2.9	2	1	0	25.8	25.6	2	4	2	44.0	43.7	2	7	11	6.6	6.4
1	10	-5	11.0	-12.1	2	1	1	147.2	155.4	2	4	3	53.4	-53.3	2	7	12	-4.7	5.7
1	10	-4	17.3	-18.2	2	1	2	36.7	-34.7	2	4	4	58.3	55.4	2	7	13	-4.7	4.1
1	10	-3	20.7	19.9	2	1	3	31.2	-31.9	2	4	5	6.3	-7.0	2	8	-13	13.3	12.6
1	10	-2	29.5	-29.4	2	1	4	46.4	45.4	2	4	6	51.0	-50.7	2	8	-12	15.0	-14.6
1	10	-1																	

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
2	8	2	16.9	-16.4	2	13	-1	-0.9	1.2	3	3	-1	11.7	-11.1	3	6	7	23.1	23.4
2	8	3	47.5	48.0	2	13	0	17.2	-14.2	3	3	0	75.7	-73.9	3	6	8	15.3	15.8
2	8	4	11.3	10.4	2	13	1	14.2	15.0	3	3	1	25.8	27.0	3	6	9	13.2	-13.3
2	8	5	56.7	57.2	2	13	2	20.8	21.4	3	3	2	26.7	25.3	3	6	10	34.2	34.4
2	8	6	0.0	1.1	2	13	3	8.2	7.0	3	3	3	19.8	-20.1	3	6	11	0.0	-0.4
2	8	7	-4.6	-6.5	2	13	4	9.5	8.6	3	3	4	11.7	11.7	3	6	12	19.2	-15.7
2	8	8	-5.6	5.9	3	C	-14	17.2	17.8	3	3	5	112.9	-112.7	3	6	13	11.5	10.3
2	8	9	-2.2	0.5	3	0	-12	-4.0	-5.9	3	3	6	55.2	-56.0	3	7	-13	-4.9	-5.9
2	8	10	22.3	21.6	3	0	-10	77.7	-78.4	3	3	7	9.7	9.5	3	7	-12	8.8	-7.8
2	8	11	9.9	-8.8	3	0	-8	-3.2	-1.0	3	3	8	0.0	-0.3	3	7	-11	8.0	-8.2
2	8	12	7.3	-7.3	3	0	-6	58.1	57.5	3	3	9	9.6	-9.8	3	7	-10	-6.1	5.7
2	9	-12	6.7	4.3	3	0	-4	66.2	-61.7	3	3	10	68.6	70.8	3	7	-9	-3.9	2.7
2	9	-11	18.3	-17.7	3	0	-2	41.5	45.6	3	3	11	13.5	13.4	3	7	-8	26.9	-27.3
2	9	-10	7.0	-4.1	3	0	0	23.6	25.8	3	3	12	0.0	2.6	3	7	-7	20.3	19.7
2	9	-9	10.7	-10.5	3	0	2	151.1	-152.9	3	3	13	38.1	37.7	3	7	-6	23.2	23.2
2	9	-8	11.0	10.5	3	0	4	31.4	29.9	3	3	14	-2.2	-1.9	3	7	-5	46.2	57.8
2	9	-7	23.2	23.6	3	0	6	53.6	-52.7	3	4	-15	-4.8	4.6	3	7	-4	28.2	28.2
2	9	-6	7.4	-8.0	3	0	8	105.8	-108.8	3	4	-14	-2.9	4.4	3	7	-3	-4.3	-4.3
2	9	-5	21.9	22.1	3	0	10	65.1	65.8	3	4	-13	23.5	21.9	3	7	-2	33.3	-34.2
2	9	-4	28.2	-28.8	3	0	12	47.9	43.6	3	4	-12	-3.9	-2.4	3	7	-1	-2.8	-2.1
2	9	-3	17.6	17.3	3	0	14	11.5	10.3	3	4	-11	17.5	-17.8	3	7	0	45.4	46.3
2	9	-2	65.2	65.7	3	1	-15	-1.3	1.5	3	4	-10	6.7	-8.1	3	7	1	36.1	-36.1
2	9	-1	6.3	5.5	3	1	-14	25.7	-24.9	3	4	-9	11.3	-10.8	3	7	2	24.0	24.2
2	9	0	-4.0	-0.3	3	1	-13	-1.5	7.4	3	4	-8	71.2	21.0	3	7	3	20.5	20.7
2	9	1	41.5	-42.3	3	1	-12	34.3	34.7	3	4	-7	-2.9	4.0	3	7	4	48.7	-49.8
2	9	2	42.6	-43.0	3	1	-11	10.8	10.1	3	4	-6	32.6	-32.3	3	7	5	8.5	8.8
2	9	3	8.7	-9.6	3	1	-10	37.6	37.8	3	4	-5	45.0	-44.9	3	7	6	25.0	25.2
2	9	4	0.0	-3.4	3	1	-9	28.6	-28.8	3	4	-4	-4.1	4.1	3	7	7	13.1	-12.6
2	9	5	15.2	14.1	3	1	-8	-4.5	3.5	3	4	-3	29.6	29.9	3	7	8	-3.6	-5.8
2	9	6	18.6	-18.8	3	1	-7	19.9	-20.3	3	4	-2	42.1	39.8	3	7	9	0.0	-1.4
2	9	7	0.0	-1.1	3	1	-6	16.1	17.0	3	4	-1	48.5	47.5	3	7	10	18.0	-18.3
2	9	8	-4.9	-4.0	3	1	-5	25.3	27.3	3	4	0	14.0	12.9	3	7	11	14.7	13.8
2	9	9	10.5	9.9	3	1	-4	76.4	-77.2	3	4	1	9.2	-9.7	3	7	12	9.0	8.2
2	9	10	23.9	24.0	3	1	-3	21.5	19.8	3	4	2	14.7	15.0	3	8	-12	-3.8	4.2
2	9	11	5.7	-9.9	3	1	-2	124.0	-129.1	3	4	3	34.4	34.4	3	8	-11	6.8	6.3
2	10	-11	0.0	0.4	3	1	-1	15.5	18.5	3	4	4	9.7	-8.6	3	8	-10	28.3	28.3
2	10	-10	0.0	-2.0	3	1	0	100.4	100.7	3	4	5	5.5	5.7	3	8	-9	17.5	17.7
2	10	-9	12.0	-11.5	3	1	1	46.7	43.4	3	4	6	26.7	25.9	3	8	-8	42.0	-42.4
2	10	-8	21.7	21.6	3	1	2	31.2	-27.4	3	4	7	14.4	-15.7	3	8	-7	-5.0	3.5
2	10	-7	20.0	20.1	3	1	3	39.5	35.3	3	4	8	29.4	29.0	3	8	-6	37.9	-39.5
2	10	-6	0.0	-3.4	3	1	4	10.2	-10.7	3	4	9	6.5	-5.5	3	8	-5	17.8	18.6
2	10	-5	-3.5	3.4	3	1	5	6.8	6.9	3	4	10	12.7	-12.4	3	8	-4	46.4	47.5
2	10	-4	22.5	-22.2	3	1	6	-4.7	-1.3	3	4	11	23.9	-24.2	3	8	-3	0.0	-2.2
2	10	-3	39.7	-40.6	3	1	7	26.8	-24.2	3	4	12	-1.3	-1.5	3	8	-2	23.7	23.9
2	10	-2	0.0	2.8	3	1	8	0.0	0.2	3	4	13	12.2	-11.7	3	8	-1	34.8	-34.7
2	10	-1	-4.4	-2.6	3	1	9	30.6	29.9	3	4	14	-5.9	-4.6	3	8	0	40.5	41.8
2	10	0	17.3	-17.5	3	1	10	9.1	-9.9	3	5	-14	-3.8	-3.1	3	8	1	20.7	-21.3
2	10	1	-3.5	-2.8	3	1	11	7.7	9.2	3	5	-13	16.1	15.4	3	8	2	0.0	2.9
2	10	2	13.2	-13.1	3	1	12	31.2	31.8	3	5	-12	32.0	-31.7	3	8	3	26.4	-26.5
2	10	3	26.5	26.4	3	1	13	27.1	-22.4	3	5	-11	24.6	-24.8	3	8	4	63.8	-65.9
2	10	4	16.4	16.6	3	1	14	-4.5	0.3	3	5	-10	26.1	-26.6	3	8	5	9.0	-8.2
2	10	5	24.8	25.0	3	2	-15	7.4	-6.0	3	5	-9	28.3	-28.6	3	8	6	17.5	-17.3
2	10	6	-4.8	3.9	3	2	-14	-1.4	1.4	3	5	-8	65.2	66.5	3	8	7	17.0	16.5
2	10	7	14.5	-15.5	3	2	-13	20.7	-21.0	3	5	-7	66.9	68.5	3	8	8	24.9	25.3
2	10	8	10.0	10.6	3	2	-12	21.6	-20.1	3	5	-6	9.8	9.4	3	8	9	20.7	20.2
2	10	9	9.7	-9.3	3	2	-11	-3.9	2.5	3	5	-5	-1.8	2.5	3	8	10	-5.5	4.1
2	10	10	9.5	7.3	3	2	-10	-5.5	6.0	3	5	-4	18.4	-18.0	3	8	11	22.2	23.1
2	11	-9	-5.5	-3.6	3	2	-9	69.3	-70.1	3	5	-3	43.7	42.8	3	9	-11	0.0	-2.3
2	11	-8	-6.3	-5.7	3	2	-8	9.3	-10.2	3	5	-2	6.9	7.6	3	9	-10	-1.5	-2.8
2	11	-7	10.0	10.6	3	2	-7	17.1	-16.9	3	5	-1	42.1	41.9	3	9	-9	24.5	-24.0
2	11	-6	0.0	2.5	3	2	-6	42.4	41.7	3	5	0	-1.6	1.7	3	9	-8	8.5	-9.2
2	11	-5	-6.9	5.7	3	2	-5	88.9	89.4	3	5	1	30.9	-31.0	3	9	-7	29.0	-28.2
2	11	-4	6.5	-7.3	3	2	-4	49.2	49.0	3	5	2	27.7	-26.6	3	9	-6	14.4	-14.7
2	11	-3	19.7	19.0	3	2	-3	11.7	11.5	3	5	3	43.1	-41.9	3	9	-5	7.6	6.4
2	11	-2	25.3	-25.5	3	2	-2	32.3	-31.6	3	5	4	17.5	-17.2	3	9	-4	10.2	10.0
2	11	-1	-2.7	-1.5	3	2	-1	38.0	37.6	3	5	5	7.0	8.1	3	9	-3	-0.9	0.1
2	11	0	15.6	16.7	3	2	0	-2.6	-2.4	3	5	6	38.0	-38.2	3	9	-2	28.2	28.4
2	11	1	0.0	-2.6	3	2	1	50.9	48.8	3	5	7	52.4	-53.7	3	9	-1	20.7	-21.4
2	11	2	-1.2	-2.3	3	2	2	44.4	43.3	3	5	8	31.0	31.9	3	9	0	11.5	-11.5
2	11	3	-2.8	-3.5	3	2	3	96.2	-96.1	3	5	9	-6.1	-5.2	3	9	1	31.0	31.6
2	11	4	0.0	0.7	3	2	4	46.0	-44.5	3	5	10	37.6	37.9	3	9	2	10.4	11.0
2	11	5	-5.9	-6.4	3	2	5	5.9	7.3	3	5	11	27.4	26.5	3	9	3	24.6	-25.3
2	11	6	17.4	17.4	3	2	6	15.1	-14.6	3	5	12	-6.1	6.4	3	9	4	26.7	26.1
2	11	7	10.0	10.2	3	2	7	35.7	35.6	3	5	13	20.4	20.1	3	9	5	0.0	-2.4
2	11	8	18.4	18.4	3	2	8	7.5	8.2	3	6	-14	-5.8	6.2	3	9	6	10.1	-9.4
2	11	9	-6.5	6.0	3	2	9	18.0	-18.5	3	6	-13	8.5	9.4	3	9	7	8.1	7.6
2	12	-7	-2.1	-3.8	3	2	10	14.6	-14.9	3	6	-12	17.4	17.7	3	9	8	7.8	-6.9
2	12	-6	-5.1	5.1	3	2	11	22.4	-23.2	3	6	-11	14.5	14.3	3	9	9	-6.3	-4.7
2	12	-5	23.8	23.8	3	2	12	23.7	23.6	3	6	-10	16.4	-15.9	3	9	10	10.4	-10.6
2	12	-4	20.9	20.4	3	2	13	-9.1	-2.9	3	6	-9	10.3	9.9	3	10	-10	-2.0	0.4
2	12	-3	-1.6	-1.0	3	2	14	13.8	14.5	3	6	-8	52.0	-54.0	3	10	-9	15.0	14.7
2	12	-2	11.5	-11.3	3	3	-15	19.5	18.4	3	6	-7	11.4	-10.6	3	10	-8	18.0	18.8
2	12	-1	16.5	-17.1	3	3	-1												

H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC
3	10	6	14.1	13.5	4	2	-9	95.9	-98.2	4	5	0	-3.1	6.3	4	9	-5	20.6	-20.1
3	10	7	18.3	-18.3	4	2	-8	0.0	2.6	4	5	1	10.6	10.6	4	9	-4	13.5	-14.5
3	10	8	-4.8	-5.4	4	2	-7	52.2	53.1	4	5	2	46.9	46.3	4	9	-3	34.0	-33.9
3	10	9	31.3	30.0	4	2	-6	43.0	-42.2	4	5	3	72.3	73.0	4	9	-2	6.4	6.3
3	11	-9	12.4	-12.6	4	2	-5	60.8	-60.3	4	5	4	95.0	-95.6	4	9	-1	8.1	6.3
3	11	-8	-4.6	-5.1	4	2	-4	-3.6	-0.3	4	5	5	-3.0	-3.6	4	9	0	21.5	-21.9
3	11	-7	12.3	-11.8	4	2	-3	72.6	-70.2	4	5	6	21.6	-21.9	4	9	1	16.9	17.2
3	11	-6	18.1	18.2	4	2	-2	33.5	-32.1	4	5	7	51.0	-51.2	4	9	2	-2.8	3.3
3	11	-5	24.7	-24.1	4	2	-1	86.4	86.9	4	5	8	12.6	12.8	4	9	3	13.2	13.4
3	11	-4	-5.1	2.4	4	2	0	34.4	33.9	4	5	9	19.0	-19.0	4	9	4	47.7	48.0
3	11	-3	-8.1	5.2	4	2	1	53.5	-51.1	4	5	10	12.4	-13.3	4	9	5	13.2	13.3
3	11	-2	7.5	7.6	4	2	2	49.5	48.1	4	5	11	6.8	-6.3	4	9	6	-3.6	0.4
3	11	-1	36.0	36.2	4	2	3	12.3	12.1	4	5	12	13.9	15.4	4	9	7	18.8	-18.4
3	11	0	9.6	-9.1	4	2	4	39.1	37.4	4	5	13	0.0	1.2	4	9	8	8.2	-8.4
3	11	1	7.3	-8.1	4	2	5	62.7	63.0	4	6	-13	10.3	-9.4	4	9	9	0.0	-3.7
3	11	2	34.9	-34.2	4	2	6	48.3	-48.4	4	6	-12	30.5	31.1	4	9	10	9.7	9.2
3	11	3	0.0	0.1	4	2	7	80.5	-82.5	4	6	-11	14.9	-14.4	4	10	-10	9.5	-9.4
3	11	4	-3.7	5.8	4	2	8	12.9	-12.6	4	6	-10	14.7	-15.2	4	10	-9	-3.7	5.1
3	11	5	-3.1	-3.2	4	2	9	16.1	-16.2	4	6	-9	-4.1	0.9	4	10	-8	-5.2	5.5
3	11	6	10.4	11.3	4	2	10	-5.4	-4.6	4	6	-8	0.0	3.9	4	10	-7	11.8	-11.2
3	11	7	-2.5	-1.3	4	2	11	14.5	15.0	4	6	-7	24.2	24.4	4	10	-6	9.7	-10.1
3	11	8	7.8	7.6	4	2	12	-2.3	-1.2	4	6	-6	10.1	-10.0	4	10	-5	7.0	-7.7
3	12	-7	13.6	12.3	4	2	13	0.0	0.0	4	6	-5	24.6	25.3	4	10	-4	-4.1	-2.3
3	12	-6	-2.4	3.3	4	2	14	-4.7	2.6	4	6	-4	13.6	-12.3	4	10	-3	17.3	17.9
3	12	-5	6.7	4.6	4	3	-15	14.2	-13.4	4	6	-3	7.6	7.3	4	10	-2	37.3	38.3
3	12	-4	-1.3	2.8	4	3	-14	19.7	-19.4	4	6	-2	38.6	-38.9	4	10	-1	14.6	13.9
3	12	-3	14.4	-13.7	4	3	-13	12.9	12.6	4	6	-1	34.3	-35.1	4	10	0	-5.1	5.9
3	12	-2	14.9	13.3	4	3	-12	-4.1	-4.6	4	6	0	11.3	10.4	4	10	1	14.8	14.8
3	12	-1	10.2	9.5	4	3	-11	30.1	30.9	4	6	1	30.3	29.9	4	10	2	7.1	-5.0
3	12	0	10.2	-10.6	4	3	-10	27.0	28.1	4	6	2	12.8	13.0	4	10	3	14.4	-14.1
3	12	1	17.3	17.3	4	3	-9	10.7	10.8	4	6	3	24.7	-24.3	4	10	4	10.1	9.2
3	12	2	9.3	-8.9	4	3	-8	22.7	23.4	4	6	4	-4.9	-2.2	4	10	5	20.2	-20.1
3	12	3	-5.6	-5.5	4	3	-7	32.7	-32.9	4	6	5	9.1	10.0	4	10	6	16.7	-17.0
3	12	4	-2.3	-0.7	4	3	-6	10.1	10.2	4	6	6	15.1	15.3	4	10	7	0.0	-2.5
3	12	5	0.0	1.5	4	3	-5	23.4	-24.0	4	6	7	13.6	12.3	4	10	8	16.3	-15.4
3	12	6	17.9	-17.6	4	3	-4	13.9	13.6	4	6	8	-4.4	4.7	4	11	-8	18.8	-18.2
3	12	7	12.5	12.8	4	3	-3	15.7	14.7	4	6	9	24.7	-25.0	4	11	-7	0.0	-2.6
3	13	-3	16.1	15.4	4	3	-2	34.3	34.7	4	6	10	18.1	-17.7	4	11	-6	-3.2	5.4
3	13	-2	12.0	-11.4	4	3	-1	12.9	12.3	4	6	11	0.0	0.1	4	11	-5	31.5	-31.0
3	13	-1	-2.1	-3.6	4	3	0	43.0	-41.0	4	6	12	-3.7	3.4	4	11	-4	15.0	13.6
3	13	0	15.1	-15.4	4	3	1	12.4	12.9	4	7	-13	9.3	-8.6	4	11	-3	0.0	-0.3
3	13	1	-2.1	2.9	4	3	2	26.1	-26.6	4	7	-12	6.8	7.0	4	11	-2	11.1	-13.2
3	13	2	9.0	-9.0	4	3	3	62.4	61.8	4	7	-11	0.0	-3.4	4	11	-1	11.9	-12.2
3	13	3	-5.6	7.0	4	3	4	-1.7	0.7	4	7	-10	25.3	-25.0	4	11	0	13.8	13.6
4	0	-14	9.7	10.2	4	3	5	13.8	13.8	4	7	-9	9.1	-8.2	4	11	1	11.1	-8.2
4	0	-12	15.3	-15.0	4	3	6	44.5	-44.5	4	7	-8	-1.7	4.6	4	11	2	-5.2	2.3
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4	0	-6	6.4	6.1	4	3	9	27.4	-28.6	4	7	-5	12.1	11.1	4	11	5	0.0	-0.2
4	0	-4	114.1	-114.0	4	3	10	26.6	27.4	4	7	-4	29.0	-29.1	4	11	6	6.7	-6.2
4	0	-2	12.5	10.2	4	3	11	30.3	-30.3	4	7	-3	37.5	-37.9	4	11	7	-3.0	-0.3
4	0	0	110.2	110.4	4	3	12	9.0	-10.2	4	7	-2	8.2	7.1	4	12	-6	18.3	-18.9
4	0	2	109.3	108.0	4	3	13	-5.2	7.3	4	7	-1	18.0	18.0	4	12	-5	-3.9	-1.5
4	0	4	40.3	38.5	4	4	-14	21.3	20.8	4	7	0	27.4	27.1	4	12	-4	0.0	-1.4
4	0	6	0.0	-1.2	4	4	-13	11.6	-12.3	4	7	1	58.8	59.0	4	12	-3	8.3	-8.9
4	0	8	92.6	-93.7	4	4	-12	9.9	7.8	4	7	2	-2.8	-2.4	4	12	-2	7.0	5.5
4	0	10	22.3	-22.3	4	4	-11	74.1	-23.9	4	7	3	7.5	-7.7	4	12	-1	-5.3	6.2
4	0	12	0.0	0.7	4	4	-10	0.0	-4.1	4	7	4	26.6	27.3	4	12	0	-4.6	4.1
4	0	14	7.1	-5.6	4	4	-9	-4.0	6.0	4	7	5	17.2	-17.2	4	12	1	9.9	9.0
4	1	-15	-2.4	3.2	4	4	-8	25.9	5.7	4	7	6	21.6	21.5	4	12	2	29.8	29.9
4	1	-14	27.0	-26.5	4	4	-7	9.6	-8.8	4	7	7	10.7	-11.0	4	12	3	6.1	-8.9
4	1	-13	28.7	28.6	4	4	-6	52.7	-53.4	4	7	8	-2.9	-5.6	4	12	4	-3.4	0.4
4	1	-12	30.6	31.5	4	4	-5	27.7	-27.6	4	7	9	10.9	-12.5	5	0	-14	14.6	-14.8
4	1	-11	36.9	37.6	4	4	-4	3.4	-3.3	4	7	10	-2.2	1.7	5	0	-12	21.8	-22.2
4	1	-10	24.3	-24.3	4	4	-3	26.8	26.7	4	7	11	10.4	8.9	5	0	-10	33.8	34.7
4	1	-9	33.4	-32.9	4	4	-2	50.2	-49.4	4	8	-12	16.3	16.7	5	0	-8	4.0	4.6
4	1	-8	30.1	31.4	4	4	-1	37.7	37.0	4	8	-11	0.0	-3.1	5	0	-6	14.1	-14.1
4	1	-7	37.4	-38.0	4	4	0	52.2	-51.9	4	8	-10	18.8	19.1	5	0	-4	27.8	-29.4
4	1	-6	73.6	72.8	4	4	1	4.0	2.2	4	8	-9	-4.2	-4.2	5	0	-2	31.4	-30.7
4	1	-5	46.4	45.3	4	4	2	68.1	68.3	4	8	-8	31.1	-31.3	5	0	0	7.9	8.8
4	1	-4	26.9	-28.5	4	4	3	6.7	-4.2	4	8	-7	0.0	0.4	5	0	2	-5.1	-5.4
4	1	-3	0.0	-0.6	4	4	4	16.0	15.7	4	8	-6	13.5	14.1	5	0	4	56.7	55.5
4	1	-2	28.1	27.4	4	4	5	9.1	-9.4	4	8	-5	10.2	-10.2	5	0	6	57.4	58.8
4	1	-1	25.0	-24.4	4	4	6	24.3	25.0	4	8	-4	6.2	-5.2	5	0	8	17.2	17.6
4	1	0	14.0	14.2	4	4	7	14.6	14.4	4	8	-3	11.4	11.6	5	0	10	26.6	25.4
4	1	1	50.5	-31.0	4	4	8	19.2	-20.1	4	8	-2	36.6	-37.0	5	0	12	23.2	-23.7
4	1	2	42.1	-44.0	4	4	9	13.8	13.0	4	8	-1	40.7	40.6	5	1	-15	0.0	2.0
4	1	3	76.9	-75.4	4	4	10	9.4	-9.7	4	8	0	39.7	40.2	5	1	-14	-4.4	5.4
4	1	4	44.2	42.0	4	4	11	-7.0	1.9	4	8	1	31.5	-31.3	5	1	-13	-4.1	-4.6
4	1	5	28.4	26.5	4	4	12	-6.3	7.4	4	8	2	7.4	7.6	5	1	-12	-4.4	1.2
4	1	6	6.8	7.7	4	4	13	-3.3	2.2	4	8	3	6.2	-5.8	5	1	-11	-2.8	-0.6
4	1	7	43.2	43.5	4	4	14	-3.5	-0.6	4	8	4	14.9	-14.8	5	1	-10	7.2	-6.7
4	1	8	-3.5	4.1	4	4	1												



H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC
5	1	4	43.1	-43.4	5	5	-11	-9.6	-4.8	5	9	-8	10.9	10.1	6	2	-14	7.4	-8.2
5	1	5	24.2	26.4	5	5	-10	10.9	10.2	5	9	-7	13.8	13.8	6	2	-13	-6.5	-6.3
5	1	6	4.3	-6.7	5	5	-9	21.8	22.2	5	9	-6	6.5	4.8	6	2	-12	11.2	11.6
5	1	7	24.1	-24.5	5	5	-8	13.2	-12.7	5	9	-5	-3.9	-0.7	6	2	-11	-5.5	5.7
5	1	8	15.1	14.6	5	5	-7	-3.7	-0.7	5	9	-4	-2.5	-1.6	6	2	-10	0.0	2.9
5	1	9	20.2	-20.4	5	5	-6	21.6	-27.2	5	9	-3	6.6	-7.1	6	2	-9	12.0	-11.6
5	1	10	11.7	-12.4	5	5	-5	55.2	-56.4	5	9	-2	-5.3	-3.7	6	2	-8	23.2	-23.1
5	1	11	-2.2	4.8	5	5	-4	30.3	-30.6	5	9	-1	-6.1	4.0	6	2	-7	90.4	94.8
5	1	12	-4.4	1.5	5	5	-3	-3.6	-4.3	5	9	0	17.6	-17.9	6	2	-6	-5.9	-6.9
5	1	13	-3.9	0.7	5	5	-2	9.2	9.8	5	9	1	-1.5	-7.4	6	2	-5	11.5	11.9
5	2	-15	-4.8	-3.7	5	5	-1	15.9	15.8	5	9	2	8.2	7.6	6	2	-4	35.6	34.9
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5	2	-13	-3.4	-5.3	5	5	1	18.0	-18.2	5	9	4	-4.4	1.8	6	2	-2	8.3	-8.4
5	2	-12	6.7	7.5	5	5	2	6.7	-5.5	5	9	5	-3.3	3.4	6	2	-1	58.0	58.8
5	2	-11	8.1	8.7	5	5	3	20.9	21.5	5	9	6	21.6	-20.7	6	2	0	5.7	3.2
5	2	-10	13.0	12.8	5	5	4	42.2	43.7	5	9	7	11.1	11.4	6	2	1	55.1	-56.1
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5	2	-1	42.6	-43.5	5	6	-13	-5.3	-7.7	5	10	-2	0.0	0.6	6	2	10	8.0	-9.0
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5	2	5	-2.9	0.3	5	6	-7	4.0	8.9	5	10	4	14.2	15.2	6	3	-11	16.0	-15.1
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5	2	8	8.8	8.5	5	6	-4	14.0	14.2	5	10	7	-6.0	-6.9	6	3	-8	34.6	-35.6
5	2	9	-4.4	3.4	5	6	-3	-3.1	2.7	5	11	-7	23.0	23.3	6	3	-7	-2.6	-0.4
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5	2	13	11.6	11.3	5	6	1	25.8	26.0	5	11	-3	0.7	1.4	6	3	-3	45.3	45.4
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5	3	-11	-1.7	-1.0	5	6	5	-3.8	-2.4	5	11	1	18.3	-17.3	6	3	1	6.8	6.8
5	3	-10	14.9	-15.3	5	6	6	31.3	31.5	5	11	2	-5.0	-4.9	6	3	2	30.1	30.5
5	3	-9	10.2	10.8	5	6	7	0.0	-1.9	5	11	3	-3.5	-2.0	6	3	3	15.1	-14.4
5	3	-8	47.2	-42.0	5	6	8	7.9	-7.1	5	11	4	21.2	21.5	6	3	4	53.5	54.8
5	3	-7	27.3	28.4	5	6	9	16.5	-16.5	5	11	5	-4.1	2.9	6	3	5	44.9	-45.6
5	3	-6	9.9	-9.0	5	6	10	10.3	8.8	5	12	-4	-3.3	-4.0	6	3	6	-2.4	0.5
5	3	-5	19.9	19.8	5	6	11	14.7	13.8	5	12	-3	-2.9	0.6	6	3	7	6.5	7.4
5	3	-4	28.7	28.9	5	7	-12	0.0	1.0	5	12	-2	7.0	-7.4	6	3	8	8.2	-9.4
5	3	-3	10.2	-9.5	5	7	-11	24.7	24.8	5	12	-1	-3.4	6.0	6	3	9	19.9	19.3
5	3	-2	41.6	41.9	5	7	-10	17.9	16.6	5	12	0	-4.1	7.5	6	3	10	11.4	-11.5
5	3	-1	70.2	-70.8	5	7	-9	10.8	11.7	5	12	1	8.1	-8.2	6	3	11	-6.3	6.6
5	3	0	25.5	25.6	5	7	-8	9.5	10.2	5	12	2	9.9	10.0	6	4	-13	16.3	-15.8
5	3	1	9.5	-9.1	5	7	-7	34.4	-35.8	6	0	-14	8.8	10.1	6	4	-12	21.3	-21.0
5	3	2	7.5	-6.5	5	7	-6	15.0	-15.0	6	0	-12	16.5	15.8	6	4	-11	0.0	1.9
5	3	3	28.8	28.1	5	7	-5	24.1	-24.6	6	0	-10	8.3	8.8	6	4	-10	8.5	-8.8
5	3	4	6.5	-4.0	5	7	-4	6.5	6.9	6	0	-8	29.6	-29.2	6	4	-9	45.4	45.8
5	3	5	12.3	12.1	5	7	-3	21.6	-21.7	6	0	-6	-5.2	5.7	6	4	-8	18.4	18.3
5	3	6	-1.0	1.4	5	7	-2	33.9	-33.7	6	0	-4	41.2	41.5	6	4	-7	25.3	25.5
5	3	7	63.4	64.7	5	7	-1	18.1	18.4	6	0	-2	102.3	104.0	6	4	-6	13.4	-13.1
5	3	8	-5.6	3.9	5	7	0	14.2	-13.6	6	0	0	26.1	-26.5	6	4	-5	-4.8	2.2
5	3	9	14.6	15.2	5	7	1	43.0	44.0	6	0	2	104.2	-104.4	6	4	-4	-2.1	1.9
5	3	10	10.7	-11.9	5	7	2	10.3	10.9	6	0	4	29.8	-29.3	6	4	-3	28.7	23.1
5	3	11	22.9	-21.8	5	7	3	10.7	-10.4	6	0	6	26.7	27.6	6	4	-2	20.8	20.5
5	3	12	22.9	-23.1	5	7	4	21.5	-21.6	6	0	8	-4.0	2.5	6	4	-1	28.6	-29.1
5	4	-14	-3.3	4.5	5	7	5	14.3	-14.9	6	0	10	36.9	37.7	6	4	0	43.1	-43.2
5	4	-13	-1.9	-2.3	5	7	6	14.6	14.5	6	0	12	-4.2	0.8	6	4	1	17.9	16.9
5	4	-12	14.6	15.3	5	7	7	-6.3	3.9	6	1	-14	-5.3	7.9	6	4	2	27.2	26.9
5	4	-11	11.4	-11.6	5	7	8	8.4	7.6	6	1	-13	18.6	-18.6	6	4	3	19.4	19.9
5	4	-10	10.2	-10.7	5	7	9	0.0	-1.0	6	1	-12	32.8	31.5	6	4	4	8.9	8.6
5	4	-9	21.5	21.8	5	7	10	6.7	-7.4	6	1	-11	20.5	-20.0	6	4	5	61.6	-62.0
5	4	-8	15.0	14.6	5	8	-11	0.0	-0.9	6	1	-10	44.2	-44.9	6	4	6	10.9	-11.5
5	4	-7	34.9	34.8	5	8	-10	-3.4	-4.0	6	1	-9	14.9	-15.1	6	4	7	-4.0	4.9
5	4	-6	11.4	11.1	5	8	-9	6.9	6.0	6	1	-8	14.5	-15.5	6	4	8	8.2	7.0
5	4	-5	13.8	-14.1	5	8	-8	-1.4	0.8	6	1	-7	20.2	20.2	6	4	9	9.4	8.6
5	4	-4	9.2	8.9	5	8	-7	32.9	-33.5	6	1	-6	22.9	22.8	6	4	10	-4.4	-3.6
5	4	-3	13.9	-14.5	5	8	-6	31.7	31.5	6	1	-5	21.4	22.3	6	4	11	-6.5	-4.2
5	4	-2	-2.8	-1.9	5	8	-5	-1.8	1.7	6	1	-4	78.1	-80.8	6	5	-13	15.9	15.8
5	4	-1	-0.6	-2.4	5	8	-4	21.5	22.4	6	1	-3	33.3	-32.7	6	5	-12	23.1	-22.2
5	4	0	33.8	-33.5	5	8	-3	16.5	17.3	6	1	-2	27.6	27.4	6	5	-11	11.9	-12.5
5	4	1	30.2	-31.1	5	8	-2	43.0	-44.1	6	1	-1	7.7	-8.8	6	5	-10	0.0	2.0
5	4	2	9.8	6.7	5	8	-1	21.7	-22.1	6	1	0	58.9	59.					

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
6	5	4	0.0	1.5	6	10	-1	19.9	-19.1	7	3	6	12.4	-11.5	7	8	-3	17.8	17.5
6	5	5	-3.4	-2.1	6	10	0	32.5	-32.6	7	3	7	12.8	-11.7	7	8	-2	10.6	-10.6
6	5	6	12.7	13.1	6	10	1	9.7	-9.3	7	3	8	10.6	-11.3	7	8	-1	11.7	-11.3
6	5	7	-6.2	6.8	6	10	2	0.0	-0.2	7	3	9	17.3	-17.4	7	8	0	43.1	42.9
6	5	8	25.9	24.8	6	10	3	14.4	13.5	7	3	10	-6.4	-0.2	7	8	1	-2.9	1.2
6	5	9	32.1	32.4	6	10	4	12.8	13.2	7	4	-12	-1.8	-4.1	7	8	2	-6.8	6.0
6	5	10	16.9	-16.1	6	10	5	8.5	8.3	7	4	-11	18.1	18.2	7	8	3	11.4	11.0
6	5	11	12.8	11.2	6	11	-3	-5.4	-4.0	7	4	-10	19.1	-18.8	7	8	4	10.0	-10.6
6	6	-12	12.6	-12.7	6	11	-4	8.3	-6.5	7	4	-9	10.2	-10.0	7	8	5	20.0	-19.5
6	6	-11	-6.2	7.1	6	11	-3	24.7	24.2	7	4	-8	-1.2	3.3	7	8	6	-4.1	-4.2
6	6	-10	28.8	-26.8	6	11	-2	-3.8	1.8	7	4	-7	24.0	-24.1	7	9	-8	-5.3	-3.7
6	6	-9	0.0	2.0	6	11	-1	10.8	10.0	7	4	-6	-4.5	1.9	7	9	-7	12.3	-12.0
6	6	-8	8.9	8.8	6	11	0	0.0	-1.6	7	4	-5	8.1	6.7	7	9	-6	0.0	-3.0
6	6	-7	12.2	-11.6	6	11	1	-4.3	-5.8	7	4	-4	18.4	-18.8	7	9	-5	8.3	8.5
6	6	-6	25.8	25.3	6	11	2	-2.4	-7.3	7	4	-3	7.5	-8.6	7	9	-4	7.7	5.9
6	6	-5	11.9	-12.1	6	11	3	13.4	13.7	7	4	-2	25.3	25.2	7	9	-3	15.0	-15.0
6	6	-4	11.6	11.3	7	0	-12	12.9	-13.8	7	4	-1	14.7	14.9	7	9	-2	-6.5	6.1
6	6	-3	6.6	-6.2	7	0	-10	29.2	30.3	7	4	0	16.4	17.1	7	9	-1	7.6	9.4
6	6	-2	26.9	27.9	7	0	-8	-1.1	-7.4	7	4	1	8.2	-9.0	7	9	0	-3.9	-4.6
6	6	-1	18.1	-18.6	7	0	-6	44.9	-46.9	7	4	2	-4.3	-3.9	7	9	1	-2.1	0.5
6	6	0	25.1	24.9	7	0	-4	26.7	27.1	7	4	3	31.2	-31.9	7	9	2	0.0	-2.3
6	6	1	37.1	37.0	7	0	-2	26.6	26.8	7	4	4	6.7	-7.8	7	9	3	-6.4	4.5
6	6	2	-4.2	-1.5	7	0	0	32.1	-33.0	7	4	5	14.4	14.3	7	9	4	-1.8	0.6
6	6	3	6.2	-5.9	7	0	2	8.1	7.4	7	4	6	-2.4	-0.2	7	9	5	10.7	10.5
6	6	4	7.2	-9.7	7	0	4	13.6	14.0	7	4	7	14.0	14.1	7	10	-5	9.7	10.2
6	6	5	0.0	2.0	7	0	6	34.0	-34.2	7	4	8	12.0	12.0	7	10	-4	7.2	6.0
6	6	6	26.1	-26.7	7	0	8	21.0	-20.5	7	4	9	-4.5	-5.4	7	10	-3	16.4	-16.7
6	6	7	-3.5	4.4	7	0	10	7.9	5.5	7	4	10	-2.9	2.0	7	10	-2	8.3	9.1
6	6	8	8.1	-8.1	7	1	-13	0.0	-6.8	7	5	-12	-5.2	-4.5	7	10	-1	-1.6	-1.9
6	6	9	10.2	-9.8	7	1	-12	-3.8	-3.7	7	5	-11	8.5	-8.0	7	10	0	0.0	-3.2
6	6	10	-4.0	3.5	7	1	-11	0.0	1.4	7	5	-10	10.8	-9.0	7	10	1	-3.6	1.0
6	6	11	19.7	19.9	7	1	-10	0.0	0.7	7	5	-9	16.4	15.8	7	10	2	-6.8	-6.4
6	6	12	7.0	-7.0	7	1	-9	0.0	4.6	7	5	-8	22.0	-22.0	7	10	3	-5.6	-4.9
6	7	-9	-2.0	-4.7	7	1	-8	24.1	22.7	7	5	-7	10.8	-11.2	8	0	-12	8.9	-7.5
6	7	-8	-6.4	6.0	7	1	-7	29.2	-29.3	7	5	-6	28.3	28.2	8	0	-10	-4.3	5.0
6	7	-7	-6.1	-4.3	7	1	-6	12.5	11.4	7	5	-5	11.0	12.1	8	0	-8	0.0	-3.8
6	7	-6	20.1	27.9	7	1	-5	15.4	-14.8	7	5	-4	19.9	21.0	8	0	-6	49.1	49.0
6	7	-5	14.8	15.4	7	1	-4	44.6	-45.9	7	5	-3	43.6	43.5	8	0	-4	-4.5	5.0
6	7	-4	14.7	-14.3	7	1	-3	-3.5	-2.5	7	5	-2	0.0	1.7	8	0	-2	74.2	-74.4
6	7	-3	26.0	-26.5	7	1	-2	13.3	-11.9	7	5	-1	10.9	-11.4	8	0	0	-4.0	4.3
6	7	-2	-2.8	2.9	7	1	-1	26.3	28.0	7	5	0	27.8	28.5	8	0	2	9.9	9.6
6	7	-1	6.4	-5.1	7	1	0	32.4	-34.0	7	5	1	34.0	-34.8	8	0	4	18.1	17.7
6	7	0	12.6	13.0	7	1	1	32.0	31.2	7	5	2	9.6	9.3	8	0	6	9.4	9.4
6	7	1	-5.8	-8.2	7	1	2	-5.8	-1.5	7	5	3	19.6	20.4	8	0	8	28.6	-27.6
6	7	2	25.2	-26.1	7	1	3	0.0	-2.1	7	5	4	18.9	-20.1	8	1	-12	-5.0	-4.0
6	7	3	33.6	-33.7	7	1	4	13.9	13.5	7	5	5	23.0	-23.4	8	1	-11	28.9	28.3
6	7	4	-5.1	-5.0	7	1	5	10.3	-9.5	7	5	6	-1.8	3.7	8	1	-10	9.0	-9.2
6	7	5	16.7	16.9	7	1	6	8.8	7.5	7	5	7	13.6	-14.0	8	1	-9	0.0	-1.4
6	7	6	8.6	9.6	7	1	7	-4.5	-1.5	7	5	8	17.3	-17.1	8	1	-8	0.0	3.3
6	7	7	22.2	21.2	7	1	8	-2.0	1.4	7	5	9	-3.1	-0.4	8	1	-7	22.3	-22.8
6	7	8	21.4	-21.4	7	1	9	-6.5	7.2	7	6	-11	-3.2	1.9	8	1	-6	38.7	39.5
6	7	9	0.0	1.1	7	1	10	-1.2	2.2	7	6	-10	7.9	8.7	8	1	-5	12.1	-12.3
6	8	-10	-6.2	2.9	7	2	-13	11.8	11.2	7	6	-9	11.7	10.7	8	1	-4	7.7	-7.2
6	8	-9	13.8	-12.3	7	2	-12	13.0	12.4	7	6	-8	-5.2	-6.7	8	1	-3	14.4	-15.3
6	8	-8	21.1	-20.9	7	2	-11	10.8	-9.4	7	6	-7	-4.2	3.5	8	1	-2	15.7	16.8
6	8	-7	13.8	13.1	7	2	-10	10.5	-10.0	7	6	-6	50.0	-50.6	8	1	-1	28.8	29.8
6	8	-6	23.1	21.4	7	2	-9	16.0	-15.7	7	6	-5	12.3	-11.3	8	1	0	20.4	21.2
6	8	-5	9.5	8.9	7	2	-8	9.7	-8.4	7	6	-4	27.6	-27.5	8	1	1	10.4	9.9
6	8	-4	8.2	8.8	7	2	-7	10.5	-10.7	7	6	-3	0.0	-0.7	8	1	2	40.5	-40.9
6	8	-3	17.8	-17.6	7	2	-6	19.0	19.7	7	6	-2	-2.8	1.2	8	1	3	23.7	-23.2
6	8	-2	32.8	-33.4	7	2	-5	24.5	-24.9	7	6	-1	14.0	-13.3	8	1	4	0.0	-4.3
6	8	-1	7.4	8.2	7	2	-4	19.2	15.8	7	6	0	26.4	26.6	8	1	5	10.8	10.8
6	8	0	27.2	29.3	7	2	-3	71.7	73.6	7	6	1	15.8	-15.3	8	1	6	-0.8	1.3
6	8	1	30.6	-31.4	7	2	-2	-5.3	1.9	7	6	2	42.4	42.8	8	1	7	10.5	9.7
6	8	2	0.0	0.2	7	2	-1	74.1	75.6	7	6	3	9.4	-10.2	8	1	8	13.2	-12.5
6	8	3	9.7	8.6	7	2	0	15.8	15.6	7	6	4	-4.9	4.6	8	1	9	-4.6	4.8
6	8	4	24.1	-23.3	7	2	1	17.0	-17.1	7	6	5	15.2	15.0	8	2	-12	-6.0	-7.9
6	8	5	33.9	34.5	7	2	2	16.8	-16.6	7	6	6	15.8	-16.2	8	2	-11	12.8	12.1
6	8	6	10.6	11.9	7	2	3	0.0	0.7	7	6	7	12.0	12.1	8	2	-10	-1.3	-2.0
6	8	7	7.8	8.1	7	2	4	23.4	-25.0	7	6	8	-4.2	-4.8	8	2	-9	17.9	-17.7
6	8	8	-5.8	-4.5	7	2	5	8.6	-8.4	7	7	-10	12.5	-12.0	8	2	-8	0.0	1.5
6	8	9	0.0	-3.6	7	2	6	-1.3	0.8	7	7	-9	16.9	-15.3	8	2	-7	10.6	-11.0
6	8	10	11.7	11.4	7	2	7	12.6	-13.2	7	7	-8	8.4	8.6	8	2	-6	-5.2	6.4
6	9	-9	-6.0	-3.5	7	2	8	-2.6	0.3	7	7	-7	-1.7	4.1	8	2	-5	27.3	-27.8
6	9	-8	-6.3	-6.8	7	2	9	9.2	8.6	7	7	-6	17.8	-17.4	8	2	-4	-5.3	-1.9
6	9	-7	23.1	23.2	7	2	10	-3.4	-2.6	7	7	-5	35.0	36.1	8	2	-3	27.0	-26.6
6	9	-6	13.7	-14.2	7	3	-13	20.1	20.4	7	7	-4	12.2	11.4	8	2	-2	12.3	-12.1
6	9	-5	19.9	19.3	7	3	-12	-5.3	2.6	7	7	-3	35.9	36.7	8	2	-1	21.9	22.0
6	9	-4	-4.6	6.8	7	3	-11	20.4	18.7	7	7	-2	18.9	18.2	8	2	0	-3.1	-2.0
6	9	-3	14.6	14.1	7	3	-10	-2.8	4.2	7	7	-1	20.9	-21.7	8	2	1	15.7	-14.8
6	9	-2	11.2	12.4	7	3	-9	27.4	-28.7	7	7	0	12.5	-12.1	8	2	2	30.8	31.6
6	9	-1	8.5	9.2	7	3	-8	10.0	9.2	7	7	1	22.1	-23.2	8	2	3	20.7	20.4
6	9	0	7.5	-5.7	7	3	-7	-5.1	0.4	7	7	2	-4.7	0.7	8	2	4	12.0	11.7
6	9	1	21.7	-21.8	7														

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
8	3	-4	7.6	-7.2	8	7	-8	-6.7	-6.3	9	2	-3	13.0	-12.4	9	6	3	0.0	2.7
8	3	-3	8.2	7.2	8	7	-7	0.0	-2.1	9	2	-2	15.8	-16.3	9	6	4	0.0	0.9
8	3	-2	0.0	1.3	8	7	-6	-6.0	-7.1	9	2	-1	19.9	-19.9	9	7	-5	13.9	-14.1
8	3	-1	19.5	-18.7	8	7	-5	22.3	21.7	9	2	0	18.2	18.2	9	7	-4	9.9	-8.7
8	3	0	11.5	11.5	8	7	-4	-2.9	-0.1	9	2	1	37.3	-37.0	9	7	-3	25.3	-25.0
8	3	1	20.0	-20.1	8	7	-3	27.6	-26.6	9	2	2	-2.7	-4.6	9	7	-2	0.0	3.5
8	3	2	15.6	-16.0	8	7	-2	-6.1	5.7	9	2	3	17.1	17.0	9	7	-1	-3.3	-2.1
8	3	3	10.5	9.8	8	7	-1	8.8	8.6	9	2	4	-3.1	1.1	9	7	0	13.4	-13.2
8	3	4	19.6	-19.8	8	7	0	10.4	9.9	9	2	5	17.4	16.8	9	7	1	16.6	16.7
8	3	5	-2.0	0.2	8	7	1	36.8	36.9	9	2	6	11.8	12.3	9	7	2	-2.3	-0.9
8	3	6	17.6	-17.6	8	7	2	-1.8	3.0	9	2	7	-3.8	-4.8	10	0	-8	25.1	-24.2
8	3	7	8.2	7.9	8	7	3	9.0	-7.1	9	3	-10	-5.2	3.9	10	0	-6	23.0	-22.0
8	3	8	-4.5	-1.1	8	7	4	-1.7	2.9	9	3	-9	26.3	-25.7	10	0	-4	9.0	9.7
8	4	-11	7.9	-6.2	8	7	5	7.3	7.6	9	3	-8	14.3	-13.9	10	0	-2	21.8	-21.8
8	4	-10	-4.9	-5.3	8	8	-7	-3.6	4.1	9	3	-7	-4.3	5.8	10	0	0	38.4	37.2
8	4	-9	13.8	-13.8	8	8	-6	-6.4	4.5	9	3	-6	-4.6	-6.8	10	0	2	7.1	6.4
8	4	-8	20.7	20.2	8	8	-5	0.0	-1.6	9	3	-5	21.9	20.9	10	0	4	28.2	-26.5
8	4	-7	21.3	-21.1	8	8	-4	0.0	-1.5	9	3	-4	-2.2	1.2	10	1	-8	9.5	8.3
8	4	-6	34.9	-36.0	8	8	-3	15.7	-15.6	9	3	-3	-5.7	-5.5	10	1	-7	-2.6	4.8
8	4	-5	6.6	8.8	8	8	-2	12.0	-10.8	9	3	-2	16.2	16.9	10	1	-6	-3.0	-1.5
8	4	-4	13.7	-12.9	8	8	-1	-1.2	1.4	9	3	-1	8.4	7.4	10	1	-5	35.6	35.7
8	4	-3	31.9	32.6	8	8	0	16.5	17.1	9	3	0	26.7	26.2	10	1	-4	15.0	-15.3
8	4	-2	24.4	24.7	8	8	1	11.1	11.1	9	3	1	-1.0	4.2	10	1	-3	-4.7	-5.7
8	4	-1	19.6	-19.4	8	8	2	-0.9	-4.4	9	3	2	6.4	-6.0	10	1	-2	10.8	11.0
8	4	0	14.1	-13.7	8	8	3	9.5	-9.4	9	3	3	29.0	-28.9	10	1	-1	11.2	-11.9
8	4	1	0.0	1.6	8	8	4	-5.4	-5.6	9	3	4	13.2	-12.1	10	1	0	-3.5	-0.3
8	4	2	11.2	12.4	8	9	-5	8.9	-7.5	9	3	5	7.0	6.8	10	1	1	7.8	5.9
8	4	3	20.3	21.1	8	9	-4	10.0	10.0	9	3	6	9.0	-7.5	10	1	2	-3.3	-1.0
8	4	4	13.2	13.9	8	9	-3	8.3	-6.7	9	4	-9	-5.5	-4.9	10	1	3	-5.5	-8.2
8	4	5	0.0	-3.5	8	9	-2	7.9	8.7	9	4	-8	9.1	9.0	10	1	4	20.3	20.4
8	4	6	14.1	-15.0	8	9	-1	21.7	-21.5	9	4	-7	9.3	-10.8	10	2	-7	14.1	13.2
8	4	7	15.9	15.1	8	9	0	-3.1	-5.4	9	4	-6	9.5	8.7	10	2	-6	0.0	-2.4
8	4	8	10.5	10.2	8	9	1	9.3	-8.8	9	4	-5	16.5	16.5	10	2	-5	-5.9	-3.7
8	5	-10	18.8	18.4	8	9	2	9.7	-9.2	9	4	-4	-5.3	4.1	10	2	-4	16.7	-15.9
8	5	-9	8.2	8.0	9	0	-10	-3.8	-3.9	9	4	-3	10.6	-11.3	10	2	-3	-3.7	-1.3
8	5	-8	14.3	13.4	9	0	-8	-2.5	-0.7	9	4	-2	-9.4	-6.2	10	2	-2	18.8	18.2
8	5	-7	-4.0	2.2	9	0	-6	22.4	-21.9	9	4	-1	19.2	-19.7	10	2	-1	15.4	15.2
8	5	-6	20.3	-19.7	9	0	-4	0.0	2.1	9	4	0	17.5	-16.8	10	2	0	-2.6	0.8
8	5	-5	-3.9	-2.4	9	0	-2	8.0	8.2	9	4	1	16.3	16.6	10	2	1	17.5	-16.7
8	5	-4	11.5	-10.7	9	0	0	6.6	-5.6	9	4	2	0.0	-1.2	10	2	2	-4.3	-6.3
8	5	-3	9.0	9.6	9	0	2	19.5	18.9	9	4	3	0.0	0.3	10	2	3	10.3	-11.3
8	5	-2	17.1	-17.7	9	0	4	-2.6	5.7	9	4	4	-1.8	0.2	10	2	4	-6.8	-7.6
8	5	-1	0.0	-4.0	9	0	6	13.1	-12.7	9	4	5	-5.2	6.0	10	3	-7	12.2	11.7
8	5	0	-5.9	4.0	9	1	-10	-5.6	-6.7	9	4	6	-2.1	3.9	10	3	-6	0.0	-0.5
8	5	1	-5.5	3.0	9	1	-9	16.4	16.8	9	5	-8	-5.3	5.1	10	3	-5	25.1	-24.2
8	5	2	29.6	30.4	9	1	-8	-6.4	-3.6	9	5	-7	0.0	-2.2	10	3	-4	-5.1	-6.7
8	5	3	34.8	34.5	9	1	-7	11.1	9.8	9	5	-6	-3.6	-4.1	10	3	-3	14.2	13.6
8	5	4	13.4	-13.1	9	1	-6	12.6	-12.4	9	5	-5	17.9	-17.4	10	3	-2	-2.2	-2.7
8	5	5	-4.0	-1.9	9	1	-5	9.9	9.0	9	5	-4	-3.5	5.3	10	3	-1	12.5	11.9
8	5	6	16.4	-16.3	9	1	-4	16.1	-16.3	9	5	-3	6.9	4.1	10	3	0	9.2	9.9
8	5	7	12.1	-12.1	9	1	-3	13.1	12.2	9	5	-2	-3.8	-5.2	10	3	1	12.4	-12.9
8	6	-9	-2.7	1.7	9	1	-2	41.2	41.4	9	5	-1	9.3	-8.2	10	3	2	0.0	-1.8
8	6	-8	-1.1	-1.9	9	1	-1	10.3	-11.2	9	5	0	-2.6	-2.9	10	3	3	17.5	17.4
8	6	-7	-4.0	-4.2	9	1	0	7.4	4.0	9	5	1	0.0	-3.1	10	4	-6	-1.8	-2.3
8	6	-6	9.3	8.5	9	1	1	22.7	-23.0	9	5	2	11.7	-11.3	10	4	-5	-4.3	4.0
8	6	-5	7.1	7.8	9	1	2	0.0	0.5	9	5	3	27.2	27.3	10	4	-4	10.2	8.4
8	6	-4	22.9	-23.6	9	1	3	7.4	-6.6	9	5	4	13.3	-13.9	10	4	-3	9.2	-9.4
8	6	-3	15.9	15.3	9	1	4	10.7	10.1	9	5	5	10.2	-8.6	10	4	-2	17.5	17.1
8	6	-2	19.0	-18.7	9	1	5	-3.9	-7.1	9	6	-7	-4.1	-2.1	10	4	-1	-6.3	-3.3
8	6	-1	0.0	-2.0	9	1	6	19.9	-18.5	9	6	-6	-2.7	-0.3	10	4	0	16.8	-17.7
8	6	0	-3.2	-3.4	9	1	7	0.0	3.9	9	6	-5	8.9	-8.3	10	4	1	12.2	11.9
8	6	1	8.4	-7.8	9	2	-10	-5.7	4.8	9	6	-4	29.3	29.2	10	4	2	-5.6	-4.5
8	6	2	19.6	-19.8	9	2	-9	0.0	-2.5	9	6	-3	10.9	10.0	10	5	-4	14.2	13.2
8	6	3	10.7	-10.3	9	2	-8	-1.5	2.0	9	6	-2	20.9	20.6	10	5	-3	-4.3	2.8
8	6	4	-2.2	-1.5	9	2	-7	28.2	27.9	9	6	-1	9.4	10.4	10	5	-2	0.0	4.3
8	6	5	-3.1	-2.4	9	2	-6	11.4	9.4	9	6	0	32.3	-32.8	10	5	-1	6.8	-5.9
8	6	6	13.2	13.1	9	2	-5	-3.2	3.7	9	6	1	-5.5	2.0	10	5	0	-3.3	-4.7
8	6	7	8.4	7.8	9	2	-4	19.1	-18.7	9	6	2	14.7	-18.9	10	5	1	0.0	3.0

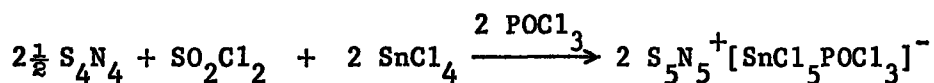
CHAPTER 6

The Crystal Structure of  $S_5N_5^+[SnCl_5POCl_3]^-$

## 6.1 Introduction.

The discovery that sulphur-nitrogen cations such as  $S_4N_3^+$  are pseudo-aromatic species has introduced theoretical justifications for the possible existence of further sulphur-nitrogen Hückel aromatic compounds. The type of compounds possible have been outlined earlier (section 2.5). One of the species predicted was  $S_4N_4^{2+}$  which ideally would be a planar eight-membered ring compound containing a  $10\pi$  system. A series of experiments were designed in an attempt to prepare this ion (Banister, 1975). These were unsuccessful in their initial aims, but were highly successful in preparing another derivative of  $S_5N_5^+$ ,  $S_5N_5^+[SnCl_5POCl_3]^-$ . The structure of this compound has been studied in an attempt to understand the difference in the shape of the cation observed in  $S_5N_5^+AlCl_4^-$  and  $S_5N_5^+S_3N_3O_4^-$ .

The compound was prepared by reacting a mixture of  $SnCl_4$  and  $SO_2Cl_2$  with a slurry of  $S_4N_4$  in  $POCl_3$  as a solvent. Initially the Lewis adduct  $(S_4N_4)_2SnCl_4$  formed and was precipitated as a red brown solid. On heating, the reaction mixture became lighter in colouration and on cooling yellow crystals were deposited. These were removed by filtration and separated in a glove box by hand from the other reaction residues. The stoichiometry of the reaction was,



Originally it was hoped that the  $SO_2Cl_2$  would oxidise the  $S_4N_4$  to give  $SO_2$  and  $S_4N_4^{2+}$ , together with producing the  $SnCl_6^{2-}$  anion. From the reaction product, it would appear that the  $(S_4N_4)_2SnCl_4$  adduct is oxidised by the  $SOCl_2$  to give  $NSCl$ , which is thought to react with the  $S_4N_4$  adduct to give  $S_5N_5^+$  and  $SnCl_5POCl_3^-$  (Banister and Durrant 1975).

## 6.2 Crystal Data.

The compound crystallised as well formed thin yellow plates showing prominent {001} faces bounded by {110} faces. It was extremely sensitive to moisture and consequently the crystals were sealed in quartz tubes. The crystal used for data collection had dimensions 0.3 x 0.25 x 0.15mm.

Preliminary studies using precession and Weissenberg methods showed the unit cell to be monoclinic. The conditions limiting reflections were,

$$h \ 0 \ l \quad l = 2n, \quad 0 \ k \ 0 \quad k = 2n$$

and these uniquely define the space group as  $P2_1/c$ . Accurate cell dimensions were obtained from a least squares treatment of the positions of twelve high order reflections, as measured on a four-circle diffractometer.

$$\begin{array}{ll} \text{S}_5\text{N}_5^+[\text{SnCl}_5\text{POCl}_3]^- & M = 679.62 \\ & a = 8.272(1)\text{\AA} \quad \alpha = 90^\circ \\ & b = 12.834(2)\text{\AA} \quad \beta = 97.083^\circ \\ & c = 18.515(3)\text{\AA} \quad \gamma = 90^\circ \\ & U = 1950.6\text{\AA}^3 \\ & Z = 4 \\ & D_m = 2.39\text{g cm}^{-3} \text{ (by floatation in} \\ & \quad \text{CH}_3\text{I/CH}_2\text{Br}_2) \\ & D_c = 2.31\text{g cm}^{-3} \end{array}$$

Absorption coefficient for MoK $\alpha$  radiation ( $\lambda = 0.7107\text{\AA}$ ) =  $29.9\text{cm}^{-1}$

### 6.3 Data Collection and Correction.

Data was collected on a four-circle diffractometer as before, using a  $2\theta - \omega$  scan technique. Each reflection was scanned in 80 steps of  $0.01^\circ$  with a counting time of 2.5 seconds per step and a stationary background count of 50 seconds at the beginning and end of each scan. Standard reflections were measured every 50 reflections and these showed no systematic variations during data measurement, indicating that the crystal was stable throughout the experiment. These standard reflections were used to place the intensities on a common scale.

One octant of the sphere of reflection was recorded for  $0 < \theta \leq 25^\circ$  giving 3440 independent reflections, of which 2054 were considered to be observed having net counts  $> 2.5$  e.s.d's. The data was corrected for Lorentz and polarisation effects, but not for absorption.

### 6.4 Solution and Refinement.

The structure was solved from its Patterson function which for the space group  $P2_1/c$  takes the form

$$P(u,v,w) = \frac{4}{V} \sum_{h=0}^{\infty} \sum_{k=0}^{\infty} \sum_{l=0}^{\infty} \{ |F(hkl)|^2 \cos 2\pi (hu + lw) + |F(hk\bar{l})|^2 \cos 2\pi (hu - lw) \} \cos 2\pi kv$$

this was computed for a quarter of the unit cell from

$$u = 0 \rightarrow 1.0 \text{ in intervals of } 0.27573\text{\AA}$$

$$v = 0 \rightarrow 0.5 \text{ in intervals of } 0.26737\text{\AA}$$

$$w = 0 \rightarrow 0.5 \text{ in intervals of } 0.30858\text{\AA}$$

The coefficients used were  $|F_{\text{obs}}|^2$  weighted by  $(Lp)^{-1}$  for each reflection. This increased the importance of the higher order planes and thus enhanced the magnitude of the tin-tin vectors in the map.

The position of the tin atom in the asymmetric unit was located from its Harker peaks. For an atom in a general position the following Harker peaks are expected

$$\begin{array}{ccc} 0 & \frac{1}{2} + 2y & \frac{1}{2} \\ 2x & \frac{1}{2} & \frac{1}{2} + 2z \end{array}$$

There were two large peaks in the map at (0, 0.052, 0.5) and (0.333, 0.5, 0.233) with peak heights of 168 and 155 with respect to the peak height of 500 at the origin. These are consistent with a tin atom at (0.333, 0.224, 0.133) and the corresponding single weight Sn-Sn vector was found at (0.666, 0.448, 0.267) with a height of 90. This position of the tin atom was refined using least squares methods with the block-diagonal approximation. Initially the tin atom was given an isotropic temperature factor of  $3.0\text{\AA}^2$  and after two cycles of refinement the R value was 0.48. The structure factors thus calculated were used to compute a difference synthesis which revealed the positions of all of the atoms except N(5). The heights of the heavier atoms varied from  $5.5 - 8.3e. \text{\AA}^{-3}$  and the lighter atoms from  $2.3 - 4.0e. \text{\AA}^{-3}$ , with the background showing spurious peaks of up to  $6e. \text{\AA}^{-3}$ . All of the atoms except N(3) were included in the



subsequent refinement with isotropic temperature factors of  $3.0\text{\AA}^2$  after which R fell to 0.20. A difference synthesis revealed the position of N(5). This was included in the further refinement during which all atoms were refined with anisotropic thermal parameters giving an R value of 0.069. The refinement was completed using full matrix least squares methods which saw R converge on its final value of 0.0630. During the last cycle all the parameter shifts were  $< 0.1$  of their e.s.d's.

A difference synthesis was computed from the final structure factors and showed no significant features above  $0.6e.\text{\AA}^{-3}$  except for a spherical ripple around the position of the tin atom. At the tin position there was a negative hole of  $-0.5e.\text{\AA}^{-3}$  around which the ripple reached a maximum height of  $1.9e.\text{\AA}^{-3}$ . This indicates that the form factors for the tin atom are not wholly satisfactory. The scattering factors for tin had been taken from International Tables Vol. III, however replacement of these by more recent values (Doyle and Turner, 1968) produced only small changes in the ripple.

The weighting scheme used in the initial stages of refinement was the same as described previously with  $P_1 = 10.0$  and  $P_2 = 0.01$ . This was replaced by one based on counting statistics as used in previous refinements. The most even distribution of  $w\Delta^2$  as a function of  $|F_o|$  was obtained with  $P = 0.09$ . The unobserved reflections were not included in the refinement. The final least squares totals are given in table 6.1. The final calculated and observed structure factors are given in table 6.8. The tin, chlorine, sulphur and phosphorus atoms were corrected for anomalous dispersion. For all atoms except tin these correction factors and their scattering factors were taken from International Tables Vol. III.

Table 6.1  $S_5N_5^+[SnCl_5POCl_3]^-$ Least Squares Totals.

$\Sigma F_o $	$\Sigma F_c $	$\Sigma \Delta $	R
109114.87	107925.06	6879.14	0.0630

Final Weighting Analysis

$ F_o $ Ranges	No.	$\Sigma w\Delta^2$	R
10 - 20	41	4.44	0.188
20 - 30	482	4.53	0.142
30 - 40	429	2.81	0.069
40 - 50	314	3.34	0.053
50 - 60	217	3.04	0.044
60 - 70	129	3.63	0.044
70 - 80	120	4.61	0.050
80 -100	137	3.47	0.040
100 - Upwards	185	5.11	0.054

Table 6.2  $S_5N_5^+[SnCl_5POCl_3]^-$ 

Final Atomic Coordinates with their Estimated Standard Deviations

 $(\times 10^5)$  and Isotropic Temperature Factors  $\text{\AA}^2$  †

Atom	x/a	y/b	z/c	B
SN	0.33097( 10)	0.22205( 7)	0.13340( 5)	2.28
Cl(1)	0.09452( 44)	0.19587( 34)	0.19157( 23)	4.29
Cl(2)	0.22047( 48)	0.15261( 33)	0.01878( 21)	4.34
Cl(3)	0.26431( 50)	0.39324( 29)	0.08880( 22)	4.29
Cl(4)	0.48114( 43)	0.29333( 32)	0.24158( 19)	3.94
Cl(5)	0.45101( 44)	0.05477( 30)	0.16466( 23)	3.92
Cl(6)	0.53858( 62)	0.29913( 74)	-0.06664( 31)	8.11
Cl(7)	0.71314(104)	0.10319( 45)	-0.00111( 40)	9.04
Cl(8)	0.85984( 52)	0.31937( 49)	0.03671( 28)	6.01
S(1)	-0.07873( 54)	0.62069( 38)	0.10641( 24)	4.90
S(2)	-0.29955( 47)	0.48029( 35)	0.17862( 22)	4.15
S(3)	-0.15348( 46)	0.37364( 37)	0.30663( 24)	4.37
S(4)	0.18577( 45)	0.43249( 38)	0.33147( 24)	4.32
S(5)	0.22387( 47)	0.58015( 34)	0.21466( 23)	4.20
P	0.65328( 46)	0.24408( 32)	0.02109( 21)	3.49
O	0.56701(118)	0.24931( 79)	0.08532( 56)	3.78
N(1)	-0.22826(162)	0.55657(119)	0.12564( 72)	5.31
N(2)	-0.16093(127)	0.44022(101)	0.23746( 61)	3.09
N(3)	0.02633(147)	0.37385(120)	0.34800( 72)	4.82
N(4)	0.15221(138)	0.50054( 98)	0.26564( 69)	3.90
N(5)	0.09546(152)	0.61699(100)	0.15047( 71)	4.40

† The temperature factors from the last cycle of isotropic refinement.

Anisotropic Thermal Parameters and their Estimated StandardDeviations (Both  $\text{\AA}^2 \times 10^5$ )

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
SN	3282( 44)	3978( 50)	3965( 49)	- 201( 46)	596( 32)	- 203( 44)
Cl(1)	3806(189)	7384(294)	7475(267)	998(217)	2137(178)	- 326(185)
Cl(2)	5881(230)	6421(268)	5282(226)	-1692(204)	-1104(182)	643(207)
Cl(3)	6679(245)	3756(204)	6587(259)	534(184)	502(204)	581(184)
Cl(4)	4822(201)	6301(261)	4467(201)	- 801(182)	- 93(155)	-898(182)
Cl(5)	4579(198)	4485(220)	7144(257)	656(190)	426(179)	662(173)
Cl(6)	5842(299)	27715(1007)	8509(373)	8965(514)	344(255)	1077(429)
Cl(7)	20330(754)	6870(378)	14419(600)	-2074(379)	9235(561)	1226(425)
Cl(8)	4578(233)	13138(466)	8720(338)	409(317)	2000(222)	-1622(271)
S(1)	6475(265)	7669(312)	5994(267)	2039(239)	314(210)	- 919(242)
S(2)	4428(211)	7004(284)	5594(247)	1126(211)	-438(177)	- 258(196)
S(3)	4154(211)	7374(294)	6574(266)	1840(230)	243(189)	- 570(206)
S(4)	3623(199)	7754(292)	6688(268)	691(236)	-342(179)	- 100(200)
S(5)	4259(206)	6356(264)	6510(261)	750(215)	1025(183)	- 640(192)
P	4342(204)	5803(263)	4488(213)	496(176)	1530(165)	62(175)
O	4567(573)	6078( 717)	6557(655)	- 840(518)	2870(492)	- 74(479)
N(1)	5904(801)	8510(1051)	6026(874)	1804( 795)	-207(666)	-1521( 791)
N(2)	3113(581)	6889(857)	4490(695)	- 346(630)	1022(510)	257(585)
N(3)	4435(722)	8442(1062)	6494(878)	1504( 768)	134(620)	-1313( 714)
N(4)	4042(669)	6058(860)	6404(842)	- 95(683)	2172(619)	- 427(603)
N(5)	5645(776)	4971( 790)	6830(886)	846(669)	404(667)	700(652)

The anomalous dispersion correction and scattering factors used for tin were those values calculated by Cromer, 1965 and Doyle and Turner, 1968. The final atomic coordinates and anisotropic thermal parameters are given in tables 6.2 and 6.3 respectively.

### 6.5 Results and Discussion.

The structure consists of discrete  $S_5N_5^+$  cations and  $[SnCl_5POCl_3]^-$  anions and it is convenient to discuss these separately. The bond distances and angles are given in tables 6.4 and 6.5 respectively.

#### 6.5.a The Structure of the $S_5N_5^+$ Cation.

The cation consists of a ten-membered ring of alternating sulphur and nitrogen atoms as shown in figure 6.1. It is immediately apparent that this ion has essentially the same shape as that found in  $S_5N_5^+S_3N_3O_4^-$  described in chapter 5. The ring is roughly planar (table 6.6) and the deviations of the atoms from their mean plane are of the same order as those seen previously. However the deviations do not show the systematic variation around the ring as clearly as before and any buckling appears to be masked by the larger errors. The bond distances on either side of the ring are the same within experimental error, eg. S(1)-N(1) and S(1)-N(5) of length 1.563(15)Å and 1.567(14)Å. The corresponding bond angles at sulphur on either side of the ring are also the same within experimental error, whereas those at the nitrogen atoms show greater differences than can be ascribed to experimental error.

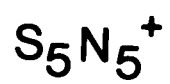
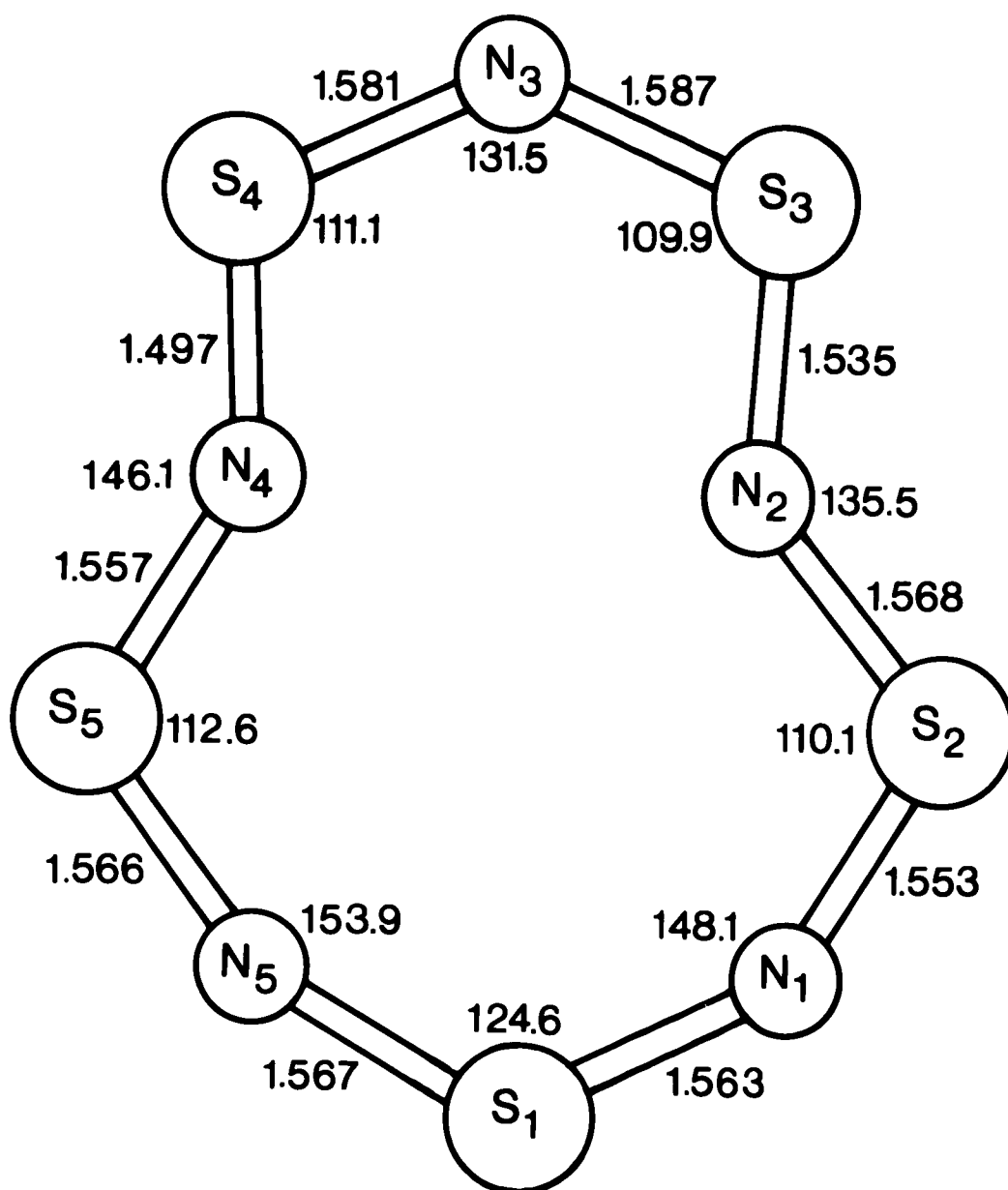


Figure 6.1

The  $S_5N_5^+$  Cation found in  $S_5N_5^+[SnCl_5POCl_3]^-$

The mean bond lengths and average bond angles found in the  $S_5N_5^+$  cations in  $S_5N_5^+[SnCl_5POCl_3]^-$  and  $S_5N_5^+S_3N_3O_4^-$  are shown in figure 6.2. Except for the mean values of S(3)-N(2) and S(4)-N(4) the mean S-N distances in the  $S_5N_5^+$  rings in these two compounds are the same within experimental error. Likewise the average bond angles are similar in the  $S_5N_5^+$  rings in both derivatives. It is significant that the greatest differences between corresponding bond distances and bond angles on either side of the ring are associated with those two parts of the ion most involved in secondary bonding, namely S(2)-N(2)-S(3) and S(4)-N(4)-S(5). As described in section 6.6, S(2) and S(3) participate in bridging interactions with two chlorine atoms, whereas S(4) and S(5) interact with only one. The smaller re-entrant angle at nitrogen is associated with the stronger secondary interactions involving S(2) and S(3). This is directly analogous to the interaction observed in  $S_5N_5^+S_3N_3O_4^-$  which is also associated with the smaller re-entrant angle at nitrogen. There may be a correlation between the angles at N(2) and N(4) because the N(2)-N(4) cross-ring distance of  $2.69\text{\AA}$  is substantially less than the nitrogen-nitrogen van der Waals distance of  $3.1\text{\AA}$  (Bondi, 1964). Both N(2) and N(4) carry lone pairs so that there must be a repulsive interaction between them. Thus any distortion that shifts the position of one nitrogen atom should result in a similar shift in the other, which may account for the small angle at N(2) and the large angle at N(4). The difference between the angle of  $148.1^\circ$  at N(1) and  $154.0^\circ$  at N(5) may be the result of a short contact of  $3.246\text{\AA}$  between N(1) and Cl(6) at  $(-x, 1-y, -z)$ .

It is not meaningful to discuss the variations in bond distances around the ring in these  $S_5N_5^+$  cations because they cannot be

Table 6.4  $S_5N_5^+[SnCl_5POCl_3]^-$ Final Bond Distances ( $\overset{\circ}{\text{A}}$ ) and their Estimated Standard Deviations( $\overset{\circ}{\text{A}} \times 10^3$ )

Sn	-	Cl(1)	2.370( 4)
Sn	-	Cl(2)	2.378( 4)
Sn	-	Cl(3)	2.388( 4)
Sn	-	Cl(4)	2.404( 4)
Sn	-	Cl(5)	2.406( 4)
Sn	-	O	2.271(10)
P	-	Cl(6)	1.913( 7)
P	-	Cl(7)	1.932( 7)
P	-	Cl(8)	1.953( 6)
P	-	O	1.462(11)
S(1)	-	N(1)	1.563(15)
S(1)	-	N(5)	1.567(14)
S(2)	-	N(1)	1.553(15)
S(2)	-	N(2)	1.568(12)
S(3)	-	N(2)	1.535(13)
S(3)	-	N(3)	1.587(13)
S(4)	-	N(3)	1.581(14)
S(4)	-	N(4)	1.497(14)
S(5)	-	N(4)	1.557(13)
S(5)	-	N(5)	1.566(14)



Table 6.5  $S_5N_5^+[SnCl_5POCl_3]^-$ Bond Angles (degrees) with their Estimated Standard Deviations(deg x 10<sup>2</sup>)

C1(1) - Sn - C1(2)	96.00(14)
C1(1) - Sn - C1(3)	96.85(14)
C1(1) - Sn - C1(4)	92.63(14)
C1(1) - Sn - C1(5)	95.94(14)
C1(1) - Sn - O	176.06(28)
C1(2) - Sn - C1(3)	89.39(14)
C1(2) - Sn - C1(4)	171.30(14)
C1(2) - Sn - C1(5)	88.97(14)
C1(2) - Sn - O	87.85(27)
C1(3) - Sn - C1(4)	90.66(13)
C1(3) - Sn - C1(5)	167.21(14)
C1(3) - Sn - O	84.02(27)
C1(4) - Sn - C1(5)	89.06(13)
C1(4) - Sn - O	83.51(27)
C1(5) - Sn - O	83.25(27)
C1(6) - P - C1(7)	106.16(36)
C1(6) - P - C1(8)	106.04(32)
C1(6) - P - O	115.67(50)
C1(7) - P - C1(8)	104.59(33)
C1(7) - P - O	112.31(50)
C1(8) - P - O	111.27(48)
N(1) - S(1) - N(5)	124.64(76)
N(1) - S(2) - N(2)	110.09(72)
N(2) - S(3) - N(3)	109.92(71)
N(3) - S(4) - N(4)	111.09(74)
N(4) - S(5) - N(5)	112.63(70)
SN - O - P	147.29(64)
S(1) - N(1) - S(2)	148.08(102)
S(2) - N(2) - S(3)	135.50(83)
S(3) - N(3) - S(4)	131.46(93)
S(4) - N(4) - S(5)	146.10(91)
S(1) - N(5) - S(5)	153.96(94)

Table 6.6  $S_5N_5^+[SnCl_5POCl_3]^-$ 

The mean plane of the  $S_5N_5^+$  cation.

$$0.3151X - 0.7597Y - 0.5689Z + 7.4534 = 0$$

Atom	S(1)	S(2)	S(3)	S(4)	S(5)
P	0.0081	-0.0054	-0.0151	0.0179	-0.0173
$\sigma(P)$	0.0047	0.0043	0.0045	0.0047	0.0043

Atom	N(1)	N(2)	N(3)	N(4)	N(5)
P	0.0286	0.0891	-0.0105	0.0026	0.0060
$\sigma(P)$	0.0145	0.0122	0.0144	0.0126	0.0129

Where P and  $\sigma(P)$  are the distance and its e.s.d. of an atom from the mean plane.

X, Y and Z are orthogonal coordinates in  $\text{\AA}$  oriented in the direction of  $\underline{a}$ ,  $\underline{b}$ , and  $\underline{c}^*$  respectively.

adequately described in classical terms.

6.5.b Discussion on the variations in shape observed for the  $S_5N_5^+$  cation.

The  $S_5N_5^+$  cation found originally in  $S_5N_5^+AlCl_4^-$  (shape I) differs markedly from that found in  $S_5N_5^+S_3N_3O_4^-$  and  $S_5N_5^+[SnCl_5POCl_3]^-$  (shape II), as shown in figure 6.2. In both cases the sulphur atoms have approximately the same distribution and the main differences are in the positions of two nitrogen atoms. There is also a far wider variation in the S-N bond distances and angles at nitrogen in shape I than in II i.e. 1.465 - 1.590Å and 129 - 177° as compared to the variation in the mean bond lengths of 1.543 - 1.580Å and average bond angles of 133-151° in  $S_5N_5^+S_3N_3O_4^-$ .

There are two possible explanations for this difference; firstly that the  $S_5N_5^+$  cation can exist in more than one conformation or secondly that the shape observed in  $S_5N_5^+AlCl_4^-$  represents the mean positions of two disordered  $S_5N_5^+$  cations of the type seen in  $S_5N_5^+S_3N_3O_4^-$  or  $S_5N_5^+[SnCl_5POCl_3]^-$ .

The difference between I and II cannot be explained by intermolecular forces, because the only significant interactions in all three of these structures occur between the sulphur atoms and atoms in the anion carrying some negative charge whereas the distribution of sulphur atoms is approximately the same in shapes I and II. Conversely there are no short contacts involving the nitrogen atoms which could account for the differences observed. So that there do not appear to be any reasons why the forces in the crystal should compel the ion to take up different conformations.

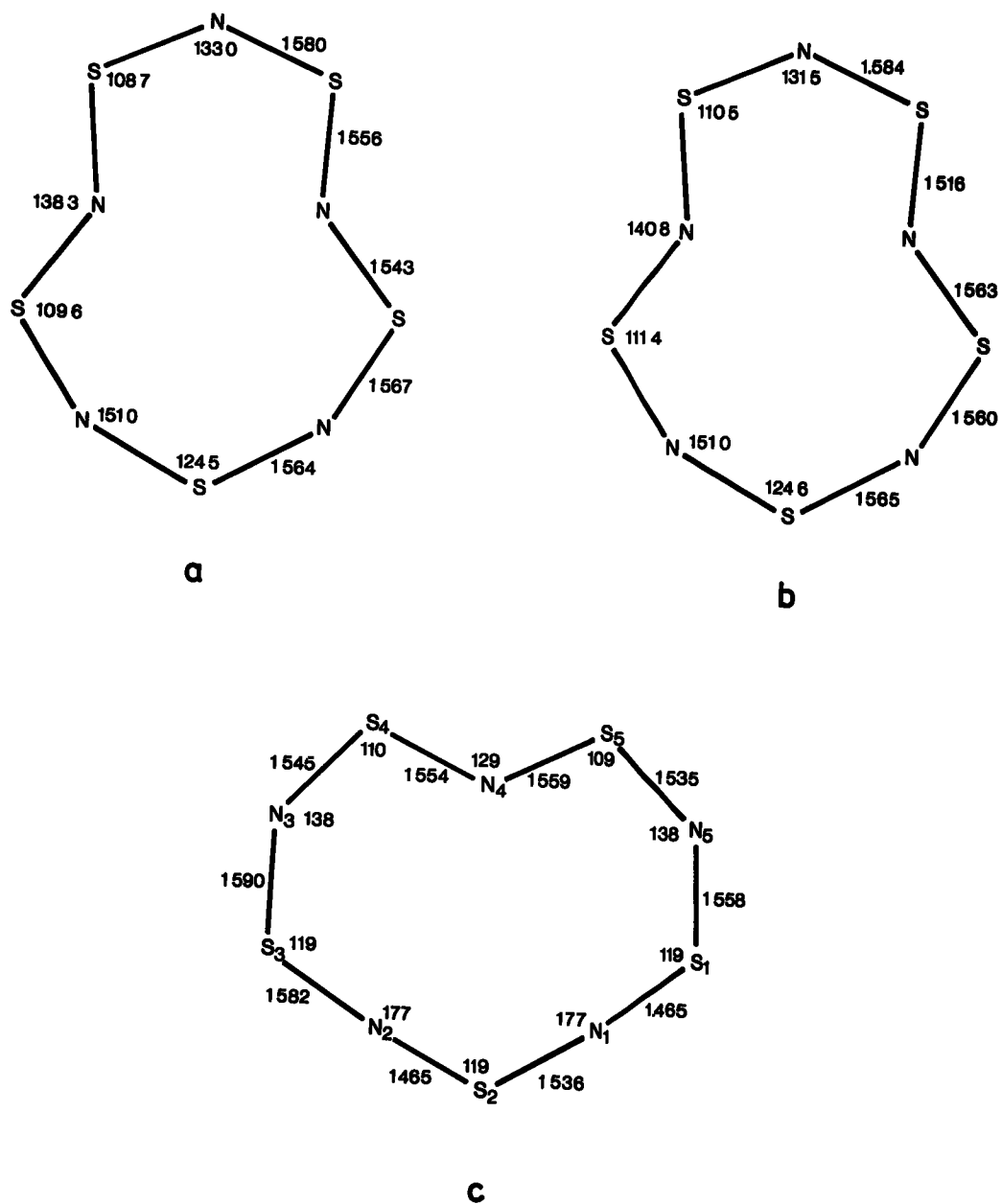
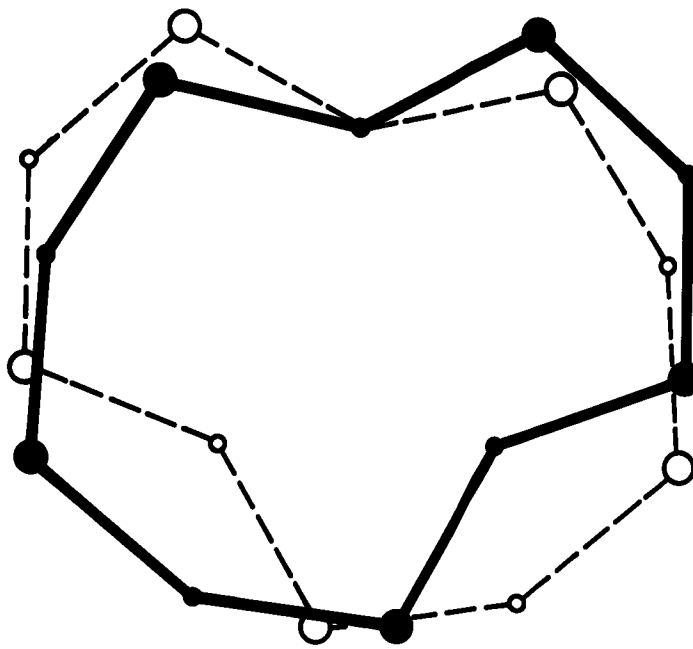


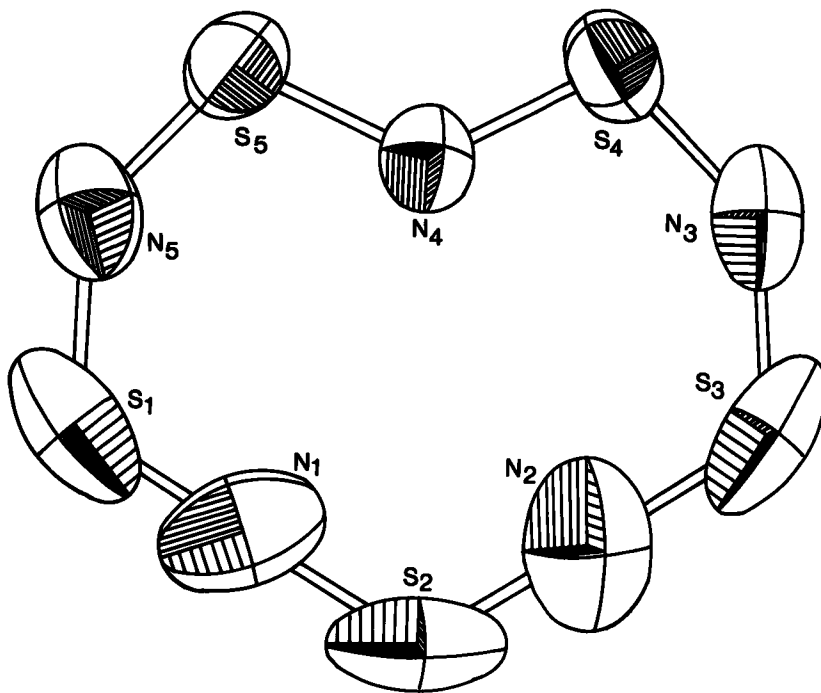
Figure 6.2

The  $S_5N_5^+$  Cations in (a)  $S_5N_5^+S_3N_3O_4^-$

(b)  $S_5N_5^+[SnCl_5POCl_3]^-$  (c)  $S_5N_5^+AlCl_4^-$



a



b

Figure 6.3

- (a) Superposition of two  $S_5N_5^+$  cations as found in  $S_5N_5^+S_3N_3O_4^-$
- (b) Thermal epipsoids for  $S_5N_5^+$  in  $S_5N_5^+AlCl_4^-$

The second explanation in terms of disordering is illustrated graphically in figure 6.3. This would account for the greater range of bond lengths observed in shape I and also the larger angles at N(1) and N(2). Support for this explanation is given by the large anisotropic thermal parameters and the orientation of the thermal ellipsoids for N(1) and N(2) in  $S_5N_5^+AlCl_4^-$ , as shown in figure 6.3.

It would appear that the cation reported in  $S_5N_5^+AlCl_4^-$  could arise from the superposition of two cations of the shape observed in  $S_5N_5^+S_3N_3O_4^-$  or  $S_5N_5^+[SnCl_5POCl_3]^-$ . The best way of establishing the existence of shape I would be by further study on  $S_5N_5^+AlCl_4^-$  preferably at low temperature.

#### 6.5.c Description and Discussion of the $[SnCl_5POCl_3]^-$ anion.

The anion consists of a central tin atom coordinated to five chlorine atoms and a  $POCl_3$  molecule as shown in figure 6.4. The structures of several related compounds have been studied i.e.  $SnCl_4(POCl_3)_2$  (Brandon, 1963),  $SbCl_5POCl_3$  and  $NbCl_5POCl_3$  (Brandon and Lindqvist, 1963). The second compound is isoelectronic with  $[SnCl_5POCl_3]^-$  whilst the first and third provide examples of coordinated  $POCl_3$ .

The most interesting features in this ion concern the coordination of the  $POCl_3$  ligand and its effect on the rest of the ion. As expected the Sn-O distance of  $2.271\text{\AA}$  is longer than the normal single bond distance of  $2.11\text{\AA}$  calculated from Pauling's covalent radii or of  $2.07\text{\AA}$  seen in  $[SnCl_3OHH_2O]_2$  (Bokii and Struchov, 1971) which contains two  $SnCl_3H_2O$  units linked by bridging OH groups.

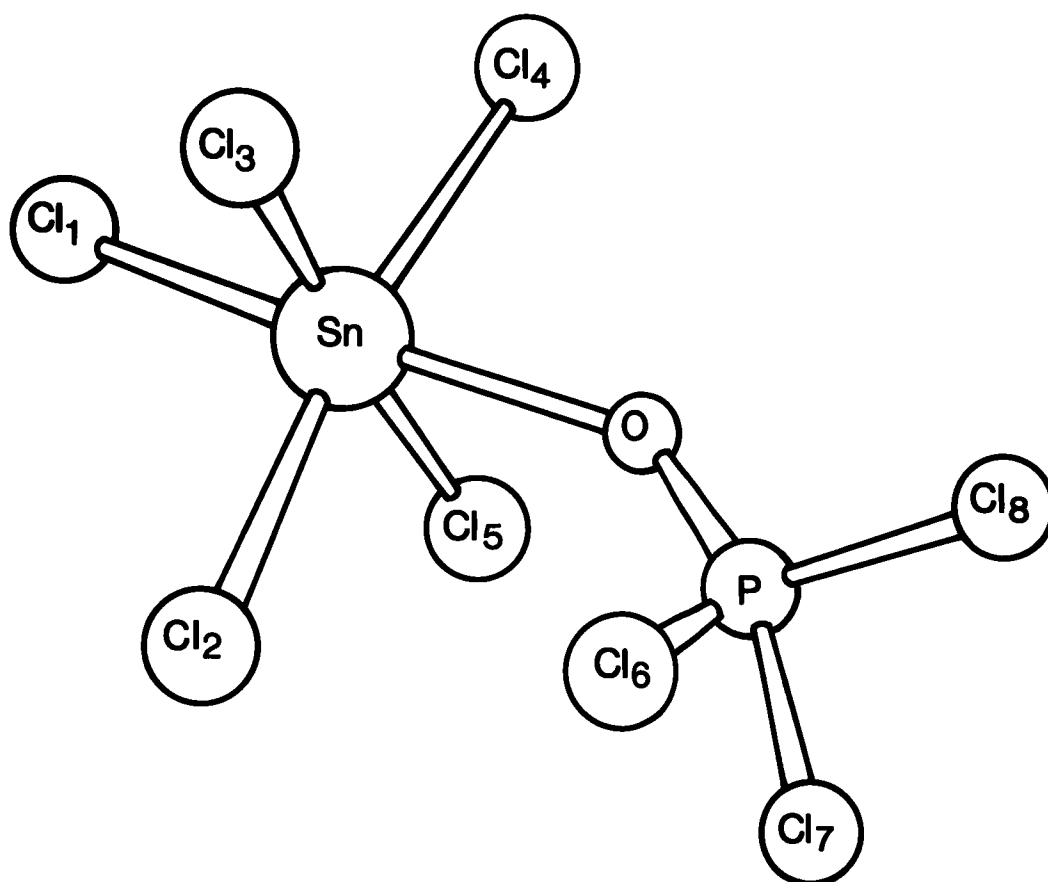


Figure 6.4

The distance is the same within experimental error as the mean value of  $2.28(3)\text{\AA}$  found in  $\text{SnCl}_4(\text{POCl}_3)_2$  but because of the large e.s.d's in this last example it is not possible to consider fine differences in structure between these two species. The Sn-O-P angle of  $147.3^\circ$  is similar to the mean value of  $148^\circ$  found in  $\text{SnCl}_4(\text{POCl}_3)_2$  and to the value of  $145^\circ$  in  $\text{SbCl}_5\text{POCl}_3$ . Since there are no contacts between the phosphorus atom and the chlorine atoms bonded to tin less than their van der Waals distance of  $3.55\text{\AA}$ , the magnitude of this angle must be governed by the distribution of electrons at the oxygen atom. The size of the angle suggests that the hybridisation of the oxygen atom lies between  $sp$  and  $sp^2$  hybrid states.

The P-O distance of  $1.462\text{\AA}$  does not differ significantly from that of  $1.447\text{\AA}$  observed in free  $\text{POCl}_3$  (Moritani et al., 1971) and is the same within experimental error as the mean value of  $1.45(5)\text{\AA}$  found in  $\text{SnCl}_4(\text{POCl}_3)_2$  and that of  $1.47(2)\text{\AA}$  found in  $\text{SbCl}_5\text{POCl}_3$ .

The P-Cl distances vary from  $1.913$  to  $1.953\text{\AA}$  and this range is greater than can be accounted for by statistical variation. All of the chlorine atoms bonded to phosphorus have large thermal parameters, e.g. in the last cycle of isotropic refinement the temperature factors of the chlorine atoms bonded to the tin atom varied from  $3.92 - 4.34\text{\AA}^2$  whereas the temperature factors for Cl(6), Cl(7) and Cl(8) were  $8.11$ ,  $9.04$  and  $6.01\text{\AA}^2$ . It is noticeable that the shortest bond lengths, namely P-Cl(6) and P-Cl(7) of length  $1.913(7)\text{\AA}$  and  $1.932(7)\text{\AA}$ , are associated with the chlorine atoms with the largest temperature factors so that the variation in the P-Cl distances



may be a result of contraction of the observed values of the bond distances due to thermal motion.

The P-Cl distances are all significantly shorter than that of  $1.991(1)\text{\AA}$  observed in free  $\text{POCl}_3$  but are close to the mean values of  $1.94(3)\text{\AA}$  in  $\text{SnCl}_4(\text{POCl}_3)_2$  and  $1.95(1)\text{\AA}$  in  $\text{SbCl}_5\text{POCl}_3$ . This may be the result of reduced  $\pi$  bonding between the oxygen and phosphorus atoms allowing the chlorine atoms to bond more strongly.

The coordination about phosphorus is roughly tetrahedral. The Cl-P-O angles vary from  $111.3$ - $115.7^\circ$  and this range is greater than can be accounted for by statistical variation. Cl(7) and Cl(8) which are involved in the smallest Cl-P-O angles, have Cl---Cl contacts less than or close to the normal van der Waals distance of  $3.50\text{\AA}$ , namely  $3.351\text{\AA}$  between Cl(7) and Cl(2) at  $1-x, -y, -z$  and  $3.497\text{\AA}$  between Cl(8) and Cl(3) at  $1+x, y, z$ , whereas there are no short contacts to Cl(6). Movement of Cl(7) and Cl(8) towards the other atom in the contact increases the Cl-P-O angle, suggesting that the variation may be caused by packing. The Cl-P-Cl angles range from  $104.6^\circ$ - $106.2^\circ$  with a mean value of  $105.6^\circ$ . The Cl-P-O angles and Cl-P-Cl angles observed here are close to the values of  $115.1^\circ$  and  $103.3^\circ$  in free  $\text{POCl}_3$ .

The environment of the tin is that of a distorted octahedron. The Sn-Cl bond distances range from  $2.370$ - $2.406\text{\AA}$ , and their average of  $2.389\text{\AA}$  is shorter than the Sn-Cl distance of  $2.43\text{\AA}$  in  $\text{SnCl}_6^{2-}$  (Schaffer, 1954). The shortening can be attributed to the orbital contraction caused by the presence of only one negative charge.

The two longest Sn-Cl bonds, namely Sn-Cl(4) and Sn-Cl(5) of length 2.404Å and 2.406Å, are involved in S---Cl contacts less than the van der Waals distance of 3.55Å, as given in table 6.7. These interactions may account for the large variation found in the Sn-Cl bond distances.

The coordination at the tin atom appears to be governed by steric effects since the four chlorine atoms adjacent to the oxygen atom have Cl-Sn-O angles less than 90° ranging from 83.3-87.9°, and the Cl-Sn-Cl angles involving the chlorine atom trans to the oxygen atom are all greater than 90°, ranging from 92.6-96.9°. This overall distortion can be explained by the larger size of the chlorine atom as compared to oxygen, so that it is sterically favourable for the chlorine atoms to spread towards the oxygen.

#### 6.6 Intermolecular Interactions.

The packing of the  $S_5N_5^+$  cations and  $[SnCl_5POCl_3]^-$  anions is characterised by a large number of intermolecular contacts less than the appropriate van der Waals distance. This is to be expected on account of the ionic nature of the structure. As mentioned before contacts between sulphur and chlorine atoms are likely to lower the potential energy of the structure, so that it is not surprising that all the sulphur atoms have S---Cl contacts less than the van der Waals distance of 3.55Å (Bondi, 1964); these are shown in table 6.7. The shortest intermolecular contacts involve the interaction of one chlorine with two sulphur atoms. Both S(2) and S(3) interact with Cl(4<sup>I</sup>) at (x-1, y, z) and Cl(5<sup>II</sup>) at ( $\bar{x}$ ,  $\frac{1}{2}+y$ ,  $\frac{1}{2}-z$ ), and their interactions

are fairly symmetrical as shown by their distances, namely 3.306 Å and 3.279 Å for S(2)---Cl(4<sup>I</sup>) and S(3)---Cl(4<sup>I</sup>), and 3.435 Å and 3.474 Å for S(2)---Cl(5<sup>II</sup>) and S(3)---Cl(5<sup>II</sup>). In these two interactions Cl(4<sup>I</sup>) and Cl(5<sup>II</sup>) lie 0.54 Å and 2.88 Å away from the mean plane of the S<sub>5</sub>N<sub>5</sub> ring. There is a similar interaction involving S(4) and S(5) with Cl(5<sup>III</sup>) at (1-x,  $\frac{1}{2}$ +y,  $\frac{1}{2}$ -z) with distances of 3.383 Å and 3.294 Å respectively, where Cl(5<sup>III</sup>) lies 0.27 Å away from the mean plane of the S<sub>5</sub>N<sub>5</sub> ring. This type of interaction is possible because the intervening nitrogen is inset into the ring and a short N---Cl contact does not occur. It is of interest that the shortest S---Cl contacts occur with the two chlorine atoms which are closest to the mean plane of the S<sub>5</sub>N<sub>5</sub> ring, and this suggests that these interactions may involve the overlap of a lone pair on a chlorine atom with a vacant orbital on the S<sub>5</sub>N<sub>5</sub> ring. These interactions are analogous to that seen in S<sub>5</sub>N<sub>5</sub><sup>+</sup>S<sub>3</sub>N<sub>3</sub>O<sub>4</sub><sup>-</sup> between two sulphur atoms and an oxygen atom described in section 5.6 and are related to the interaction between an oxygen atom and two sulphurs in [S<sub>3</sub>N<sub>2</sub>]<sub>2</sub><sup>2+</sup>(ClS<sub>2</sub>O<sub>6</sub>)<sub>2</sub><sup>-</sup> described in section 3.6.

There are very few Cl---Cl contacts less than their van der Waals distance of 3.5 Å. Those present are between the chlorine atoms on the POCl<sub>3</sub> group and those bonded to tin, and have been used in section 6.5.c to account for the variations in the angles seen in the POCl<sub>3</sub> group. Likewise there is only one N---Cl distance less than the van der Waals distance of 3.330 Å, namely N(1)---Cl(6) at ( $\bar{x}$ , 1-y,  $\bar{z}$ ) of distance 3.246 Å.

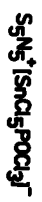
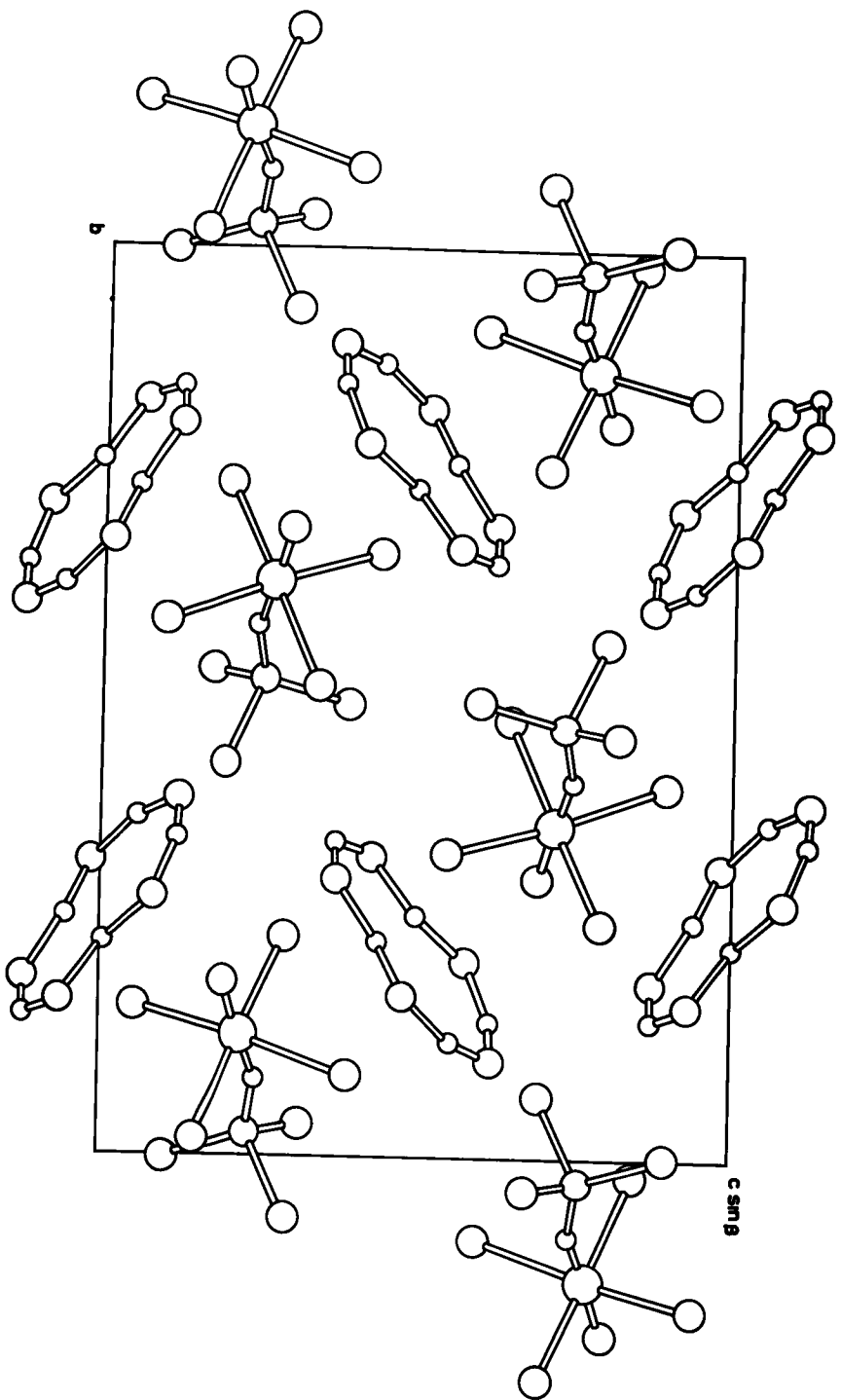
A projection along a of the contents of a unit cell is shown in figure 6.5.

Some Intermolecular Contacts ( $\text{\AA}$ )  $< 3.8\text{\AA}$ .

Atom A	Atom B	Equivalent	Cell	A-B
S(1)	Cl(3)	2	(0, 1, 0)	3.753
S(1)	Cl(8)	2	(1, 1, 0)	3.475
S(2)	Cl(4)	1	(-1, 0, 0)	3.306
S(2)	Cl(5)	3	(0, 0, 0)	3.435
S(2)	Cl(8)	1	(-1, 0, 0)	3.710
S(3)	Cl(4)	1	(-1, 0, 0)	3.279
S(3)	Cl(5)	3	(0, 0, 0)	3.474
S(4)	Cl(2)	4	(0, 0, 0)	3.613
S(4)	Cl(5)	3	(1, 0, 0)	3.383
S(5)	Cl(1)	3	(0, 0, 0)	3.645
S(5)	Cl(4)	3	(1, 0, 0)	3.689
S(5)	Cl(5)	3	(1, 0, 0)	3.294
Cl(1)	Cl(8)	1	(-1, 0, 0)	3.623
Cl(2)	Cl(7)	2	(1, 0, 0)	3.351
Cl(3)	Cl(8)	1	(1, 0, 0)	3.497
N(1)	Cl(6)	2	(0, 1, 0)	3.244
N(3)	Cl(2)	4	(0, 0, 0)	3.382
N(4)	Cl(1)	3	(0, 0, 0)	3.388

The intermolecular contacts refer to the position of atom A as in the original coordinates list and B as obtained from this using the symmetry operations given

Equivalent	1	x	y	z
2	$\bar{x}$	$\bar{y}$	$\bar{z}$	
3	$\bar{x}$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	
4	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	



projection on the [001] plane

Figure 6.5

Table 6.8  $S_5N_5^+[SnCl_5POCl_3]^-$

Final Calculated and Observed Structure Factors (Both x 10)

H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC
0	0	2	599	-642	0	5	20	221	202	0	12	6	0	-24	1	2	-3	377	408
0	0	4	604	-707	0	6	0	1513	-1431	0	12	7	212	-74	1	2	-2	1721	-1845
0	0	6	1394	1900	0	6	1	1054	-965	0	12	8	217	-180	1	2	-1	575	-564
0	0	8	641	881	0	6	2	-102	31	0	12	9	307	389	1	2	0	1962	1453
0	0	10	151	-143	0	6	3	964	-882	0	12	10	-157	210	1	2	1	181	-172
0	0	12	0	-33	0	6	4	931	801	0	12	11	-87	137	1	2	2	1754	1940
0	0	14	0	-17	0	6	5	1314	1293	0	12	12	-131	76	1	2	3	855	1000
0	0	16	399	328	0	6	6	-48	-31	0	12	13	-92	-131	1	2	4	1282	-1451
0	0	18	627	-576	0	6	7	-123	-113	0	13	1	464	430	1	2	5	1213	-1309
0	0	20	372	-324	0	6	8	638	-616	0	13	2	186	142	1	2	6	2070	-2249
0	1	1	0	154	0	6	9	-96	36	0	13	3	-117	-148	1	2	7	258	303
0	1	2	1833	-1814	0	6	10	-104	-47	0	13	4	-147	-182	1	2	8	1365	1467
0	1	3	0	-74	0	6	11	193	-215	0	13	5	373	-363	1	2	9	542	574
0	1	4	321	-377	0	6	12	197	-27	0	13	6	294	-273	1	2	10	219	-173
0	1	5	1280	1456	0	6	13	873	870	0	13	7	399	349	1	2	11	617	405
0	1	6	328	346	0	6	14	376	-360	0	13	8	-123	136	1	2	12	479	-447
0	1	7	1271	1395	0	6	15	265	-220	0	13	9	188	162	1	2	13	330	-363
0	1	8	945	-1092	0	6	16	-61	116	0	13	10	261	237	1	2	14	253	-225
0	1	9	513	-903	0	6	17	599	-950	0	13	11	189	-205	1	2	15	-125	45
0	1	10	1487	-1496	0	6	18	-156	159	0	14	0	251	246	1	2	16	398	374
0	1	11	156	180	0	6	19	-174	132	0	14	1	-125	-137	1	2	17	0	47
0	1	12	0	-21	0	6	20	-135	130	0	14	2	368	-325	1	2	18	-171	158
0	1	13	199	148	0	7	1	803	-756	0	14	3	-130	-64	1	2	19	-126	149
0	1	14	0	-58	0	7	2	-123	-129	0	14	4	-144	-178	1	2	20	469	-443
0	1	15	219	197	0	7	3	1366	1330	0	14	5	0	-26	1	2	21	-211	86
0	1	16	997	-981	0	7	4	1014	955	0	14	6	239	125	1	2	22	-108	17
0	1	17	0	-28	0	7	5	595	594	0	14	7	0	143	1	2	23	-20	278
0	1	18	532	-921	0	7	6	640	-605	0	14	8	247	246	1	2	24	-19	0
0	1	19	0	-63	0	7	7	1313	-1261	0	15	1	-61	-81	1	2	25	-18	-162
0	1	20	604	556	0	7	8	177	-139	0	15	2	241	-245	1	2	26	-17	457
0	2	0	0	-56	0	7	9	365	364	0	15	3	-140	-56	1	2	27	-16	893
0	2	0	2091	-1909	0	7	10	285	262	0	15	4	-86	49	1	2	28	-15	-85
0	2	1	402	-351	0	7	11	208	169	1	0	-22	0	-144	1	2	29	-14	564
0	2	1	1647	-1596	0	7	12	223	-207	1	0	-20	-137	-80	1	2	30	-13	202
0	2	2	792	-801	0	7	13	237	238	1	0	-18	329	319	1	2	31	-12	1125
0	2	3	342	346	0	7	14	-20	-78	1	0	-16	633	636	1	2	32	-11	922
0	2	4	792	740	0	7	15	348	-378	1	0	-14	1063	-1028	1	2	33	-10	758
0	2	5	401	425	0	7	16	368	333	1	0	-12	853	-868	1	2	34	-9	435
0	2	6	171	195	0	7	17	0	-67	1	0	-10	1472	1564	1	2	35	-8	742
0	2	7	1166	-1257	0	7	18	-148	53	1	0	-8	1066	-1136	1	2	36	-7	395
0	2	8	639	-583	0	7	19	-124	198	1	0	-6	224	-257	1	2	37	-6	742
0	2	9	453	480	0	8	0	310	318	1	0	-4	220	-257	1	2	38	-5	648
0	2	10	595	-615	0	8	1	822	762	1	0	-2	1031	787	1	2	39	-4	705
0	2	11	902	889	0	8	2	720	671	1	0	0	845	-703	1	2	40	-3	-125
0	2	12	543	542	0	8	3	379	337	1	0	2	2328	-2072	1	2	41	-2	1082
0	2	13	485	-503	0	8	4	291	-288	1	0	4	762	745	1	2	42	-1	965
0	2	14	325	-495	0	8	5	916	-922	1	0	6	1152	1120	1	2	43	0	948
0	2	15	230	-197	0	8	6	166	-144	1	0	8	203	-229	1	2	44	1	746
0	2	16	852	781	0	8	7	-55	-66	1	0	10	-6	196	1	2	45	2	586
0	2	17	-71	-117	0	8	8	298	307	1	0	12	173	38	1	2	46	3	478
0	2	18	240	-229	0	8	9	383	378	1	0	14	167	194	1	2	47	4	619
0	2	19	20	-146	0	8	10	431	432	1	0	16	1212	-1198	1	2	48	5	630
0	2	20	0	-44	0	8	11	347	281	1	0	18	-124	126	1	2	49	6	844
0	3	1	484	-420	0	8	12	-104	-95	1	0	20	535	500	1	2	50	7	904
0	3	2	2528	2451	0	8	13	842	-816	1	1	-21	-79	7	1	2	8	724	698
0	3	3	944	1004	0	8	14	0	7	1	1	-20	348	332	1	2	9	974	1050
0	3	4	1194	-1192	0	8	15	0	7	1	1	-19	-161	-112	1	2	10	1089	-1161
0	3	5	1133	-1132	0	8	16	0	-23	1	1	-18	197	162	1	2	11	1367	410
0	3	6	588	-593	0	8	17	302	309	1	1	-17	436	394	1	2	12	1515	-540
0	3	7	968	-1020	0	8	18	217	-225	1	1	-16	498	-495	1	2	13	1489	-478
0	3	8	431	430	0	8	19	1	309	1	1	-15	277	-255	1	2	14	1719	684
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H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC				
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1	0	4	317	-307	1	12	-11	256	-199	2	1	1	2	421	385	2	4	-9	264	299	2	7	-14	-63	-52			
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1	0	7	323	334	1	12	-8	-74	-45	2	1	4	5	1026	-1016	2	4	-6	-103	86	2	7	-11	0	-45			
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1	0	25	334	-344	1	12	10	255	-184	2	1	22	23	-157	-81	2	4	12	-156	-136	2	7	7	475	460			
1	0	26	-114	116	1	12	11	-73	-171	2	1	23	24	-18	-17	2	4	13	705	-721	2	7	8	230	250			
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1	0	31	491	-479	1	12	16	-203	216	2	1	28	-13	-175	149	2	4	18	0	109	2	7	13	556	546			
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1	0	34	583	-545	1	12	19	-6	222	145	2	1	31	-10	314	338	2	4	21	-20	282	2	7	16	301	-314		
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1	0	42	288	315	1	12	27	2	274	-246	2	1	39	-2	1770	1650	2	4	29	-12	-174	-233	2	7	24	-13	356	-335
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4 K L FD FC					H K L FO FC					M K L FO FC					H K L FO FC					M K L FO FC											
2	0	7	669	-678	2	13	7	396	-344	3	2	14	612	-620	3	9	8	425	-437	3	8	11	272	299							
2	0	8	-86	-156	2	13	8	-167	-164	3	2	15	-199	149	3	9	9	-170	-198	3	8	12	237	224							
2	0	9	529	349	2	13	9	0	97	3	2	16	0	-23	3	9	10	512	-917	3	8	13	-168	-201							
2	0	10	213	228	2	13	10	-155	-93	3	2	17	-144	-140	3	9	11	550	-965	3	8	14	0	94							
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2	0	12	-132	75	2	14	-7	0	80	3	2	19	0	158	3	9	13	-101	167	3	8	16	-24	-61							
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5	3	34	-136	-64	5	6	43	10	0	51	5	11	17	-1	222	195	6	2	32	757	-716	6	5	47	-13	-64		
5	3	35	-120	89	5	6	44	11	243	-294	5	11	18	0	-202	303	6	2	33	-1	485	-435	6	5	48	12	-151	
5	3	36	729	-686	5	6	45	12	-27	198	5	11	19	-1	135	-217	6	2	34	0	-93	-152	6	5	49	11	526	
5	3	37	559	-562	5	6	46	13	-174	160	5	11	20	2	311	-321	6	2	35	1	-117	-41	6	5	50	269	-251	
5	3	38	738	720	5	6	47	14	-135	-51	5	11	21	3	-64	89	6	2	36	861	788	6	5	51	-9	-133		
5	3	39	406	360	5	6	48	15	-127	135	5	11	22	4	-124	37	6	2	37	533	511	6	5	52	-8	259		
5	3	40	707	174	5	6	49	16	-114	-279	5	11	23	5	304	368	6	2	38	4	245	-198	6	5	53	7	506	
5	3	41	363	349	5	6	50	17	0	87	5	11	24	6	-155	34	6	2	39	5	401	405	6	5	54	-6	-202	
5	3	42	996	-959	5	6	51	18	-276	-200	5	11	25	-4	-90	112	6	2	40	6	708	-708	6	5	55	-5	-192	
5	3	43	309	-332	5	6	52	19	-108	68	5	11	26	-3	-135	89	6	2	41	7	-169	-181	6	5	56	-4	-94	
5	3	44	-130	-33	5	6	53	20	-111	379	49	5	11	27	0	-71	5	2	42	8	373	306	6	5	57	-3	358	
5	3	45	240	128	5	6	54	21	0	81	5	11	28	-1	-206	-236	6	2	43	9	0	-54	6	5	58	-2	418	
5	3	46	433	454	5	6	55	22	-148	81	5	11	29	0	-127	0	6	2	44	10	387	376	6	5	59	-1	310	
5	3	47	110	228	5	6	56	23	-112	-149	5	11	30	1	0	14	6	2	45	11	0	-36	6	5	60	0	-151	
5	3	48	-141	-163	5	6	57	24	-329	-328	6	11	31	-1	498	-495	6	2	46	12	-191	-147	6	5	61	1	512	
5	3	49	398	431	5	6	58	25	-6	0	-141	6	11	32	-16	331	336	6	2	47	13	326	286	6	5	62	2	0
5	3	50	-139	-218	5	6	59	26	-131	-176	6	11	33	-14	-49	145	6	2	48	14	0	88	6	5	63	3	336	
5	3	51	-61	-88	5	6	60	27	-62	640	6	11	34	-12	347	-337	6	2	49	15	-34	-204	6	5	64	4	207	
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5	3	53	-18	379	-347	5	6	62	-2	425	-395	6	11	36	-9	745	704	6	2	51	17	0	-44	6	5	66	6	-151
5	3	54	-179	-53	5	6	63	-1	-191	-203	6	11	37	-8	942	929	6	2	52	18	0	-8	6	5	67	7	722	
5	3	55	-15	0	72	5																						

4	K	L	PO	FC	H	K	L	PO	FC	H	K	L	PO	FC	H	K	L	PO	FC						
6	9	6	-143	44	7	2	8	299	327	7	6	8	-190	126	8	2	-14	0	-92	8	7	-9	-89	100	
6	9	7	403	397	7	2	9	-211	194	7	6	9	231	225	8	2	-13	-132	12	8	7	-8	0	-18	
6	9	8	-152	-38	7	2	10	-108	147	7	6	10	-144	61	8	2	-12	472	-492	8	7	-7	250	319	
6	9	9	242	218	7	2	11	328	388	7	7	-13	226	293	8	2	-11	0	11	8	7	-6	3	43	
6	10	-11	-133	71	7	2	12	222	-253	7	7	-12	-166	-196	8	2	-10	-200	169	8	7	-5	497	-525	
6	10	-10	-118	-177	7	2	13	0	-77	7	7	-11	-187	-194	8	2	-9	0	-72	8	7	-4	256	276	
6	10	-9	485	464	7	3	-18	360	364	7	7	-10	0	36	8	2	-8	382	393	8	7	-3	-187	-197	
6	10	-8	303	293	7	3	-19	-140	-86	7	7	-9	440	-425	8	2	-7	-93	81	8	7	-2	0	35	
6	10	-7	-129	-72	7	3	-14	-210	225	7	7	-8	502	459	8	2	-6	603	-598	8	7	-1	532	534	
6	10	-6	0	-6	7	3	-13	258	242	7	7	-7	480	454	8	2	-5	-184	278	8	7	0	-195	221	
6	10	-5	244	-274	7	3	-12	444	-440	7	7	-6	264	237	8	2	-4	312	-335	8	7	1	0	46	
6	10	-4	-212	-224	7	3	-11	376	-314	7	7	-5	243	236	8	2	-3	539	-571	8	7	2	-95	10	
6	10	-3	-201	188	7	3	-10	-194	138	7	7	-4	273	-246	8	2	-2	590	562	8	7	3	-593	-614	
6	10	-2	0	-14	7	3	-9	299	-291	7	7	-3	528	-533	8	2	-1	-133	141	8	7	4	-163	153	
6	10	-1	363	367	7	3	-8	697	642	7	7	-2	-113	-7	8	2	0	-133	13	8	7	5	492	502	
6	10	0	-27	-20	7	3	-7	449	455	7	7	-1	0	-91	8	2	1	412	380	8	7	6	-265	-333	
6	10	1	-197	-266	7	3	-6	357	-329	7	7	0	-144	72	8	2	2	338	-308	8	7	7	-6	391	366
6	10	2	-145	-139	7	3	-5	323	335	7	7	1	310	311	8	2	3	-183	-57	8	7	8	-5	0	-7
6	10	3	376	-389	7	3	-4	725	-650	7	7	2	-168	-141	8	2	4	358	-383	8	7	9	-4	-193	-121
6	10	4	-129	126	7	3	-3	-72	-25	7	7	3	-156	76	8	2	5	-171	237	8	7	0	-3	531	571
6	10	5	372	351	7	3	-2	555	545	7	7	4	-135	-12	8	2	6	215	219	8	7	1	-2	-95	99
6	10	6	0	27	7	3	-1	354	361	7	7	5	531	-533	8	2	7	-197	-144	8	7	2	0	-16	-16
6	10	7	-85	130	7	3	0	301	283	7	7	6	-107	54	8	2	8	210	243	8	7	3	0	0	-26
6	10	8	0	18	7	3	1	-199	243	7	7	7	0	-89	8	2	9	238	96	8	7	4	1	461	-469
6	10	9	-99	153	7	3	2	497	-517	7	7	8	-179	-167	8	2	10	-160	-244	8	7	5	2	-114	-179
6	11	-7	362	-395	7	3	3	423	460	7	7	9	369	391	8	3	-14	408	-410	8	7	6	3	-216	255
6	11	-6	381	-412	7	3	4	-195	-181	7	8	-12	0	112	8	3	-13	-192	-159	9	0	-10	465	-662	
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6	11	-4	0	15	7	3	6	0	-77	7	8	-10	-127	175	8	3	-11	0	-13	9	0	-8	-159	246	
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6	11	-2	-182	-153	7	3	8	549	539	7	8	-8	318	-247	8	3	-9	-132	62	9	0	-6	2	298	237
6	11	-1	278	-235	7	3	9	-194	221	7	8	-7	-184	261	8	3	-8	252	-268	9	0	-5	0	642	648
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6	11	2	0	-66	7	3	12	278	-239	7	8	-4	-106	-176	8	3	-5	435	-434	9	0	-2	6	254	235
6	11	3	243	254	7	4	-16	-143	59	7	8	-3	0	-199	8	3	-4	318	403	9	1	-1	-11	-24	-12
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6	11	5	-212	233	7	4	-14	244	-240	7	8	-1	473	467	8	3	-2	592	646	9	1	-9	0	5	5
6	12	-3	-131	-138	7	4	-13	-135	-53	7	8	0	0	62	8	3	-1	324	283	9	1	-8	1	257	191
6	12	-2	246	217	7	4	-12	-190	-208	7	8	1	214	-120	8	3	0	264	-294	9	1	-7	2	274	311
6	12	-1	0	-196	7	4	-11	352	-351	7	8	2	310	331	8	3	1	0	-19	9	1	-6	-92	-147	
6	12	0	-204	-137	7	4	-10	369	351	7	8	3	353	-401	8	3	2	-30	-101	9	1	-5	-156	-157	
7	0	-16	-75	122	7	4	-9	521	475	7	8	4	-114	141	8	3	3	-184	-238	9	1	-4	-192	-165	
7	0	-14	586	-624	7	4	-8	0	-6	7	8	5	0	-174	8	3	4	306	309	9	1	-3	0	-28	0
7	0	-12	209	-178	7	4	-7	571	583	7	8	6	0	4	8	3	5	305	287	9	1	-2	6	683	695
7	0	-10	522	475	7	4	-6	741	-717	7	8	7	412	439	8	3	6	370	386	9	1	-1	-134	73	
7	0	-8	467	-463	7	4	-5	718	-691	7	8	8	-77	-173	8	3	7	-138	75	9	1	0	260	321	
7	0	-6	835	-857	7	4	-4	-88	45	7	9	-10	268	-215	8	3	8	291	-332	9	1	1	-115	158	
7	0	-4	270	279	7	4	-3	372	380	7	9	-9	-185	278	8	3	9	-69	-66	9	1	2	343	-406	
7	0	-2	488	454	7	4	-2	487	444	7	9	-8	-153	-6	8	3	-13	0	-21	9	1	3	-161	12	
7	0	0	332	-337	7	4	-1	0	85	7	9	-7	252	-275	8	3	-12	292	227	9	1	4	-251	127	
7	0	1	472	-452	7	4	0	-106	-145	7	9	-6	-207	-203	8	3	-11	0	107	9	1	5	0	-16	0
7	0	2	-95	-136	7	4	1	-40	19	7	9	-5	232	-267	8	3	-10	-53	61	9	1	6	413	437	
7	0	3	592	582	7	4	2	507	-499	7	9	-4	-163	70	8	3	-9	279	237	9	1	7	-10	-134	120
7	0	4	739	-703	7	4	3	-185	-205	7	9	-3	513	545	8	3	-8	262	118	9	1	8	-9	-114	55
7	0	5	434	-414	7	4	4	-46	8	7	9	-2	0	-11	8	3	-7	226	-221	9	1	9	-8	-184	-74
7	0	6	586	586	7	4	5	-204	-191	7	9	-1	247	224	8	3	-6	-181	241	9	1	10	-7	0	65
7	1	-17	-79	41	7	4	6	435	429	7	9	0	-66	178	8	3	-5	-133	49	9	1	11	-6	-61	-64
7	1	-16	445	-457	7	4	7	-134	-173	7	9	1	343	-364	8	3	-4	558	588	9	1	12	-5	-32	40
7	1	-15	-197	103	7	4	8	-193	-213	7	9	2	0	-57	8	3	-3	325	332	9	1	13	-4	230	200
7	1	-14	-35	-136	7	4	9	-71	-2	7	9	3	0	-135	8	3	-2	421	-427	9	1	14	-3	229	-275
7	1	-13	-178	18	7	4	10	-120	-160	7	9	4	-37	139	8	3	-1	-196	117	9	1	15	-2	-85	163
7	1	-12	296	274	7	4	11	431	-449	7	9	5	446	478	8	3	0	326	-354	9	1	16	-1	472	479
7	1	-11	-99	-32	7	4	12	374	391	7	9	6	-209	181	8	3	1	504	-519	9	1	17	0	564	-581
7	1	-10	328	-205	7	5	-15	239	-202	7	10	-7	264	-268	8	3	2	494	489	9	1	18	1	447	-675
7	1	-9	214	228	7	5	-14	-126	-32	7	10	-6	-190	42	8	3	3	0	167	9	1	19	2	325	-301
7	1	-8	1025	-1041	7	5	-13	-178	-112	7	10	-5	500	487	8	3	4	-117	98	9	1	20	3	-115	-228
7	1	-7	-133	-167	7	5	-12	-169	228	7	10	-4	225	186	8	3	5	241	203	9	1	21	4	456	521
7	1	-6	-177	-172	7	5	-11	-22	93	7	10	-3	-91	87	8	3	6	395							

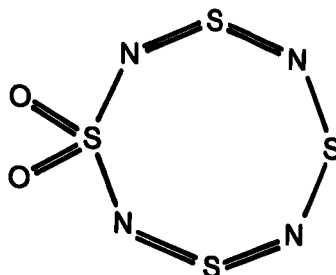
CHAPTER 7

The Crystal Structure of  $S_4N_4O_2$

### 7.1 Introduction.

This section describes the work performed on the second compound isolated from the reaction between  $(\text{CH}_3)_3\text{Si-N=S=N-Si}(\text{CH}_3)_3$  and  $\text{FSO}_2\text{-N=S=O}$  as described in section 5.1. This compound gave an analysis and mass spectrum corresponding to the formulation  $\text{S}_4\text{N}_4\text{O}_2$ . The compound was found to be monomeric in the gas phase and also its molecular weight as determined cryoscopically corresponded to  $\text{S}_4\text{N}_4\text{O}_2$ .

The infrared spectrum could be interpreted in terms of the structure



This compound was of interest because it represented the second known oxide of  $\text{S}_4\text{N}_4$ .

### 7.2 Crystal Data.

The crystals were obtained as orange needles elongated along  $\underline{c}$  and bounded by prominent  $\{120\}$  faces. Individual crystals were

cut to appropriate lengths and sealed in quartz tubes to prevent hydrolysis. The crystal used for data collection had dimensions  $0.5 \times 0.25 \times 0.25$  mm. Preliminary work using precession and Weissenberg methods showed the unit cell to be orthorhombic with systematic absences

h k l	$k + l = 2n$
0 k l	$k = 2n$
h 0 l	$(l = 2n)$
h k 0	$(k = 2n)$
h 0 0	no conditions
0 k 0	$(k = 2n)$
0 0 l	$(l = 2n)$

These are consistent with the noncentrosymmetric space group Abm2 (No.39) and also with the centrosymmetric space group Abmm (a non-standard representation of Cmma No.67) the reflections observed on the precession and Weissenberg photographs could be interpreted in terms of two superimposed reciprocal lattices each showing the absences of the space group and the same relative intensity to each other but differing slightly in orientation. This suggested that there were two pieces of crystal present which were slightly misaligned with respect to each other. The apparent splitting of the reflections on the films was most evident on the Okl net, although it was evident on all other nets except for the hk0 net. The separation of the two parts of the reflections became more noticeable with increasing values of l and for the 00l reflections was about  $2^\circ$ .

Several attempts were made to recrystallise the material. It was originally crystallised from methylene chloride, in which it is highly soluble. This was replaced by chloroform in which it is only slightly soluble, in order to recrystallise from a less concentrated solution. In this way several batches of very well formed crystals were obtained, a large number of which were examined, but all showed the apparent splitting of the reflections when photographed. The imperfections were not a consequence of the cutting since they were also shown by tiny uncut crystals. Data was finally collected from a split crystal.

Cell dimensions were obtained from the positions of twelve reflections measured on a diffractometer. Because for many reflections both parts overlapped, it was impossible to obtain accurate dimensions from the reflections from one part of the crystal. Consequently for the reflections which were split the positions of both parts were found and averaged, and where broadening was observed the mean position was taken. This work showed that each part of the reflection had the same  $\theta$  value and differed only in orientation. It also showed that the ratio of the intensities of the two parts was constant for all reflections. The unit cell dimensions were obtained from a least squares treatment of these positions. The dimensions shown correspond to  $\alpha$ ,  $\beta$  and  $\gamma$  being constrained to  $90^\circ$ , however refinement without this constraint gave values for the angles very close to  $90^\circ$  (within  $0.07(7)^\circ$ ).



$$\begin{aligned}
 \text{S}_4\text{N}_4\text{O}_2 \quad M &= 216.28 \\
 a &= 8.088(5)\text{\AA} \\
 b &= 18.920(10)\text{\AA} \\
 c &= 8.683(7)\text{\AA} \\
 U &= 1328.7\text{\AA}^3 \\
 Z &= 8 \\
 D_m &= 2.15\text{g cm}^{-3} \text{ (by floatation in C}_2\text{H}_5\text{I/C}_2\text{H}_4\text{Br}_2\text{)} \\
 D_c &= 2.16\text{g cm}^{-3}
 \end{aligned}$$

Absorption coefficient for MoK $\alpha$  radiation ( $\lambda = 0.7107\text{\AA}$ ) =  $13.7\text{cm}^{-1}$ .

### 7.3 Data Collection and Correction.

The intensity data were collected on a Hilger and Watts Y290 four-circle diffractometer using Zr-filtered MoK $\alpha$  radiation. To record both parts of the reflection an  $\omega$  scan of 160 steps of  $0.01^\circ$  together with an open counter was used. Counting times of 2 seconds per step were allowed with a stationary background count of 80 seconds at the beginning and end of each scan. Reflections which showed a splitting of greater than  $0.8^\circ$  were recorded in steps of  $0.01^\circ$  over  $2.0^\circ$  and the middle 40 steps were removed so that the background:count ratio was retained. Three reflections were measured as standards every 30 reflections, and showed no systematic variations indicating that the crystal was stable throughout the experiment. Two sets of equivalent reflections were recorded for  $0 < \theta \leq 25^\circ$ . These gave a total of 657 independent reflections, of these 505 were taken as observed having net counts  $> 2$  e.s.d's. The intensities were corrected for Lorentz and polarisation effects but not for absorption.

#### 7.4 Solution and Refinement.

An attempt was made initially to solve the structure in the centrosymmetric space group  $Cmma$  using symbolic addition procedures since the statistical distribution of the normalised structure factors, as shown in table 7.1 seemed to match better with the centrosymmetric case than the noncentrosymmetric. A multisolution program was used as described earlier and this gave several sets of highly self-consistent phases; however the E-maps calculated from these could not be interpreted in terms of a meaningful structure. This was later shown to be due to the wrong choice of space group. Finally the structure was solved from its Patterson function.

The Patterson function for the space groups  $Abm2$  and  $Abmm$  takes the form

$$P(uvw) = \frac{8}{V} \sum_0^{\infty} \sum_0^{\infty} \sum_0^{\infty} |F(hkl)|^2 \cos 2\pi hu \cos 2\pi kv \cos 2\pi lw$$

this was calculated from

$$u = 0 \rightarrow \frac{1}{4} \text{ intervals of } 0.29526\text{\AA}$$

$$v = 0 \rightarrow \frac{1}{8} \text{ intervals of } 0.27134\text{\AA}$$

$$w = 0 \rightarrow \frac{1}{8} \text{ intervals of } 0.25275\text{\AA}$$

The coefficients used were  $|F_{\text{obs}}|^2$  weighted by  $(Lp)^{-1}$  for each reflection. The vector map could only be interpreted in terms of the noncentrosymmetric space group.

The positions of all sulphur atoms were determined from their

Harker peaks. For an atom in a general position  $x, y, z$  in the space group  $Abm2$  the following Harker peaks should be observed in the Patterson function

$$\begin{array}{rcl} 2x & 2y & 0 \\ 2x & \frac{1}{2} & 0 \\ 0 & \frac{1}{2} - 2y & 0 \end{array}$$

and for atoms on the mirror planes at  $x = \frac{1}{4}$  and  $\frac{3}{4}$

$$\frac{1}{2} \quad 0 \quad 2z$$

The density measurements showed that there was one molecule per asymmetric unit corresponding to four sulphur atoms in general positions. The vector map was characterised by having very few large peaks in general positions, indicating that some of the sulphur atoms may be in special positions, and that the distribution of the sulphur atoms might have a higher symmetry than required by the space group. The two most significant peaks were at 0.219, 0.109, 0.125 and 0.281, 0.141, 0.25; the first of these corresponds to the vector between adjacent sulphur atoms in the same  $S_4N_4O_2$  molecule, and the second to a vector between sulphur atoms in adjacent molecules. Although there are two crystallographically independent types of molecules per cell, they have approximately the same orientation so that only one intramolecular S-S vector is seen in a general position in the vector map.

The first sulphur atom was found at 0.218, 0,0 from its Harker peaks at

0.436	0	0	(62)
0.436	$\frac{1}{2}$	0	(73)
0	$\frac{1}{2}$	0	(114)

The position of the origin on the z axis for this space group is not specified by symmetry requirements, and was fixed by setting  $z = 0$  for this atom. Harker peaks were found for four further sulphur atoms (two of these were in special positions on a mirror plane). The value of the z-coordinates relative to S(1) was found by generating the vectors between these atoms and S(1) and searching for a peak with the appropriate coordinates in a u and v. The positions found were

	x	y	z
S(1)	0.218	0.0	0.0
S(2)	-0.01	0.108	0.125
S(3)	0.05	0.141	0.250
S(4)	0.281	0.25	0.375
S(5)	0.719	0.25	0.375

These positions were refined by least squares methods using the block-diagonal approximation. The sulphur atoms were given isotropic temperature factors of  $3.0\text{\AA}^2$ , and at the end of two cycles the R value was 0.40. An  $F_o$  map was calculated, which

revealed the positions of the four nitrogen atoms. Further refinement and calculation of difference syntheses gave the positions of the four oxygen atoms. The molecules of  $S_4N_4O_2$  occupy two different crystallographic positions in the cell; half the molecules lie on mirror planes and the other half are disordered about two-fold axes to produce the observed symmetry. Two of the oxygen atoms lie on a mirror plane at  $y = \frac{1}{4}$  whereas the other two lie in general positions with an occupation factor of 0.5 due to disordering. With the inclusion of these R fell to 0.20. A difference map at this stage showed that the sulphur atoms were vibrating anisotropically; this was allowed for during the subsequent refinement after which R fell to 0.148.

The atomic coordinates for the ring atoms in the disordered molecule correspond to the mean positions of two superimposed  $S_4N_4$  rings. Calculation of a difference synthesis showed that this approximation was satisfactory for all the ring atoms except S(1), for which a more accurate description was that of two sulphur atoms each with an occupation factor of 0.5 separated by about  $0.7\text{\AA}$ . These were included with isotropic temperature factors in the subsequent refinement, which resulted in an R value of 0.125. Further refinement using full matrix least squares methods saw R stand at 0.117. The parameter shifts in the last cycle were all  $< 0.2\sigma$ . A difference synthesis calculated from the final structure factors showed no prominent features associated with the atomic positions; however the map did contain ripples of  $\pm 1.2 \text{ e.\AA}^{-3}$ .

The initial weighting scheme used was the same as in previous refinements, with values of  $P_1 = 35.0$  and  $P_2 = 0.01$ . This was replaced in the final stages of refinement by a weighting scheme of the form

$$\sqrt{w} = [1 - \exp(-P_2 \cdot \sin^2 \theta / \lambda^2)] / [P_1 + |F_o|]^{\frac{1}{2}}$$

This was found to give a more uniform distribution of  $w\Delta^2$  than the previous scheme and the scheme based on counting statistics mentioned earlier. The optimum values of the parameters were  $P_1 = 30.0$   $P_2 = 60.0$ .  $w\Delta^2$  was analysed as a function of the magnitude of  $|F_o|$  and also as a function of  $\theta$ . The latter was performed in order to investigate whether the imperfections of the crystals produced any systematic errors dependent on the magnitude of  $\theta$ , but none were observed. The final least squares totals and weighting analysis are given in table 7.1. The final calculated and observed structure factors are given in table 7.7 the sulphur atoms were not corrected for anomalous dispersion. The scattering factors used were taken from International tables Vol. III. The final atomic coordinates, isotropic thermal parameters and anisotropic thermal parameters are given in table 7.2. This structure determination is less accurate than others described in this thesis, due to the poor quality of the data, to the disorder and to the large number of parameters relative to the number of observed reflections.

Table 7.1  $S N O$   
4 4 2Least squares totals

Number of observed reflections 505

$\Sigma F_o $	$\Sigma F_c $	$\Sigma \Delta $	$\Sigma w \Delta^2$	R
19282.46	18855.80	2253.84	237.76	.117

Weighting Analysis

$ F_o $ ranges	N	$\Sigma w \Delta^2 / N$	R
0 - 20	145	0.46	0.230
20 - 30	140	0.47	0.159
30 - 40	68	0.43	0.129
40 - 50	45	0.49	0.126
50 -100	82	0.54	0.082
100 -200	22	0.33	0.046
200-upwards	3	0.47	0.060

The Statistical Distribution of the Normalised Structure Factors

	Centrosymmetric	Noncentrosymmetric	Observed
$\langle  E  \rangle$	0.798	0.886	0.824
$\langle  E ^2 \rangle$	1.00	1.00	1.060
$\langle  E^2 - 1  \rangle$	0.968	0.736	0.982
$ E  > 3$	0.3%	0.01%	0.43%
$ E  > 2$	5.0%	1.8%	4.41%
$ E  > 1$	32.0%	37.0%	32.86%

Table 7.2

S N O  
4 4 2Final Atomic Coordinates with their Estimated Standard Deviations  
( $\times 10^4$ ) and Isotropic Thermal Parameters ( $\text{\AA}^2$ )

Atom	$x/a$	$y/b$	$z/c$	B	Occupation Factor
S(11)	0.2497(21)	0.0202(7)	0.0035(27)	3.34(30)	0.5
S(12)	0.1894(20)	0.0050(9)	-0.0229(25)	3.27(30)	0.5
S(2)	-0.0338( 8)	0.1077(3)	0.0996(13)	2.6 †	1.0
S(3)	0.4996(14)	0.1433(3)	0.2658 *	3.7 †	1.0
S(4)	0.2506(11)	0.25	0.3621(19)	4.3 †	1.0
S(5)	0.7034( 9)	0.25	0.3763(17)	2.6 †	1.0
O(1)	0.1004(40)	-0.0074(20)	-0.1481(49)	3.08(68)	0.5
O(2)	0.3757(56)	0.0191(23)	-0.0453(69)	4.89(94)	0.5
O(3)	0.5889(28)	0.25	0.5129(37)	2.53(41)	1.0
O(4)	0.8718(32)	0.25	0.4016(40)	3.58(54)	1.0
N(1)	0.1447(29)	0.0791(13)	0.0636(32)	3.82(48)	1.0
N(2)	-0.1871(28)	0.0566(12)	0.0665(30)	3.27(43)	1.0
N(3)	0.3398(28)	0.1732(13)	0.3255(36)	3.83(51)	1.0
N(4)	0.6619(27)	0.1863(13)	0.2541(32)	3.40(46)	

\* This parameter was used to fix the origin on c.

† The isotropic temperature factor before anisotropic refinement.

Anisotropic Thermal Parameters and their Estimated Standard Deviations  
(Both  $\text{\AA}^2 \times 10^4$ )

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
S(2)	377(43)	296(28)	746(73)	- 18(42)	168(40)	41(24)
S(3)	865(51)	264(26)	663(74)	16(44)	-197(51)	-127(41)
S(4)	37(33)	1059(88)	655(87)		- 45(49)	
S(5)	197(35)	212(32)	334(47)		- 14(42)	



Table 7.3

S N O  
4 4 2Final Bond Distances ( $\text{\AA}$ ) and their Estimated Standard Deviations( $\text{\AA} \times 10^2$ )

S(11 <sup>II</sup> )	- N(1 <sup>II</sup> )	1.49(3)
S(11 <sup>II</sup> )	- N(2)	1.63(3)
S(12)	- O(1)	1.33(4)
S(12)	- O(2)	1.54(5)
S(12)	- N(1)	1.63(3)
S(12)	- N(2 <sup>II</sup> )	1.40(3)
S(2)	- N(1)	1.57(2)
S(2)	- N(2)	1.60(2)
S(3)	- N(3)	1.50(3)
S(3)	- N(4)	1.55(2)
S(4)	- N(3)	1.65(3)
S(5)	- O(3)	1.51(3)
S(5)	- O(4)	1.38(3)
S(5)	- N(4)	1.64(3)

Table 7.3 continued...

Table 7.3 continued

Some Non-bonding Intramolecular Distances ( $\text{\AA}$ ) and their Estimated  
Standard Deviations ( $\text{\AA} \times 10^2$ )

S(11)	---S(12)	0.61(2)
S(11 <sup>II</sup> )	---S(12)	3.59(2)
S(11)	---S(2)	2.95(2)
S(12)	---S(2)	2.86(2)
S(2)	---S(2 <sup>II</sup> )	4.11(2)
N(1)	---N(1 <sup>II</sup> )	3.80(3)
N(1)	---N(2)	2.72(3)
N(1)	---N(2 <sup>II</sup> )	2.59(3)
N(2)	---N(2 <sup>II</sup> )	3.71(3)
S(3)	---S(3 <sup>I</sup> )	4.04(1)
S(3)	---S(4)	2.97(1)
S(3)	---S(5)	2.78(1)
S(4)	---S(5)	3.62(1)
N(3)	---N(3 <sup>I</sup> )	2.91(4)
N(4)	---N(4 <sup>I</sup> )	2.41(3)
N(3)	---N(4 <sup>I</sup> )	3.77(3)

Where I and II refer to atoms in the equivalent positions respectively  $x, \frac{1}{2}-y, z$  and  $-x, -y, z$  with respect to the original coordinates.

Table 7.4  $S_4N_4O_2$ Final Bond Angles (degrees) and their Estimated Standard Deviations(deg. x 10)

N(1 <sup>II</sup> ) - S(11 <sup>II</sup> ) - N(2)	111.7(17)
O(1) - S(12) - O(2)	117.3(28)
O(1) - S(12) - N(1)	114.2(22)
O(1) - S(12) - N(2 <sup>II</sup> )	107.5(23)
O(2) - S(12) - N(1)	97.2(23)
O(2) - S(12) - N(2 <sup>II</sup> )	103.1(24)
N(1) - S(2) - N(2 <sup>II</sup> )	117.9(13)
S(11 <sup>II</sup> ) - N(1 <sup>II</sup> ) - S(2 <sup>II</sup> )	147.9(20)
S(12) - N(1) - S(2)	126.2(18)
S(11 <sup>II</sup> ) - N(2) - S(2)	147.0(18)
S(12) - N(2 <sup>II</sup> ) - S(2 <sup>II</sup> )	127.8(18)
N(1) - S(12) - N(2 <sup>II</sup> )	117.2(18)
N(3) - S(3) - N(4)	123.6(15)
N(3) - S(4) - N(3 <sup>I</sup> )	123.1(15)
O(3) - S(5) - O(4)	118.8(15)
O(3) - S(5) - N(4)	112.6(14)
O(4) - S(5) - N(4)	107.8(15)
N(4) - S(5) - N(4 <sup>I</sup> )	94.6(15)
S(3) - N(3) - S(4)	140.6(19)
S(3) - N(4) - S(5)	121.2(16)

### 7.5 The Structure and Bonding in $S_4N_4O_2$

The unit cell contains two crystallographically independent sets of  $S_4N_4O_2$  molecules. One set is situated on the mirror planes at  $y = \frac{1}{4}$  and  $\frac{3}{4}$  and the other half are situated about the two-fold axes at  $(0,0,z)$  and  $(0, \frac{1}{2}, z)$  and are disordered to produce the observed symmetry. The bond lengths and angles are given in tables 7.3 and 7.4 respectively.

Both types of molecule consist of an eight-membered  $S_4N_4$  ring with both oxygen atoms attached to the same sulphur atom. The ordered molecule which sits on the mirror plane is shown in figure 7.1. The dimensions of both the ordered and disordered molecules are shown on figure 7.2.

The atomic arrangement about the two-fold axis corresponds to the mean positions of two superimposed  $S_4N_4O_2$  molecules of the dimensions seen in the molecule on the mirror plane. This can be shown by a comparison of the S---S and N---N intramolecular distances. The cross-ring distances S(4)---S(5) and S(3)---S(3<sup>I</sup>) of length 3.62(1)Å and 4.04(1)Å should not be affected by disordering. This is observed in the disordered molecule where the corresponding distances S(11<sup>II</sup>)---S(12) and S(2)---S(2<sup>II</sup>) are 3.59 Å and 4.11(2)Å. Similarly the N(3)---N(4<sup>I</sup>) cross ring distance of 3.77(3)Å in the ordered molecule is the same within experimental error as the length of 3.80(3)Å for N(1)---N(1<sup>II</sup>) and 3.71(3)Å for N(2)---N(2<sup>II</sup>). The N(3)---N(3<sup>I</sup>) and N(4)---N(4<sup>I</sup>) distances of length 2.91(4)Å and 2.41(3)Å are averaged on disordering and their average of 2.66Å is not

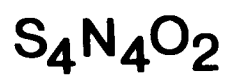
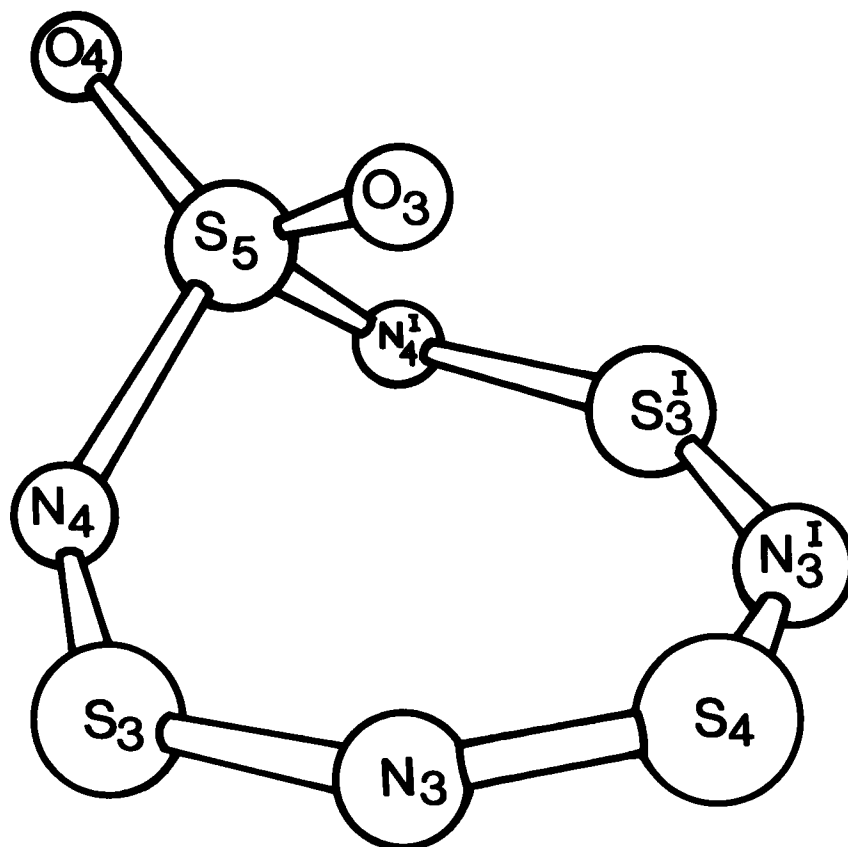
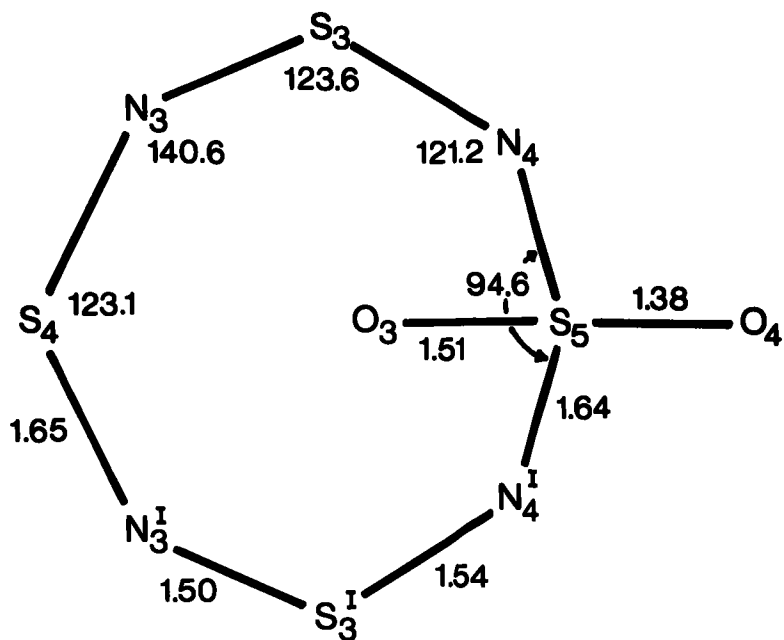
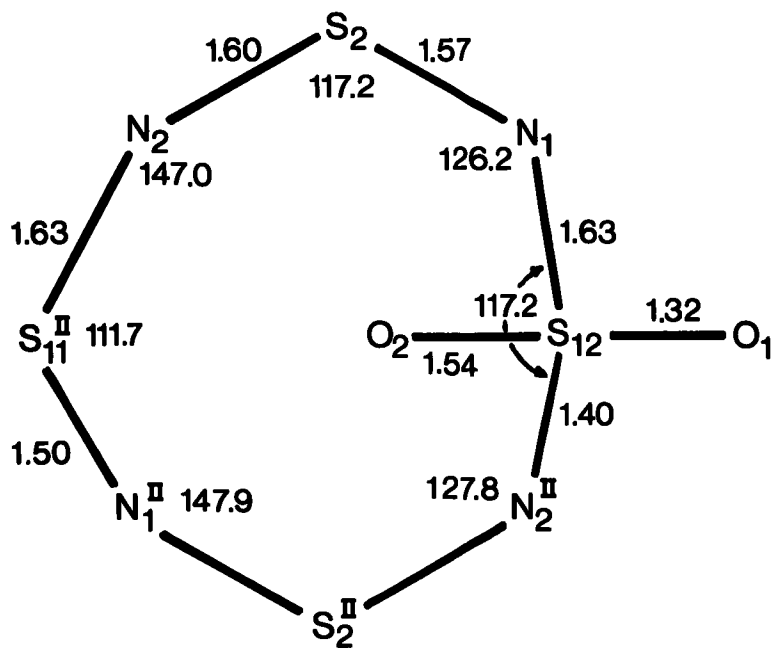


Figure 7.1



a



b



Figure 7.2

Some bond distances and angles for (a) the ordered  
(b) the disordered molecules

significantly different from the  $N(1)\text{---}N(2^{\text{II}})$  distance of  $2.59(3)\text{\AA}$  in the disordered molecule. The averaging of the  $S\text{---}S$  distances around the ring on disordering is not observed because of the separate treatment of  $S(11)$  and  $S(12)$ .

The averaging of the nitrogen positions is reflected in the differences in angle between the  $S_4N_4$  rings in the ordered and disordered molecule. In the ordered molecule the angles  $N(4)\text{---}S(5)\text{---}N(4^{\text{I}})$  and  $N(3)\text{---}S(4)\text{---}N(3^{\text{I}})$  have magnitudes of  $95^\circ$  and  $123^\circ$  respectively, whereas the corresponding angles in the disordered molecule,  $N(1)\text{---}S(12)\text{---}N(2^{\text{II}})$  and  $N(1^{\text{II}})\text{---}S(11^{\text{II}})\text{---}N(2)$  are  $117^\circ$  and  $112^\circ$  the averaging increases the separation of the nitrogen atoms bonded to the sulphur which carries the oxygen atoms and hence accounts for the increase in the angle at  $S(12)$ , and conversely the decrease at  $S(11)$ .

The following discussion of the molecular shape and dimensions is confined to the ordered molecule. The  $S_4N_4$  ring is not planar. The sulphur atom  $S(5)$  which is attached to the two oxygen atoms, and its adjacent nitrogen atoms  $N(4)$  and  $N(4^{\text{I}})$  lie  $1.52\text{\AA}$  and  $0.41\text{\AA}$  above the mean plane of the remaining ring atoms. The maximum deviation from the mean plane of  $S(3)$ ,  $S(3^{\text{I}})$ ,  $S(4)$ ,  $N(3)$  and  $N(3^{\text{I}})$  is  $0.014\text{\AA}$  as shown in table 7.5. The estimated standard deviations for all bond lengths are large (about  $0.03\text{\AA}$ ) so that a detailed discussion of the differences in bond distances is not warranted.

$S(3)\text{---}N(3)$  and  $S(3)\text{---}N(4)$  of lengths  $1.55\text{\AA}$  and  $1.50\text{\AA}$  are significantly shorter than the normal single bond distance of  $1.73\text{\AA}$  and indicate considerable multiple bonding across this part of the molecule. Conversely  $S(5)\text{---}N(4)$  of length  $1.64\text{\AA}$  does not differ

Table 7.5  $S_4N_4O_2$ 

The Equation of the Mean Plane of S(3), S(3<sup>I</sup>), S(4), N(3) and N(3<sup>I</sup>)

$$-0.3822X + 0.0Y - 0.9241Z + 3.6765 = 0$$

Atom	S(3)	S(3 <sup>I</sup> )	S(4)	S(5)†	N(3)	N(3 <sup>I</sup> )	N(4)†
P	-0.0004	-0.0004	-0.0030	-1.517	0.0140	0.0140	-0.409
$\sigma(P)$	0.0044	0.0044	0.0159	0.014	0.0305	0.0305	0.027

Where P and  $\sigma(P)$  are the distance and its standard deviation from the mean plane.

X, Y and Z refer to orthogonal coordinates in Å which lie in the direction of a, b and c respectively.

† This atom was not included in the calculation of the mean plane.

significantly from the normal single bond distance, although some shortening of this bond might be expected on account of the  $sp^2$  hybridisation at N(4) and the contraction of the orbitals on S(5) caused by the oxygen atoms bonded to it. Similarly S(4)-N(3) of length 1.65Å is not significantly different from the normal single bond distance and likewise some shortening might be expected on account of the hybridisation at N(3).

The S-O distances are the same within experimental error and the mean value of 1.45Å is similar to that of 1.449Å found in  $[(CH_3)_2N]_2SO_2$  (Jordan, et al., 1963) and 1.391Å in  $(H_2N)_2SO_2$  (Trueblood and Mayer, 1956) and is normal for an S-O double bond.



The coordination about S(5) is roughly tetrahedral. The angle between the terminal oxygen atoms of  $118.8^\circ$  is larger than the tetrahedral angle; this is a consequence of the multiple bonding in the S-O bonds. Conversely the angle in the ring at S(5), i.e. N(4)-S(5)-N(4<sup>I</sup>) has a magnitude of  $94.6^\circ$  which suggests that the S(5)-N(4) bond has a large proportion of p character and is essentially a single bond. Further support for this is given from the N-S-N angle of  $113^\circ$  in  $[(\text{CH}_3)_2\text{N}]_2\text{SO}_2$  in which there is  $\pi$ -bonding to the central sulphur atom. The N-S-O bond angles are intermediate between the O-S-O and N-S-N angles with values of  $112.6^\circ$  and  $107.8^\circ$  for N(4)-S(5)-O(3) and N(4)-S(5)-O(4).

The bonding in the  $\text{S}_4\text{N}_4$  ring could be described in terms of two sulphur diimide fragments i.e., N(3)-S(3)-N(4), and N(3<sup>I</sup>)-S(3<sup>I</sup>)-N(4<sup>I</sup>), which are similar to that seen in  $\text{S}_3\text{N}_3\text{O}_4^-$  (section 5.5.b), linked together by single bonds to a sulphur atom and an  $-\text{SO}_2-$  group. This description fits the short S-N distances in the N(3)-S(3)-N(4) part and also the angles at N(4) of  $121.2^\circ$  and S(3) of  $123.6^\circ$ . The angle in the ring at N(3) of  $140.6^\circ$  is larger than necessitated by  $\pi$ -bonding to S(3) alone, and suggests that the  $\pi$ -bonding may extend to S(4) giving delocalisation over the whole of the  $\text{S}_3\text{N}_4$  fragment.  $\text{S}_3\text{N}_4$  represents, using the electron counting rule a  $10\pi$  system, and in view of the rough planarity of this part of the molecule, the bonding could be described as a delocalised  $10\pi$ -system bridged by an  $\text{SO}_2$  unit. The  $\text{SO}_2$  unit would then be analogous to the S-Cl or S=N- units in  $\text{S}_3\text{N}_2\text{Cl}^+$  and  $-\text{N}-\text{S}_3\text{N}_2$  described earlier in section 4.5.b in that they stabilise the formation of a ring system.

## 7.6 Molecular Packing.

The most significant feature in the packing of the  $S_4N_4O_2$  molecules is a very short oxygen-oxygen contact between the molecules around the two-fold axis at the origin and those disordered about the two-fold axis at (1,0,0). Specifically this is the distance of  $2.14\text{\AA}$  between  $O(2)$  and  $O(2^V)$  at  $1-x, -y, z$  and may be viewed as the contact between the oxygen atom  $O(2)$  on one molecule of  $S_4N_4O_2$  and that on another rotated through  $180^\circ$  and translated through (1,0,0). It is unreasonable to expect this interaction to actually occur implying that the  $S_4N_4O_2$  molecules around the two-fold axes are ordered in rows parallel to a, although the rows are disordered with respect to one another.

If an individual  $S_4N_4O_2$  molecule is considered to be sitting at the origin then the equivalent positions  $x, -y, \frac{1}{2}+z$  and  $-x, y, \frac{1}{2}+z$  would give two orientations for the molecule situated above the first along c. In the first of these orientations the  $S_4N_4O_2$  molecule is approximately superimposed, in projection along c, on the molecule beneath because the plane of the molecule, which contains S(11), S(12), O(1) and O(2), lies roughly in the a b plane. In the second orientation the molecule is rotated approximately  $180^\circ$  with respect to that at the origin. As shown in table 7.6 there are two short N---O intermolecular contacts between the molecule at the origin and that directly above it along c, namely N(1)---O(1<sup>III</sup>) and N(2)---O(1<sup>IV</sup>) of length  $2.87\text{\AA}$  and  $2.85\text{\AA}$ . Because of the disordering the nitrogen positions represent the mean positions of

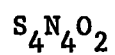
the nitrogen atoms in two superimposed  $S_4N_4O_2$  molecules. Consequently the same contacts are observed for both orientations and from these it is not possible to predict which orientation is more favourable. In the ordered molecule N(3) and N(4) lie  $0.34\text{\AA}$  and  $1.06\text{\AA}$  respectively below the plane which passes through S(4) and S(5) and lies perpendicular to the mirror plane. Since the observed contact corresponds to the mean of these two positions a longer contact will arise between the molecule at the origin and one above it, if the latter is rotated  $180^\circ$  with respect to the first. The alternative orientation will result in much shorter intermolecular contacts than are observed. This implies that there should be alternation in the orientation of the  $S_4N_4O_2$  molecules along the two-fold axes. Together with the ordering mentioned initially, this suggests that the packing of the molecules in the a c planes at  $y = 0, \frac{1}{2}, \dots$  tends to be ordered although the planes are randomly oriented with respect to each other. The imperfections in the crystals may be related to this ordering. If one row of  $S_4N_4O_2$  molecules parallel to a was superimposed directly on the row beneath, then because of the increased repulsions between the oxygen and nitrogen atoms, the separation of the rows along c would increase. This would produce a misalignment in the lattice which would be greatest in the b c plane and would account for the separation of the two parts of each reflection being most noticeable on the  $0kl$  reciprocal lattice net.

Apart from the contacts just mentioned all others which are less than the appropriate van der Waals distance involve sulphur atoms

with either oxygen or nitrogen atoms. This is expected on account of the small positive charge on the sulphur atoms and the small negative charge on the oxygen and nitrogen atoms. It is significant that there are few interactions between the molecules on the mirror planes and those about the two-fold axes which may account for the disordering being energetically possible.

A projection on the  $[00\bar{1}]$  plane of half of the contents of the unit cell is shown in figure 7.3. The equivalent positions shown correspond to the projection of the contents of the unit cell without the centering,  $(0, \frac{1}{2}, \frac{1}{2})$ .

Table 7.6

Some Intermolecular Contacts < 3.35Å

S(11) - O(1 <sup>III</sup> )	3.27
S(11) - O(2 <sup>V</sup> )	3.15
S(12) - O(1 <sup>III</sup> )	3.33
S(2) - O(1 <sup>IV</sup> )	3.14
S(2) - O(1 <sup>III</sup> )	3.10
S(2) - N(4 <sup>VI</sup> )	3.17
S(3) - O(2 <sup>VII</sup> )	3.04
S(3) - O(3 <sup>VIII</sup> )	3.07
S(4) - O(3 <sup>VIII</sup> )	3.30
S(4) - O(4 <sup>VI</sup> )	3.08
N(1) - O(1 <sup>III</sup> )	2.87
N(2) - O(1 <sup>IV</sup> )	2.85
O(2) - O(2 <sup>V</sup> )	2.14

The equivalent positions with respect to an atom at x,y,z

III x, -y,  $\frac{1}{2}+z$

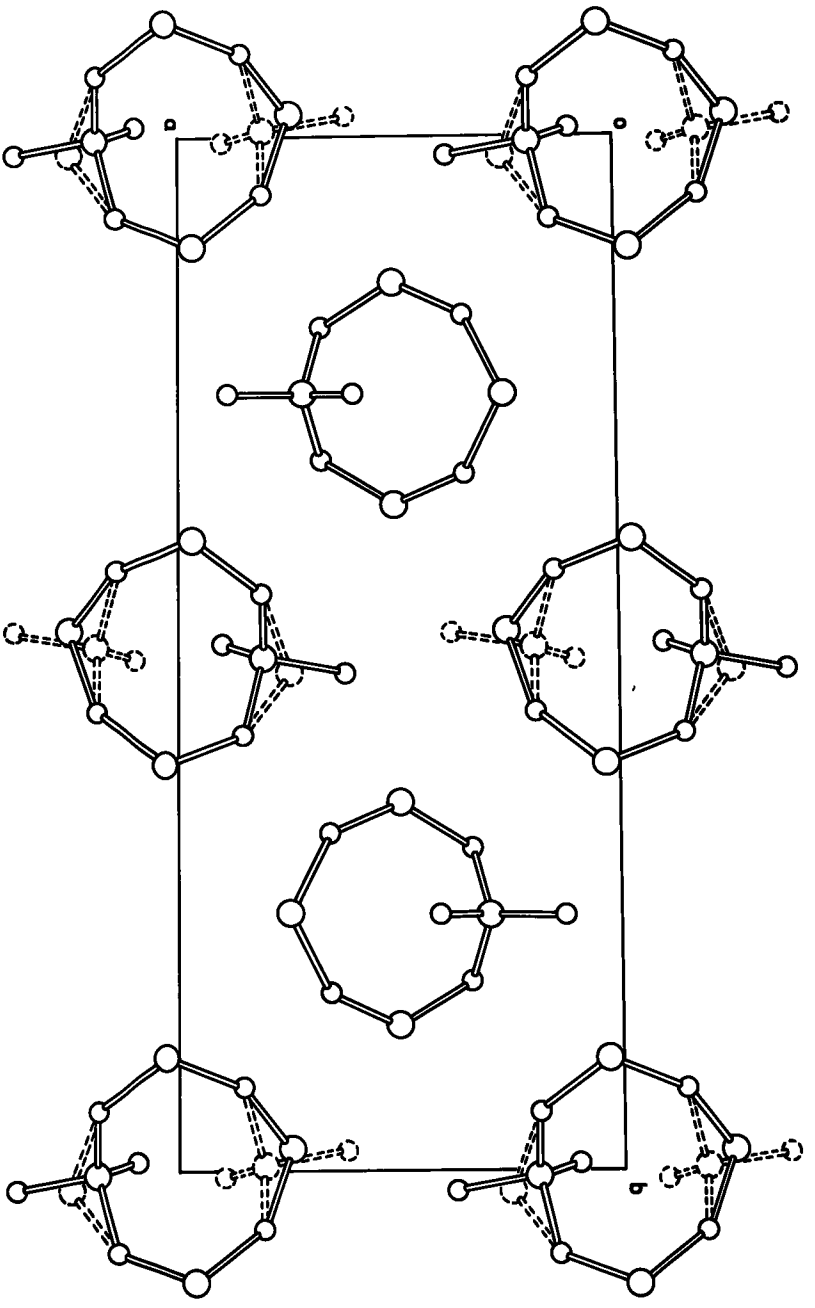
VI -1+x, y, z

IV -x, y,  $\frac{1}{2}+z$

VII 1-x, y,  $\frac{1}{2} + z$

V 1-x, -y, z

VIII 1-x, y,  $-\frac{1}{2} + z$



projection of half of the contents of the unit cell  
on the  $[001]$  plane

Figure 7.3

Table 7.7  $S_4N_4O_2$

Final Calculated and Observed Structure Factors

H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC	H	K	L	FO	FC
0	2	0	11.5	2.3	1	10	2	31.9	30.7	2	22	0	-3.5	12.5	2	9	9	-0.9	4.0
0	4	0	92.1	86.8	1	12	2	-10.3	13.9	2	1	1	34.4	21.9	2	0	10	-0.9	13.0
0	6	0	24.2	7.7	1	14	2	47.5	51.7	2	3	1	33.4	21.0	2	2	10	-0.9	11.0
0	8	0	177.6	191.5	1	16	2	15.6	9.4	2	5	1	47.9	41.4	3	0	0	11.9	11.3
0	10	0	53.4	35.2	1	18	2	20.1	21.1	2	7	1	27.4	27.0	3	2	0	97.6	102.7
0	12	0	103.3	102.3	1	20	2	78.2	24.6	2	9	1	47.1	37.6	3	4	0	11.3	9.5
0	14	0	28.2	39.2	1	1	3	47.0	49.4	2	11	1	-5.6	17.4	3	6	0	42.2	39.4
0	16	0	53.3	54.6	1	3	3	-1.6	15.3	2	13	1	11.9	10.5	3	8	0	-5.5	15.1
0	18	0	18.0	26.2	1	5	3	48.1	44.9	2	15	1	30.7	30.1	3	10	0	73.2	62.7
0	20	0	51.2	59.1	1	7	3	38.0	47.7	2	17	1	26.1	29.9	3	12	0	-6.0	0.7
0	22	0	21.7	19.8	1	9	3	52.9	54.7	2	19	1	-8.1	11.5	3	14	0	125.1	127.3
0	0	2	99.7	100.6	1	11	3	36.4	32.6	2	21	1	25.2	21.5	3	16	0	-7.3	7.5
0	2	2	240.3	294.6	1	13	3	29.6	41.4	2	0	2	167.7	176.5	3	18	0	22.6	23.6
0	4	2	261.7	275.5	1	15	3	37.8	38.4	2	2	2	124.5	132.3	3	20	0	19.7	7.9
0	6	2	113.4	109.8	1	17	3	-10.9	12.0	2	4	2	31.6	24.0	3	1	1	60.8	35.8
0	8	2	99.6	98.2	1	19	3	23.5	24.4	2	6	2	123.4	123.8	3	3	1	86.6	64.8
0	10	2	111.8	113.0	1	21	3	29.6	25.5	2	8	2	109.2	104.9	3	5	1	48.7	39.1
0	12	2	84.4	87.9	1	0	4	121.6	133.2	2	10	2	50.6	40.3	3	7	1	37.0	41.1
0	14	2	28.2	33.7	1	2	4	55.8	59.5	2	12	2	38.3	33.7	3	9	1	-9.8	7.0
0	16	2	38.3	42.6	1	4	4	74.8	71.5	2	14	2	99.8	105.1	3	11	1	76.0	66.0
0	18	2	59.9	62.3	1	6	4	48.2	42.8	2	16	2	19.4	22.3	3	13	1	28.2	29.1
0	20	2	-0.8	14.0	1	8	4	52.0	50.6	2	18	2	79.4	30.3	3	15	1	13.4	15.5
0	22	2	25.2	29.5	1	10	4	47.4	41.6	2	20	2	21.7	25.9	3	17	1	14.6	11.9
0	0	4	128.4	128.8	1	12	4	-9.2	16.2	2	1	3	33.2	46.4	3	19	1	16.7	12.2
0	2	4	89.8	76.0	1	14	4	73.8	19.7	2	3	3	14.0	17.2	3	21	1	25.5	19.0
0	4	4	79.8	80.8	1	16	4	-9.6	7.7	2	5	3	-8.2	17.9	3	0	2	23.4	27.7
0	6	4	161.5	159.7	1	18	4	23.3	21.4	2	7	3	20.6	20.6	3	2	2	26.3	33.4
0	8	4	26.9	32.5	1	20	4	19.4	21.1	2	9	3	12.2	8.4	3	4	2	95.3	94.6
0	10	4	20.4	14.4	1	1	5	36.4	31.7	2	11	3	29.2	26.3	3	6	2	-0.5	7.8
0	12	4	11.6	21.7	1	3	5	31.9	35.9	2	13	3	-0.7	3.9	3	8	2	88.0	85.8
0	14	4	85.9	84.8	1	5	5	11.8	15.9	2	15	3	26.0	29.2	3	10	2	63.8	75.0
0	16	4	18.5	17.9	1	7	5	43.4	45.9	2	17	3	-8.3	14.7	3	12	2	47.2	47.3
0	18	4	28.8	28.9	1	9	5	13.2	11.3	2	19	3	-5.9	4.7	3	14	2	15.8	19.0
0	20	4	16.8	14.7	1	11	5	40.9	46.3	2	21	3	-0.9	10.1	3	16	2	39.1	35.6
0	0	6	23.4	29.2	1	13	5	-5.3	4.0	2	0	4	23.3	25.6	3	18	2	33.3	36.1
0	2	6	50.8	54.7	1	15	5	15.8	20.2	2	2	4	122.6	126.0	3	20	2	-10.4	15.5
0	4	6	121.8	114.9	1	17	5	-2.8	3.6	2	4	4	27.6	33.0	3	1	3	23.4	22.6
0	6	6	76.8	83.9	1	19	5	26.8	24.0	2	6	4	48.6	46.9	3	3	3	17.4	11.0
0	8	6	13.5	18.0	1	0	6	12.8	12.6	2	8	4	57.3	54.5	3	5	3	15.2	18.0
0	10	6	45.5	49.0	1	2	6	10.9	7.5	2	10	4	124.5	123.4	3	7	3	43.2	35.6
0	12	6	35.7	40.3	1	4	6	-0.6	7.4	2	12	4	21.7	20.4	3	9	3	14.8	11.9
0	14	6	34.9	26.0	1	6	6	66.1	63.4	2	14	4	22.4	20.9	3	11	3	35.6	36.2
0	16	6	21.2	23.1	1	8	6	14.6	14.2	2	16	4	-11.1	14.8	3	13	3	13.8	17.8
0	18	6	17.2	22.0	1	10	6	35.1	28.5	2	18	4	46.4	49.9	3	15	3	26.7	19.6
0	0	8	74.6	60.8	1	12	6	-10.2	5.4	2	20	4	19.4	25.3	3	17	3	29.3	26.8
0	2	8	33.0	37.9	1	14	6	50.0	50.8	2	1	5	14.9	16.7	3	19	3	24.5	15.6
0	4	8	35.2	35.9	1	16	6	-9.9	6.5	2	3	5	34.6	26.8	3	0	4	84.7	87.6
0	6	8	99.6	51.1	1	18	6	25.7	24.1	2	5	5	38.3	32.9	3	2	4	23.5	27.4
0	8	8	53.9	54.6	1	1	7	46.3	37.5	2	7	5	22.0	25.8	3	4	4	37.9	36.7
0	10	8	44.4	37.8	1	3	7	20.9	20.4	2	9	5	38.7	30.2	3	6	4	18.0	17.0
0	12	8	21.9	18.9	1	5	7	12.5	16.7	2	11	5	13.7	12.0	3	8	4	76.4	79.6
0	14	8	-8.0	15.7	1	7	7	-0.7	15.4	2	13	5	12.0	7.5	3	10	4	35.9	36.0
0	0	10	26.9	31.4	1	9	7	23.5	24.1	2	15	5	-7.3	9.3	3	12	4	-9.7	16.5
0	2	10	-0.7	5.6	1	11	7	-10.7	17.2	2	17	5	-0.8	8.7	3	14	4	16.3	32.2
0	4	10	-9.5	13.5	1	13	7	18.9	21.2	2	19	5	-8.0	4.8	3	16	4	-5.8	6.2
0	0	0	-4.0	0.9	1	15	7	20.6	19.8	2	0	6	85.7	94.9	3	18	4	22.6	20.7
0	2	0	162.1	163.9	1	0	8	42.8	40.5	2	2	6	39.6	40.9	3	1	5	23.9	14.2
0	4	0	-0.4	4.5	1	2	8	20.0	16.0	2	4	6	16.3	18.9	3	3	5	20.6	11.4
0	6	0	142.6	133.9	1	4	8	16.5	18.6	2	6	6	52.0	31.5	3	5	5	-9.6	18.4
0	8	0	10.9	11.5	1	6	8	-9.7	7.1	2	8	6	59.3	60.8	3	7	5	38.8	46.6
0	10	0	128.9	134.7	1	8	8	21.1	22.2	2	10	6	43.0	35.7	3	9	5	19.1	15.9
0	12	0	-4.5	1.2	1	10	8	24.4	22.5	2	12	6	-0.8	5.7	3	11	5	-4.1	16.8
0	14	0	53.8	53.1	1	12	8	-8.9	2.3	2	14	6	24.3	20.8	3	13	5	-7.8	7.6
0	16	0	-0.7	3.5	1	14	8	-8.4	7.6	2	16	6	-3.7	11.7	3	15	5	30.9	30.2
0	18	0	70.0	76.6	1	1	9	16.5	17.7	2	1	7	-0.7	25.9	3	17	5	16.5	12.9
0	20	0	-0.8	2.4	1	3	9	23.3	11.4	2	3	7	21.3	24.7	3	0	6	-4.3	11.8
0	22	0	23.5	25.0	1	5	9	15.3	19.3	2	5	7	12.7	12.2	3	2	6	23.2	23.7
0	0	1	41.5	26.6	1	7	9	-0.8	7.3	2	7	7	28.4	21.2	3	4	6	30.7	30.4
0	2	1	41.5	21.0	1	9	9	-7.2	19.6	2	9	7	19.2	10.3	3	6	6	14.5	17.3
0	4	1	80.8	76.0	1	0	10	-12.0	10.8	2	11	7	23.4	20.7	3	8	6	28.8	33.8
0	6	1	14.6	9.3	1	2	10	-5.1	7.8	2	13	7	-9.4	10.4	3	10	6	56.5	56.1
0	8	1	95.7	59.0	1	4	10	18.6	13.6	2	15	7	-8.4	8.9	3	12	6	12.9	15.8
0	10	1	12.3	14.8	2	0	0	59.0	56.9	2	0	8	13.6	18.3	3	14	6	29.4	25.5
0	12	1	65.7	58.0	2	2	0	12.7	1.1	2	2	8	-0.8	9.2	3	16	6	-10.1	13.6
0	14	1	45.9	39.5	2	4	0	271.6	290.2	2	4	8	55.6	40.3	3	1	7	16.2	16.1
0	16	1	55.5	52.7	2	6	0	26.1	13.4	2	6	8	24.3	16.7	3	3	7	-0.7	17.1
0	18	1	-5.3	16.0	2	8	0	39.6	35.0	2	8	8	19.7	19.9	3	5	7	-0.7	16.9
0	20	1	24.7	18.7	2	10	0	10.2	20.2	2	10	8	17.3	18.4	3	7	7	27.5	27.4
0	22	2	180.4	223.1	2	12	0	73.2	75.5	2	12	8	24.5	19.3	3	9	7	-5.7	7.2
0	0	2	19.0	13.8	2	14	0	26.7	27.7	2	1	9	22.5	18.6	3	11	7	12.2	11.8
0	2	2	172.5	172.5	2	16	0	51.7	49.2	2	3	9	-0.8	5.1	3	13	7	-11.3	8.4
0	4	2	67.8	70.4	2	18	0	-4.1	14.9	2	5	9	-8.6</						





CHAPTER 8

The Crystal Structure of  $(\text{BCH}_3)_6(\text{CH})_4$

### 8.1 Introduction

Studies of boron hydrides and carboranes have been responsible for a considerable improvement in the understanding of chemical bonding. When diborane was first prepared in 1912 by Stock it was realised that there were insufficient valence electrons in the molecule for its bonding to be explained in terms of two-centre two electron bonds. The subsequent discovery of further boron hydrides and carboranes, which showed the same feature, caused this class of compounds to be called electron deficient compounds. The bonding in these molecules is based on multicentre bonds so that there are sufficient electrons in the molecule to completely fill all the bonding orbitals and this accounts for their stability (Rudolph and Pretzer, 1972). The chemistry of carboranes has been reviewed recently by Snaith and Wade (1972), which gives references to the earlier reviews.

The structures of both boron hydrides and carboranes are based on triangular faced, n-cornered polyhedra, and are classified as closo, nido or arachno according to the number of corners on the polyhedra occupied by a cage atom.

In closo structures all n corners are occupied; this form is taken up by cage species of the general formula  $C_a B_m H_{m+2}$ , where  $m = 5-12$ ,  $a = 0, 1, 2$  and  $a + m = n$ . For example compounds such as  $B_{12}H_{12}^{2-}$  and  $C_2B_{10}H_{12}$  have cage structures based on a regular icosahedron.

In nido structures all n corners except one in the polyhedra are occupied by cage atoms, and this form is taken up by compounds of the general formula  $C_a B_m H_{m+4}$ , where  $n = a + m + 1$ . Examples of this type include a series of carboranes, for which  $a + m = 6$  and  $a = 0 \rightarrow 4$ ,

based on the pentagonal bipyramid in which one apical position is vacant giving a pentagonal prism. Similarly in arachno structures all but two corners of the  $n$ -cornered polyhedra are occupied; this form is taken up by compounds of the general formula  $C_a B_m H_{m+6}$  where  $n = a + m + 2$ .

These structures may be rationalised according to the number of skeletal bonding electrons they contain. Molecular orbital treatments of closo  $B_n H_n^{2-}$  anions have shown that  $n$  atoms at the corners of an  $n$ -cornered polyhedron give rise to  $n+1$  bonding molecular orbitals (Klanberg et al., 1967) and therefore require  $n+1$  electron pairs for stability. In these boron hydride anions  $n$  pairs of skeletal electrons are provided by the boron atoms, and one pair by the charge. This requirement also applies to carboranes except that each carbon contributes three electrons to the skeletal bonding.

In nido species, which are formally derived from the hypothetical  $B_n H_n^{4-}$  species, there are  $n+2$  pairs of electrons available for skeletal bonding, which give rise to a structure based on an  $(n+1)$ -cornered polyhedron. Likewise the arachno compounds contain  $n+3$  electron pairs available for cage bonding and possess structures based on  $(n+2)$ -cornered polyhedra. This theory has been seen to apply to all delocalised boron-carbon cage systems and has been extended to clusters involving transition metals (Wade 1972a, 1972b). It was therefore of considerable interest that a boron-carbon compound,  $(C_4 B_6)H_4 Me_6$ , was prepared which did not appear to fit these rules.

This compound was prepared by the thermal decomposition of trimethyl borane (Brown et al., 1975). A sample of  $(CH_3)_3 B$  sealed in a pyrex tube was heated in a furnace at  $450^\circ C$  for about 40 minutes.

The products were separated by vacuum distillation and sublimation, giving as the major product the boron-carbon compound just mentioned in approximately 18% yield. The product was characterised by its mass spectrum and n.m.r. spectrum. The latter was particularly simple; the  $^1\text{H}$  spectrum showed only two singlet resonances with the correct relative intensities and positions corresponding to  $\text{BCH}_3$  and  $\text{CH}$ . The  $^{11}\text{B}$  spectrum showed only one resonance. This indicated that all the boron atoms were magnetically equivalent as were the methyl groups and also the cage carbon atoms. This information is consistent with an adamantane type structure whereas the electron counting rules would have suggested a nido structure based on the 11 cornered octadecahedron. The n.m.r. spectra of the latter would not be expected to be as simple as that observed. A structure determination was undertaken in order to provide further information about a molecule which appeared to be an exception to the electron counting rule.

## 8.2 Crystal Data.

The crystals were grown by vacuum sublimation at room temperature and were obtained as prisms elongated along  $c$  with well formed  $\{110\}$  faces. The crystals were extremely sensitive to oxygen and so were sealed in quartz capillary tubes. The crystal used for data collection had dimensions  $0.4 \times 0.3 \times 0.2\text{mm}$ .

Preliminary work using precession methods showed the unit cell to be orthorhombic, and that the conditions limiting reflections were:  $0k1$   $k+1 = 2n$ ,  $hk0$   $h = 2n$ . These are consistent with the space groups  $\text{Pnma}$  and  $\text{Pn}2_1\text{a}$ . Solution of the structure showed that the

space group was Pnma. Accurate cell dimensions were obtained from a least squares treatment of the positions of twelve high order reflections as measured on a four-circle diffractometer.

$$\begin{array}{l}
 \text{C}_{10}\text{H}_{22}\text{B}_6 \quad M = 207.02 \\
 \quad \quad \quad a = 16.184(1)\text{\AA} \\
 \quad \quad \quad b = 13.251(1)\text{\AA} \\
 \quad \quad \quad c = 6.999(1)\text{\AA} \\
 \quad \quad \quad U = 1501.0\text{\AA}^3 \\
 \quad \quad \quad D_m = 0.87\text{g cm}^{-3} \text{ (by floatation in isooctane and chlorobenzene)} \\
 \quad \quad \quad Z = 4 \\
 \quad \quad \quad D_c = 0.905\text{g cm}^{-3}
 \end{array}$$

Absorption coefficient for  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418\text{\AA}$ ) =  $3.2\text{cm}^{-1}$ .

### 8.3 Data Collection and Correction.

The data were collected as before using a  $2\theta$ - $\omega$  scan technique. Each peak was scanned in 70 steps of  $0.01^\circ$  at 2 seconds per step. A background count of 35 seconds was allowed at the beginning and end of each scan.

Three reflections were measured as standards every 40 ordinary reflections; these showed a general decrease throughout the data collection. Part of this was due to slight movements of the crystal within the capillary tube and part due to the compound's volatility at room temperature. As a result the orientation of the crystal was redetermined whenever the intensity of the standards had fallen by 15%.

The standard reflections were not used to scale the data.

A quarter of the sphere of reflection was recorded for  $0 < \theta \leq 50^\circ$  and one octant was measured for  $50 < \theta \leq 55^\circ$ . After averaging, 993 independent reflections were obtained, of which 639 were considered observed having net counts  $> 3$  esd's. The intensities were corrected for Lorentz and polarisation effects but not for absorption.

#### 8.4 Solution and Refinement.

The structure was solved using the symbolic addition procedure as described earlier. A set of normalised structure factors was calculated and 126 of these with  $E \geq 1.5$  were phased through iterative application of Sayre's relationship. The program used (Ahmed and Hall, 1968) chose three reflections which were arbitrarily given positive signs and hence determined the origin; then during the next stage, in which signs or symbols were given to the 69 reflections with  $E > 1.9$ , it was necessary to assign symbols to three further reflections, as shown below.

<u>Origin Determining reflections</u>				<u>Reflections to which symbols were assigned</u>					
			$ E $				$ E $	Symbol	Sign
12	5	0	5.183	10	6	0	3.925	A	-
2	3	1	3.337	4	5	5	3.439	B	+
3	5	4	2.487	7	0	5	3.087	C	+

There was only one set of signs consistent with the three symbols.

From these 69 planes the phases of the remaining 57 planes with

$1.5 \leq E \leq 1.9$  were estimated. An E-map computed from these reflections which

revealed the positions of all the non-hydrogen atoms. The peak heights of the boron and carbon atoms in the map ranged from  $2.3 - 3.3e.\text{\AA}^{-3}$  and  $2.3 - 4.1e.\text{\AA}^{-3}$  respectively, with a background fluctuation of  $\pm 0.5e.\text{\AA}^{-3}$ .

These positions were refined by least squares methods using the block-diagonal approximation. Initially all atoms were given isotropic temperature factors of  $6.8\text{\AA}^2$ , which was the overall temperature factor calculated using the Wilson plot method. The R value after two cycles was 0.21, and with further refinement, including anisotropic thermal parameters for all atoms, this fell to 0.13.

A difference synthesis revealed peaks of electron density of  $0.4e.\text{\AA}^{-3}$  which could be assigned to the hydrogen atoms attached to the cage carbon atoms. Likewise it showed annuli of electron density of height  $0.2 - 0.3e.\text{\AA}^{-3}$  associated with the methyl carbon atoms, indicating that the methyl groups were rotating about the B-C bonds. Hydrogen atoms were placed at the positions observed for those attached to the cage carbon atoms. An allowance for the rotation of the methyl groups was made by placing six hydrogen atoms, each with an occupation factor of one half, at equal intervals on a circle whose position was calculated assuming normal bond lengths and angles for the C-H bonds. All hydrogen atoms were included in the refinement with isotropic temperature factors of  $8.0\text{\AA}^2$  but their parameters were not refined. Refinement using full matrix least squares methods saw R converge to its final value of 0.0598. The parameter shifts during the last cycle were all less than  $0.15\sigma$ .

Inclusion of the hydrogen atoms lead to significant changes in the B-C bond lengths. Before their inclusion, the terminal and cage



Table 8.1       $(\text{BCH}_3)_6(\text{CH})_4$

Final Least Squares Totals

$\Sigma F_o $	$\Sigma F_c $	$\Sigma \Delta $	R
5065.37	5051.14	302.97	0.0598

Weighting Analysis

$ F_o $ Ranges	N	$\Sigma w\Delta^2/N$	R
0 - 3	172	0.03	1.62
3 - 7	256	0.01	0.66
7 -15	132	0.02	0.43
15 -20	30	0.03	0.47
20 -45	40	0.02	0.34
45 upwards	7	0.05	0.86

Table 8.2       $(\text{BCH}_3)_6(\text{CH})_4$

Final Atomic Coordinates with their Estimated Standard Deviations  
 $(\times 10^5)$  and Isotropic Thermal Parameters ( $\text{\AA}^2$ )

Atom	$x/a$	$y/b$	$z/c$	$B^\dagger$
B(1)	0.01292(32)	0.25	-0.17082(91)	6.00
B(2)	0.19157(31)	0.25	0.11520(76)	5.65
B(3)	0.14750(20)	0.15757(27)	-0.17346(60)	5.67
B(4)	0.05794(24)	0.15579(30)	0.11709(52)	6.28
C(1)	0.00709(26)	0.25	0.05125(69)	6.16
C(2)	0.10112(26)	0.25	-0.26176(63)	5.35
C(3)	0.14928(18)	0.14937(22)	0.05047(45)	6.27
C(4)	-0.06714(33)	0.25	-0.29598(90)	8.79
C(5)	0.27347(30)	0.25	0.23445(76)	7.54
C(6)	0.01870(27)	0.07159(32)	0.24610(58)	9.14
C(7)	0.19418(23)	0.07912(25)	-0.30129(59)	7.88

† Where B refers to the Isotropic Temperature Factor from the last cycle of isotropic refinement.

continued.

Table 8.2 continued

Atom	$x/a$	$y/b$	$z/c$	B	Occupation Factor
H(1)	-0.050	0.25	0.125	8.0	1.0
H(2)	0.092	0.25	-0.417	8.0	1.0
H(3)	0.183	0.083	0.083	8.0	1.0
H(41)	-0.054	0.25	-0.450	8.0	0.5
H(42)	-0.123	0.25	-0.198	8.0	0.5
H(43)	-0.106	0.182	-0.261	8.0	0.5
H(44)	-0.071	0.182	-0.387	8.0	0.5
H(51)	0.326	0.25	0.135	8.0	0.5
H(52)	0.309	0.182	0.199	8.0	0.5
H(53)	0.275	0.182	0.325	8.0	0.5
H(54)	0.258	0.25	0.388	8.0	0.5
H(61)	0.068	0.014	0.274	8.0	0.5
H(62)	0.054	0.067	0.381	8.0	0.5
H(63)	-0.003	0.104	0.381	8.0	0.5
H(64)	-0.046	0.088	0.274	8.0	0.5
H(65)	-0.033	0.035	0.168	8.0	0.5
H(66)	0.025	-0.002	0.168	8.0	0.5
H(71)	0.257	0.108	-0.331	8.0	0.5
H(72)	0.212	0.116	-0.438	8.0	0.5
H(73)	0.160	0.070	-0.438	8.0	0.5
H(74)	0.153	0.015	-0.331	8.0	0.5
H(75)	0.197	0.007	-0.225	8.0	0.5
H(76)	0.250	0.054	-0.225	8.0	0.5

Table 8.3  $(\text{BCH}_3)_6(\text{CH})_4$ Anisotropic Thermal Parameters and their Estimated StandardDeviations (both  $\text{\AA}^2 \times 10^5$ )

Atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
B(1)	7002(317)	7171(335)	10349(405)		- 632(320)	
B(2)	6972(310)	8743(347)	8286(361)		931(282)	
B(3)	6343(200)	7026(217)	10421(269)	- 535(223)	696(218)	- 769(174)
B(4)	8489(239)	8268(238)	7925(245)	- 728(218)	- 10(200)	-1638(205)
C(1)	6556(265)	10528(379)	9308(360)		1972(264)	
C(2)	7552(285)	8093(287)	7757(276)		97(226)	
C(3)	8140(211)	7066(197)	9788(239)	949(187)	- 2(183)	782(167)
C(4)	8437(340)	14037(469)	13186(495)		-1953(339)	
C(5)	8008(326)	13036(451)	10783(373)		-1303(282)	
C(6)	13499(332)	11605(312)	10468(265)	1398(260)	1570(239)	3256(259)
C(7)	10679(256)	9159(248)	12976(313)	-1315(223)	1977(241)	1223(220)

bond lengths ranged from 1.51 - 1.64Å, which is far greater than the final range of 1.552 - 1.570Å and illustrates the importance of including hydrogen atoms in the refinement of light atom compounds.

A difference map calculated at the end of the refinement showed no peaks greater than 0.2e.Å<sup>-3</sup>. The weighting scheme used was

$$\sqrt{w} = 1/[P_1 + |F_o| + P_2|F_o|^2 + P_3|F_o|^3]^{\frac{1}{2}}$$

the parameters were varied until a uniform distribution of  $w\Delta^2$  as a function of the magnitude of  $|F_o|$  was obtained; the final values used were  $P_1 = 5.5$ ,  $P_2 = 0.015$  and  $P_3 = 0.002$ . The unobserved reflections were not included in the refinement. The final least squares totals and weighting analysis are given in table 8.1.

The final calculated and observed structure factors are given in table 8.8. The scattering factors for boron and carbon were taken from International Tables Vol. III, and those for hydrogen from Stewart, Davidson, Simpson (1966). The atomic coordinates and anisotropic thermal parameters are given in tables 8.2 and 8.3 respectively.

### 8.5 Description of the Structure of (BCH<sub>3</sub>)<sub>6</sub>(CH)<sub>4</sub>

The molecule has a structure resembling that of adamantane as previously proposed and as such is unlike a normal carborane. The framework of the molecule consists of four carbon atoms which lie near the corners of a tetrahedron bonded together by six boron atoms as shown in figure 8.1. These boron atoms lie above the six edges of the tetrahedron in an almost octahedral arrangement. There is a

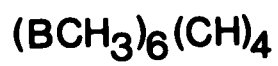
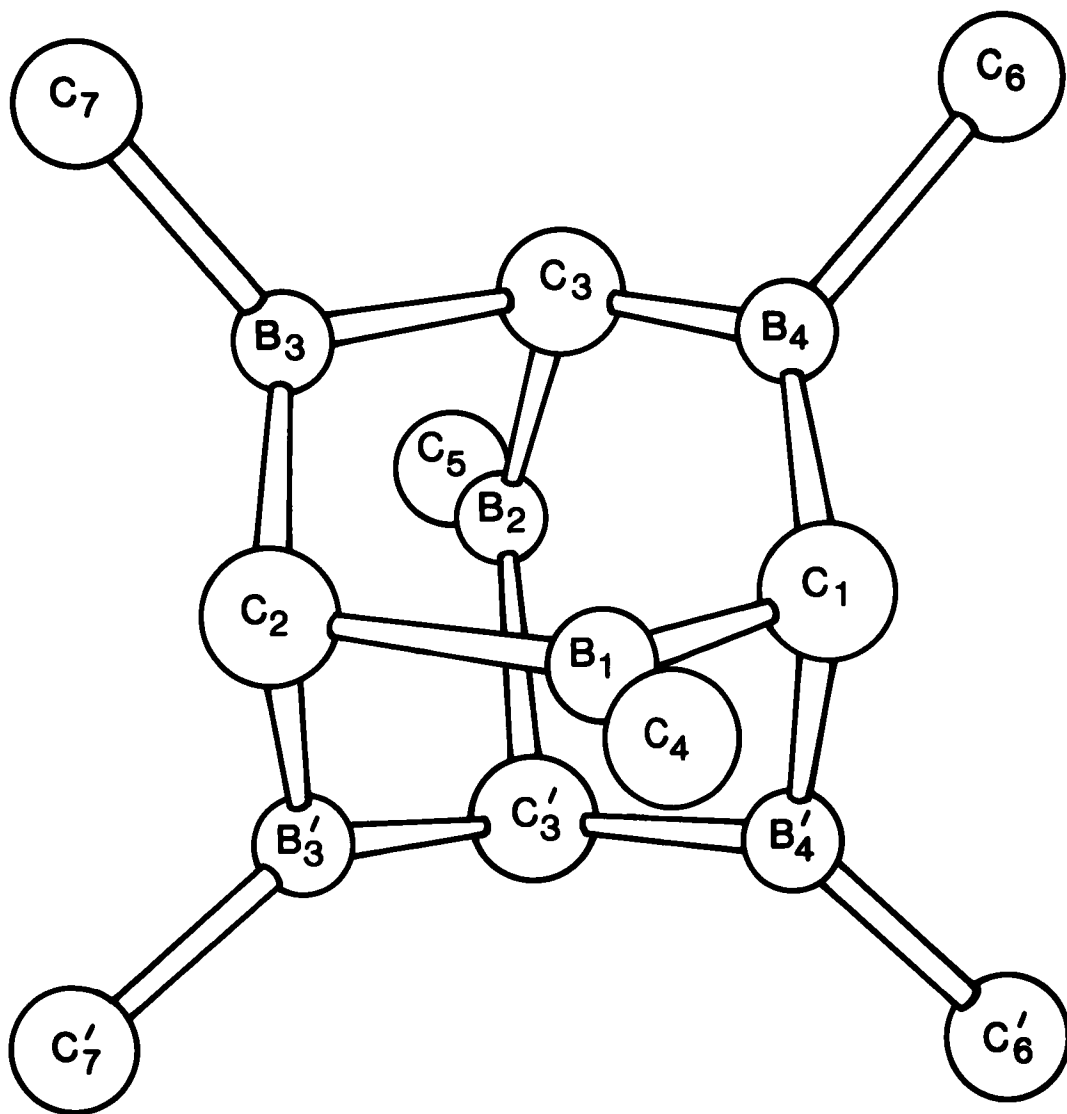


Figure 8.1

(Excluding Hydrogen Atoms)

methyl group attached to each boron and a hydrogen to each framework carbon, so that the molecular symmetry approximates to  $\bar{4}3m$ . Each carbon atom exhibits its normal covalency of four and each boron atom a covalency of three. This is in complete agreement with the structure proposed from interpretation of its n.m.r. spectra. Intramolecular bond distances and angles are given in tables 8.4 and 8.5 respectively.

Table 8.4

$(\text{BCH}_3)_6(\text{CH})_4$  Bond Distances( $\text{\AA}$ ) and their Estimated Standard Deviations ( $\text{\AA} \times 10^3$ )

B(1) - C(1)	1.557(8)
B(1) - C(2)	1.563(7)
B(1) - C(4)	1.564(8)
B(2) - C(3)	1.566(4)
B(2) - C(5)	1.566(7)
B(3) - C(2)	1.564(5)
B(3) - C(3)	1.571(5)
B(3) - C(7)	1.566(5)
B(4) - C(1)	1.565(5)
B(4) - C(3)	1.552(5)
B(4) - C(6)	1.570(6)

In the cell the molecules lie across mirror planes at  $y = 1/4$  and  $3/4$ , with the atoms B(1), B(2), C(1) and C(2) of the molecular framework situated on the mirror plane at  $y = 1/4$ . The boron-carbon distances range from 1.552(5) - 1.571(5) $\text{\AA}$  and are all the same within experimental error. The mean terminal bond distance of 1.567(3) $\text{\AA}$  is not significantly different from the mean cage bond distance of 1.563(2) $\text{\AA}$ . The overall mean boron-carbon distance of

1.564(2)Å is similar to that of 1.578(1)Å in  $B(CH_3)_3$  (Bartell and Carrol, 1965) but is shorter than that of 1.590(3)Å in tetramethyl diborane,  $B_2H_2(CH_3)_4$  (Carrol and Bartell, 1968) this difference may be accounted for by the change in hybridisation at boron on changing from threefold to fourfold coordination.

In  $(BCH_3)_6(CH)_4$  there are sufficient valence electrons available to allow the atoms to bond together by two-electron two-centre bonds. The B-C distances in carboranes are normally longer than such single bonds and are associated with a coordination at boron greater than three, eg. the B-C distance in  $B_{10}C_2H_{12}$  (1,12 dicarbaclosododecarborane 12) is 1.710Å with a coordination of six at boron and five at carbon. (Bohn and Bohn, 1971).

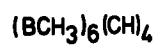
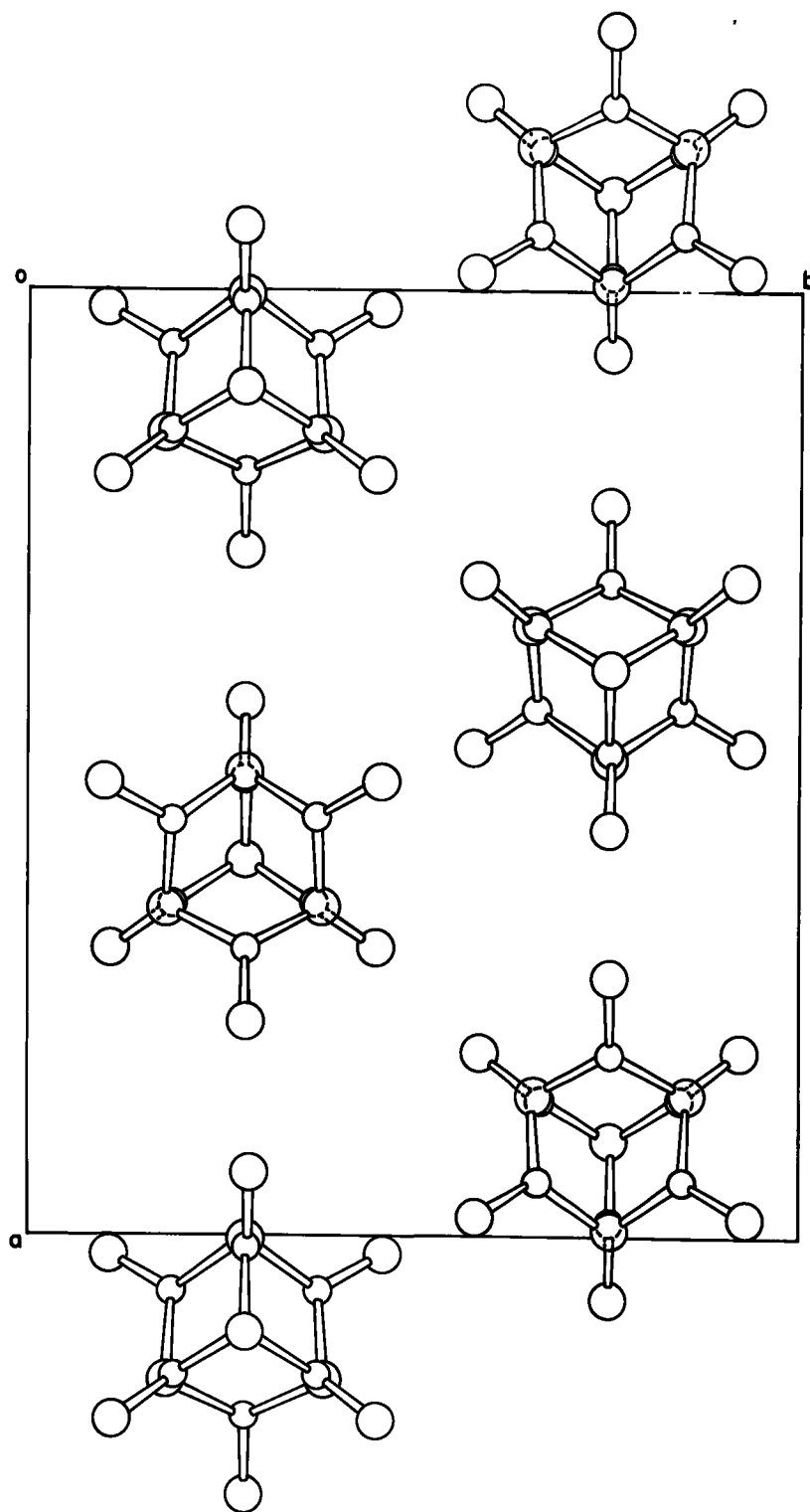
The angles at boron within the cage vary from 116.8 - 117.5° and are all equal within experimental error with a mean of 117.2°, whilst the angles at carbon lie in the range 103.1 - 106.4°. All of these angles are less than those expected for atoms in  $sp^2$  and  $sp^3$  hybrid states respectively; this feature is dictated by the structure itself. In a molecule with ideal  $\bar{4}3m$  symmetry an angle of 120° at boron necessitates an angle of 103°12' in the cage at carbon, whereas an angle of 109°28' at carbon requires the cage angle at boron also to be tetrahedral. The angles observed represent a compromise between these two extremes. The C-B- $CH_3$  angles vary from 120.6 - 121.9° and are the same within experimental error.

Departure from ideal symmetry occurs throughout the molecule. This is most evident in the distances between methyl carbon atoms, e.g. the



edges of the octahedron, which ideally should be equal but vary from 4.529 - 4.797 $\text{\AA}$ . These differences are mirrored in the corresponding boron-boron distances, but on a smaller scale. For comparison both sets of distances are given together in table 8.6. The greatest differences involve C(7) and the boron, B(3) to which it is attached, and from the distances given it can be deduced that C(7) is displaced towards C(7<sup>I</sup>) across the mirror plane at  $y = 1/4$ , and towards C(5). This distortion may be explained by the molecular packing. In the structure the shortest intermolecular contacts are close to 4 $\text{\AA}$  which is the contact distance normally accepted for rotating methyl groups. As far as the distortion is concerned the important contact appears to be that of 4.001 $\text{\AA}$  between C(7) and C(6) in the molecule at  $\bar{x}$ ,  $\bar{y}$ ,  $\bar{z}$ , (table 8.6). This distance would be decreased if the C(7) --- C(7<sup>I</sup>) separation was increased. This distortion accounts for the angles B(3) - C(2) - B(3<sup>I</sup>) and B(2) - C(3) - B(3) being less than the other cage angles at carbon, i.e. 103.1 $^\circ$  and 103.8 $^\circ$  as compared to 105.2 - 106.4 $^\circ$  for the remaining angles. It also accounts for the observation that B(3) is not coplanar with the three carbon atoms to which it is attached, as shown in table 8.7. The movement of C(7) towards the mirror plane is accompanied by a similar but smaller movement of B(3) towards B(3<sup>I</sup>) so that B(3) lies 0.024 $\text{\AA}$  above the plane of the three carbon atoms. Conversely the other boron atoms are coplanar with their attached carbon atoms.

A projection along  $\underline{c}$  of the contents of a unit cell is shown in figure 8.2.



projection on the  $[001]$  plane

Figure 8.2

Bond Angles (degrees) and their Estimated Standard Deviation (deg. x 10<sup>2</sup>)

C(1) - B(1) - C(2)	117.51(35)
C(3) - B(2) - C(3 <sup>I</sup> )	116.77(31)
C(2) - B(3) - C(3)	117.20(29)
C(1) - B(4) - C(3)	117.14(30)
B(1) - C(1) - B(4)	105.20(31)
B(4) - C(1) - B(4 <sup>I</sup> )	105.85(29)
B(1) - C(2) - B(3)	106.11(30)
B(3) - C(2) - B(3 <sup>I</sup> )	103.11(28)
B(2) - C(3) - B(3)	103.75(27)
B(2) - C(3) - B(4)	106.42(28)
B(3) - C(3) - B(4)	106.16(26)
C(1) - B(1) - C(4)	120.59(32)
C(2) - B(1) - C(4)	121.91(37)
C(3) - B(2) - C(5)	121.60(33)
C(2) - B(3) - C(7)	121.72(30)
C(3) - B(3) - C(7)	121.00(29)
C(1) - B(4) - C(6)	121.59(32)
C(3) - B(4) - C(6)	121.27(31)

I refers to the equivalent position at  $x, 1/2-y, z$ .

Table 8.6  $(\text{BCH}_3)_6(\text{CH})_4$ 

Some Non-bonding intermolecular contacts ( $\text{\AA}$ ) with their Estimated Standard Deviations ( $\text{\AA} \times 10^3$ )

B(1) - B(3)	2.499(6)	C(4) - C(7)	4.797(6)
B(1) - B(4)	2.480(7)	C(4) - C(6)	4.681(7)
B(2) - B(3)	2.468(6)	C(5) - C(7)	4.564(6)
B(2) - B(4)	2.497(6)	C(5) - C(6)	4.754(6)
B(3) - B(4)	2.497(5)	C(6) - C(7)	4.770(6)
B(3) - B(3 <sup>I</sup> )	2.450(5)	C(6) - C(6 <sup>I</sup> )	4.728(6)
B(4) - B(4 <sup>I</sup> )	2.497(6)	C(7) - C(7 <sup>I</sup> )	4.529(5)
	C(1) - C(2)	2.667(6)	
	C(1) - C(3)	2.660(5)	
	C(2) - C(3)	2.676(5)	
	C(3) - C(3 <sup>I</sup> )	2.667(4)	

Some Intermolecular Contacts  $< 4.3\text{\AA}$  for nonhydrogen atoms

C(1) - C(5 <sup>II</sup> )	4.068
C(3) - C(7 <sup>III</sup> )	4.082
C(4) - C(5 <sup>IV</sup> )	4.009
C(4) - C(6 <sup>V</sup> )	4.218
C(5) - C(7 <sup>VI</sup> )	4.163
C(6) - C(6 <sup>VII</sup> )	3.979
C(6) - C(6 <sup>VIII</sup> )	4.074
C(6) - C(7 <sup>VII</sup> )	4.001
C(6) - C(7 <sup>VI</sup> )	4.256

I	$x, \frac{1}{2}y, z$	V	$-\frac{1}{2}x, \frac{1}{2}y, -\frac{1}{2}z$
II	$-\frac{1}{2}x, \frac{1}{2}y, \frac{1}{2}z$	VI	$x, y, 1+z$
III	$\frac{1}{2}x, -y, \frac{1}{2}z$	VII	$-x, -y, -z$
IV	$x, y, -1+z$	VIII	$-x, -y, 1-z$

Table 8.7  $(\text{BCH}_3)_6(\text{CH})_4$ 

## Mean Planes

$0.5400X + 0.0Y - 0.8416Z - 1.0058 = 0$				
Atom	B(2)	C(3)	C(3')	C(5)
P	-0.0100	0.0017	0.0017	0.0033
$\sigma(\text{P})$	0.0052	0.0031	0.0031	0.0052
$-0.8343X - 0.5500Y - 0.0373Z + 3.1135 = 0$				
Atom	B(3)	C(2)	C(3)	C(7)
P	0.0187	-0.0056	-0.0040	-0.0066
$\sigma(\text{P})$	0.0033	0.0035	0.0029	0.0036
$-0.8342X - 0.5502Y - 0.0382Z + 3.1178 = 0$				
Atom	B(3) <sup>†</sup>	C(2)	C(3)	C(7)
P	0.0241	0.0	0.0	0.0
$\sigma(\text{P})$	0.0033			
$-0.2889X - 0.4954Y - 0.8192Z + 1.9674 = 0$				
Atom	B(4)	C(1)	C(3)	C(6)
P	0.0025	-0.0008	-0.0005	-0.0010
$\sigma(\text{P})$	0.0037	0.0041	0.0031	0.0041

P and  $\sigma(\text{P})$  represent the distance and its estimated standard deviation of the atom from the mean plane. X, Y, and Z refer to orthogonal coordinates in Å parallel to a, b and c.

† signifies that this atom was not included in the calculation of the mean plane.

## 8.6 Discussion.

Carboranes have been defined as mixed hydrides of carbon and boron in which both carbon and boron atoms participate in a delocalised molecular framework, so that the compound discussed here is strictly not a carborane. It is exceptional in this field in that it possesses a constitution normally associated with delocalised bonding and yet is obviously held together by normal single bonds. This is possible because there is a boron:carbon ratio of 3:2 and does not require delocalisation in the bonding.

There is only one other known compound with this boron:carbon ratio, namely  $C_2B_3H_5$ . Its structure has been found by electron diffraction methods and has the form of a trigonal bipyramid with the apical positions occupied by carbon atoms (Macneil et.al., 1973). This is the shape predicted from the electron counting rule mentioned earlier. Its boron-carbon bond distance of  $1.556\text{\AA}$  is of the appropriate length for a normal single bond, and its B-B distance of  $1.853\text{\AA}$  is longer than that normally found in carboranes (e.g.  $1.720\text{\AA}$  in  $C_2B_4H_6$  Macneil et. al., 1973). The authors think however that this B-B distance does not preclude B-B interactions but suggest that it is weaker than in normal carboranes, and thus it is not possible to clearly differentiate between the two types of bonding.

It is unlikely that the next member,  $C_6B_9H_{15}$ , will exist since for a structure based on normal covalent bonds, carbon must be tetravalent; this requires that the structure would be based on a trigonal prism of carbon atoms with boron atoms along its edges. This would require either large angles at boron or at carbon, which would reduce its stability.

Table 8.8  $(\text{BCH}_3)_6(\text{CH})_4$ 

Final Calculated and Observed Structure Factors

H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC
2	0	0	34.0	36.4	8	12	0	-1.2	-0.2	7	5	1	2.1	2.7	8	12	1	0.0	-1.0
4	0	0	22.0	25.3	2	13	0	1.7	-1.5	8	5	1	12.4	-12.1	0	13	1	3.5	3.3
6	0	0	51.0	48.0	4	13	0	-0.6	0.4	9	5	1	8.0	8.5	1	13	1	0.0	0.0
8	0	0	6.2	-6.1	6	13	0	-0.6	-0.5	10	5	1	5.2	4.9	2	13	1	2.9	2.6
10	0	0	3.2	-2.8	0	14	0	2.3	1.5	11	5	1	12.0	-12.3	3	13	1	-0.7	0.1
12	0	0	5.6	4.8	1	0	1	61.6	69.9	12	5	1	-1.1	1.5	4	13	1	-1.3	-1.5
14	0	0	11.4	12.0	2	0	1	21.3	22.6	13	5	1	3.7	-6.1	5	13	1	0.0	-1.3
16	0	0	-0.8	1.2	3	0	1	9.6	-9.8	14	5	1	-1.4	-1.7	6	13	1	0.0	-0.3
2	1	0	76.4	-104.0	4	0	1	71.2	-75.6	15	5	1	-1.8	1.8	0	0	2	81.0	-88.3
4	1	0	24.9	24.9	5	0	1	17.9	18.3	1	6	1	16.5	12.8	1	0	2	43.0	-42.1
6	1	0	8.5	7.4	6	0	1	12.9	-13.0	2	6	1	8.8	-8.8	2	0	2	3.8	-3.8
8	1	0	35.2	-33.1	7	0	1	31.6	31.1	3	6	1	20.8	-20.3	3	0	2	5.1	5.8
10	1	0	3.0	-1.9	8	0	1	18.9	-17.7	4	6	1	-0.9	0.5	4	0	2	27.2	-25.4
12	1	0	6.9	-6.6	9	0	1	7.7	-6.6	5	6	1	10.5	-10.4	5	0	2	2.6	2.8
14	1	0	2.3	-2.0	10	0	1	8.1	8.3	6	6	1	7.7	-8.4	6	0	2	14.0	13.2
16	1	0	6.5	-6.8	11	0	1	3.5	-4.2	7	6	1	0.0	-0.6	7	0	2	15.5	-16.0
0	2	0	79.3	-99.6	12	0	1	2.5	2.2	8	6	1	12.0	12.8	8	0	2	3.1	2.9
2	2	0	17.3	-17.8	13	0	1	9.1	8.7	9	6	1	12.8	-13.1	9	0	2	12.5	12.4
4	2	0	11.3	11.9	14	0	1	4.6	4.8	10	6	1	0.0	-0.1	10	0	2	9.9	-9.7
6	2	0	14.8	14.3	15	0	1	4.5	4.2	11	6	1	9.8	-10.1	11	0	2	2.4	-3.0
8	2	0	8.4	-8.7	16	0	1	-1.1	0.3	12	6	1	2.0	-3.0	12	0	2	3.5	3.3
10	2	0	0.0	-1.1	17	0	1	0.0	-0.9	13	6	1	2.5	2.7	13	0	2	-1.7	1.2
12	2	0	6.1	-6.2	0	1	1	10.1	9.4	14	6	1	-1.2	0.9	14	0	2	0.0	1.5
14	2	0	6.8	-7.0	1	1	1	45.1	-48.6	15	6	1	0.0	-0.6	15	0	2	5.5	4.6
16	2	0	-1.8	-1.0	2	1	1	5.8	5.7	0	7	1	8.4	-8.2	16	0	2	2.1	1.4
2	3	0	44.8	-47.2	3	1	1	28.9	-30.5	1	7	1	4.9	-4.7	1	1	2	36.9	-36.4
4	3	0	23.9	23.1	4	1	1	46.4	-47.9	2	7	1	14.1	-13.8	2	1	2	6.6	-6.4
6	3	0	32.3	-32.1	5	1	1	11.3	11.8	3	7	1	4.3	-4.5	3	1	2	4.7	4.7
8	3	0	5.0	-4.9	6	1	1	7.4	-6.8	4	7	1	-0.9	1.3	4	1	2	7.3	6.5
10	3	0	3.0	2.4	7	1	1	21.0	-20.7	5	7	1	3.1	2.6	5	1	2	4.6	-4.0
12	3	0	13.3	13.1	8	1	1	2.3	2.2	6	7	1	7.7	7.7	6	1	2	6.2	-6.2
14	3	0	1.9	2.3	9	1	1	11.8	-10.3	7	7	1	0.0	1.4	7	1	2	18.1	19.2
16	3	0	2.1	-0.3	10	1	1	4.4	4.3	8	7	1	4.6	5.1	8	1	2	-1.3	0.4
0	4	0	12.2	12.1	11	1	1	6.6	6.7	9	7	1	2.3	-2.4	9	1	2	10.4	10.0
2	4	0	25.6	25.4	12	1	1	3.8	3.6	10	7	1	2.2	-2.5	10	1	2	1.7	2.1
4	4	0	34.4	33.1	13	1	1	2.6	3.3	11	7	1	4.7	4.6	11	1	2	2.3	-2.3
6	4	0	21.2	-19.7	14	1	1	-1.6	1.1	12	7	1	0.0	0.3	12	1	2	9.2	10.5
8	4	0	5.1	4.5	15	1	1	4.2	-4.1	13	7	1	2.8	2.8	13	1	2	4.1	3.6
10	4	0	23.4	23.1	16	1	1	-1.4	-1.6	14	7	1	-1.6	2.2	14	1	2	-1.5	-0.7
12	4	0	3.1	3.5	1	2	1	35.7	-37.7	1	8	1	8.8	8.9	15	1	2	3.3	-3.4
14	4	0	4.8	-4.9	2	2	1	-0.7	0.3	2	8	1	1.8	-0.6	16	1	2	2.3	0.7
16	4	0	2.6	2.8	3	2	1	2.3	2.7	3	8	1	0.0	-1.2	0	2	2	5.9	-5.5
2	5	0	23.7	23.0	4	2	1	12.9	-13.0	4	8	1	8.8	9.7	1	2	2	1.4	1.4
4	5	0	2.1	2.3	5	2	1	25.4	-25.0	5	8	1	7.1	7.2	2	2	2	16.2	-15.4
6	5	0	16.9	-16.5	6	2	1	9.8	9.1	6	8	1	2.2	-1.0	3	2	2	-1.0	-0.9
8	5	0	13.5	13.4	7	2	1	14.7	-15.2	7	8	1	5.0	5.0	4	2	2	20.7	-20.9
10	5	0	4.6	-4.5	8	2	1	0.0	0.3	8	8	1	0.0	0.8	5	2	2	-0.7	1.6
12	5	0	30.9	-31.5	9	2	1	-0.9	-0.8	9	8	1	2.4	1.1	6	2	2	30.8	-28.3
14	5	0	-1.3	-0.4	10	2	1	17.2	-17.7	10	8	1	7.2	7.4	7	2	2	-0.8	0.0
16	5	0	-1.1	-0.2	11	2	1	4.7	3.4	11	8	1	2.9	2.9	8	2	2	0.0	1.0
0	6	0	42.3	-41.2	12	2	1	-0.8	-1.6	12	8	1	2.0	2.3	9	2	2	4.1	-4.0
2	6	0	10.3	-9.9	13	2	1	2.6	-2.5	13	8	1	-1.4	1.2	10	2	2	1.9	-1.8
4	6	0	43.4	-43.5	14	2	1	9.3	-9.6	0	9	1	-1.6	0.8	11	2	2	2.5	2.2
6	6	0	3.0	-2.6	15	2	1	3.3	-3.4	1	9	1	11.9	-12.2	12	2	2	-1.1	-0.2
8	6	0	-1.1	-0.5	16	2	1	0.0	1.0	2	9	1	14.7	14.8	13	2	2	-0.7	-0.4
10	6	0	30.6	-30.9	0	3	1	19.8	-19.2	3	9	1	3.9	-3.8	14	2	2	-1.1	0.0
12	6	0	2.7	-2.6	1	3	1	9.4	10.0	4	9	1	-1.3	-1.4	15	2	2	-1.4	-1.9
14	6	0	4.1	4.7	2	3	1	89.2	-171.4	5	9	1	3.7	4.5	16	2	2	2.4	-2.4
2	7	0	4.7	-4.9	3	3	1	9.0	-9.4	6	9	1	2.3	1.6	1	3	2	-1.3	3.0
4	7	0	6.3	-5.9	4	3	1	6.0	5.3	7	9	1	6.1	-6.3	2	3	2	8.2	8.0
6	7	0	1.6	1.5	5	3	1	10.4	10.0	8	9	1	7.8	8.2	3	3	2	11.4	12.6
8	7	0	8.5	-9.0	6	3	1	4.9	5.2	9	9	1	2.3	-2.4	4	3	2	9.4	-7.8
10	7	0	-1.2	1.2	7	3	1	11.6	11.5	10	9	1	-0.7	0.3	5	3	2	9.6	-9.2
12	7	0	15.1	15.2	8	3	1	12.1	-12.2	11	9	1	2.0	1.8	6	3	2	28.7	28.2
14	7	0	0.0	0.8	9	3	1	5.2	-5.1	12	9	1	3.3	3.3	7	3	2	3.2	-2.7
2	8	0	16.9	16.5	10	3	1	1.7	1.1	13	9	1	0.0	1.0	8	3	2	-0.6	-0.7
4	8	0	3.8	4.1	11	3	1	7.8	7.2	1	10	1	12.7	-12.9	9	3	2	0.0	-0.9
6	8	0	-0.9	-1.6	12	3	1	5.6	-5.5	2	10	1	1.7	-0.6	10	3	2	3.1	2.8
8	8	0	3.7	-3.3	13	3	1	3.1	2.8	3	10	1	4.9	4.8	11	3	2	0.0	0.1
10	8	0	4.8	4.8	14	3	1	-1.3	-0.2	4	10	1	2.5	2.4	12	3	2	0.0	-0.4
12	8	0	3.3	3.4	15	3	1	0.0	-0.6	5	10	1	4.7	-4.5	13	3	2	0.0	-0.5
14	8	0	4.2	4.0	16	3	1	-1.1	0.7	6	10	1	7.1	6.9	14	3	2	-1.5	-0.5
2	9	0	3.7	3.0	1	4	1	-7.4	-7.4	7	10	1	5.8	-6.0	15	3	2	-1.4	0.1
4	9	0	13.4	-12.8	2	4	1	2.3	2.3	8	10	1	-1.3	0.3	16	3	2	-1.8	1.7
6	9	0	3.1	-3.2	3	4	1	27.9	29.1	9	10	1	3.1	2.9	0	4	2	26.1	-25.4
8	9	0	9.7	10.0	4	4	1	11.7	12.7	10	10	1	2.7	-2.9	1	4	2	4.4	4.4
10	9	0	6.5	-6.8	5	4	1	25.7	25.8	11	10	1	-1.2	1.1	2	4	2	6.2	6.5
12	9	0	-1.2	0.4	6	4	1	2.1	-2.2	0	11	1	3.0	-2.4	3	4	2	11.6	11.2
14	9	0	2.1	2.1	7	4	1	1.6	-1.3	1	11	1	7.2	7.2	4	4	2	15.7	14.7
0	10	0	33.1	-32.2	8	4	1	6.5	-6.5	2	11	1	2.5	2.2	5	4	2	12.7	14.1
2	10	0	6.4	-6.0	9	4	1	15.1	15.9	3	11	1	3.6	4.0	6	4	2	14.6	14.9
4	10	0	5.8	6.0	10	4	1	7.4	7.7	4	11	1	6.2	6.3	7	4	2	4.3	3.9
6	10	0	5.9	-6.1	11	4	1	12.9	12.4	5	11	1	1.8	-2.0	8	4	2	-1.4	1.4
8	10	0	-1.3	-1.5	12	4	1	2.0	1.5	6	11	1	0.0	-1.5	9	4	2	-1.0	0.1
10	10	0	5.3	5.7	13	4	1	5.1	-5.0	7	11	1							



H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC	H	K	L	FD	FC
6	7	5	-1.1	-0.6	2	13	2	2.3	1.9	2	6	3	3.5	-3.4	8	1	4	-0.9	0.5
7	5	5	3.6	-3.6	3	13	2	-1.5	0.7	3	6	3	5.5	4.8	9	1	4	0.0	-0.4
8	5	5	5.4	5.9	4	13	2	0.0	-0.5	4	6	3	10.2	-10.1	10	1	4	2.5	-2.4
9	5	5	2.3	-2.7	1	0	3	1.5	-1.9	5	6	3	-1.0	-0.4	11	1	4	2.9	2.7
10	5	5	-1.2	1.5	2	0	3	37.5	-36.6	6	6	3	2.5	2.3	12	1	4	4.1	-4.2
11	5	5	5.6	-5.7	3	0	3	12.1	-12.3	7	6	3	4.3	4.4	13	1	4	5.6	-5.6
12	5	5	6.6	7.1	4	0	3	21.5	20.0	8	6	3	11.4	-11.9	14	1	4	-1.0	-1.8
13	5	5	-1.4	1.6	5	0	3	2.8	2.6	9	6	3	3.8	3.7	0	2	4	3.5	3.5
14	5	5	-1.1	0.6	6	0	3	5.0	-5.5	10	6	3	-1.6	1.6	1	2	4	9.0	8.1
15	5	5	-0.9	-0.3	7	0	3	6.9	-6.5	11	6	3	2.9	2.7	2	2	4	4.8	4.4
0	6	2	35.1	33.5	8	0	3	3.3	3.3	12	6	3	6.5	7.0	3	2	4	5.5	5.7
1	6	2	12.8	12.4	9	0	3	2.4	1.8	13	6	3	-1.5	-0.8	4	2	4	7.5	7.3
2	6	2	-0.3	1.4	10	0	3	-1.4	0.6	0	7	3	4.0	3.5	5	2	4	-1.5	-1.4
3	6	2	16.4	-15.8	11	0	3	4.7	4.8	1	7	3	2.6	2.7	6	2	4	9.2	8.7
4	6	2	5.3	5.6	12	0	3	3.3	3.1	2	7	3	3.3	3.7	7	2	4	7.8	8.1
5	6	2	15.1	-14.8	13	0	3	1.8	-1.3	3	7	3	2.6	1.9	8	2	4	6.1	-5.9
6	6	2	1.9	-2.1	14	0	3	-0.6	1.3	4	7	3	-0.8	-0.7	9	2	4	3.0	3.1
7	6	2	0.0	-0.1	15	0	3	-1.6	-0.3	5	7	3	2.7	-3.0	10	2	4	-0.4	-1.3
8	6	2	-0.9	-1.7	0	1	3	43.4	-41.7	6	7	3	0.0	0.3	11	2	4	0.0	-0.5
9	6	2	5.5	-5.3	1	1	3	5.8	5.8	7	7	3	-0.7	-1.1	12	2	4	2.5	-2.5
10	6	2	3.3	3.6	2	1	3	10.3	-9.4	8	7	3	-1.2	-0.7	13	2	4	0.0	0.7
11	6	2	4.7	5.1	3	1	3	11.0	10.5	9	7	3	-1.2	1.8	14	2	4	0.0	-0.2
12	6	2	0.0	-0.4	4	1	3	18.5	18.3	10	7	3	6.7	6.7	1	3	4	6.3	5.6
13	6	2	2.6	2.1	5	1	3	8.2	7.5	11	7	3	0.0	-1.1	2	3	4	1.8	-1.7
14	6	2	-1.6	-0.8	6	1	3	4.3	-4.6	12	7	3	-1.5	0.9	3	3	4	4.7	4.8
1	7	2	1.5	-0.6	7	1	3	6.0	6.1	13	7	3	-1.1	-1.4	4	3	4	6.2	6.6
2	7	2	1.8	-0.8	8	1	3	7.4	6.4	1	8	3	0.0	0.3	5	3	4	15.3	15.7
3	7	2	11.4	-10.8	9	1	3	2.0	1.9	2	8	3	5.1	-4.8	6	3	4	10.4	-10.6
4	7	2	-1.0	-0.8	10	1	3	-1.0	-0.3	3	8	3	-1.0	0.7	7	3	4	2.2	2.0
5	7	2	2.4	1.8	11	1	3	3.1	-2.8	4	8	3	-1.7	-1.4	8	3	4	-0.8	-2.1
6	7	2	3.8	3.6	12	1	3	-0.4	-1.5	5	8	3	4.2	-4.3	9	3	4	6.2	6.5
7	7	2	-0.9	-1.3	13	1	3	3.7	-3.2	6	8	3	-1.1	-0.3	10	3	4	3.8	-4.7
8	7	2	1.9	2.1	14	1	3	-1.4	-1.7	7	8	3	-0.8	2.2	11	3	4	5.2	5.3
9	7	2	0.0	0.6	15	1	3	-1.2	1.5	8	8	3	-0.6	-0.6	12	3	4	-1.1	-1.2
10	7	2	0.0	0.8	1	2	3	0.0	1.1	9	8	3	1.9	0.8	13	3	4	0.0	-0.9
11	7	2	2.7	2.4	2	2	3	16.8	16.0	10	8	3	3.1	-3.6	14	3	4	0.0	-0.6
12	7	2	4.5	-4.5	3	2	3	8.7	-9.4	11	8	3	2.7	-2.4	0	4	4	9.0	8.2
13	7	2	-1.5	-0.9	4	2	3	3.0	3.4	12	8	3	2.7	-2.4	1	4	4	6.8	6.9
14	7	2	0.0	-0.1	5	2	3	6.7	6.4	0	9	3	12.5	-12.3	2	4	4	3.8	3.4
0	8	2	5.2	5.4	6	2	3	5.4	5.1	1	9	3	5.0	5.2	3	4	4	2.4	2.3
1	8	2	2.7	-3.3	7	2	3	1.8	1.1	2	9	3	8.8	-8.2	4	4	4	2.5	-2.5
2	8	2	2.1	1.6	8	2	3	2.2	2.9	3	9	3	-1.3	-0.6	5	4	4	11.0	-11.3
3	8	2	0.0	0.2	9	2	3	2.6	-2.8	4	9	3	1.8	2.4	6	4	4	9.8	-10.6
4	8	2	3.6	4.4	10	2	3	6.6	7.1	5	9	3	3.3	3.0	7	4	4	2.2	-2.8
5	8	2	-1.6	1.8	11	2	3	0.0	-0.2	6	9	3	3.4	-3.2	8	4	4	-0.8	-1.0
6	8	2	11.1	11.5	12	2	3	2.2	2.6	7	9	3	4.4	4.8	9	4	4	4.8	5.2
7	8	2	2.0	2.3	13	2	3	3.2	-2.7	8	9	3	1.7	-1.7	10	4	4	2.3	-2.2
8	8	2	0.0	0.8	14	2	3	3.1	3.3	9	9	3	2.5	-2.2	11	4	4	4.0	-4.3
9	8	2	-0.3	0.9	15	2	3	-1.4	0.7	10	9	3	-1.3	-0.2	12	4	4	0.0	1.0
10	8	2	-1.1	0.0	0	3	3	18.3	16.8	11	9	3	2.1	0.8	13	4	4	2.7	-2.7
11	8	2	-0.6	-0.3	1	3	3	18.7	-17.4	1	10	3	3.2	4.0	1	5	4	6.6	6.9
12	8	2	0.0	-0.6	2	3	3	33.9	32.9	2	10	3	8.5	8.2	2	5	4	6.2	-6.2
13	8	2	-1.6	1.0	3	3	3	4.4	4.9	3	10	3	-1.1	0.2	3	5	4	15.9	-16.2
1	9	2	3.6	-4.4	4	3	3	5.2	5.2	4	10	3	0.0	-1.1	4	5	4	11.5	-11.7
2	9	2	4.5	-4.5	5	3	3	-1.0	-1.3	5	10	3	2.7	2.6	5	5	4	5.2	-5.4
3	9	2	-1.5	-1.8	6	3	3	6.3	6.6	6	10	3	0.0	-0.6	6	5	4	-1.3	-1.6
4	9	2	5.6	6.0	7	3	3	8.8	-10.0	7	10	3	0.0	0.1	7	5	4	3.3	3.0
5	9	2	3.7	4.0	8	3	3	4.8	5.3	8	10	3	-1.2	0.9	8	5	4	-1.2	-2.2
6	9	2	4.4	-5.2	9	3	3	4.0	4.1	9	10	3	-1.1	-1.0	9	5	4	8.2	-7.9
7	9	2	2.6	2.9	10	3	3	7.6	7.3	0	11	3	8.4	8.8	10	5	4	-0.8	0.3
8	9	2	1.9	-2.0	11	3	3	5.5	-3.3	1	11	3	2.0	-1.9	11	5	4	4.5	-4.6
9	9	2	2.5	2.6	12	3	3	3.6	3.6	2	11	3	0.0	-0.3	12	5	4	0.0	0.2
10	9	2	0.0	-0.8	13	3	3	-1.3	0.3	3	11	3	2.3	-2.3	13	5	4	-1.9	7.1
11	9	2	-1.0	1.0	14	3	3	1.7	-2.0	4	11	3	3.8	-4.0	0	6	4	14.5	-14.4
12	9	2	2.2	1.8	15	3	3	-0.5	0.1	5	11	3	-0.9	-1.0	1	6	4	12.6	-12.2
0	10	2	-1.7	1.7	1	4	3	4.0	3.1	6	11	3	-0.7	0.7	2	6	4	8.9	-8.6
1	10	2	2.6	2.2	2	4	3	7.1	6.8	7	11	3	2.0	-1.3	3	6	4	-0.9	0.3
2	10	2	-0.9	1.4	3	4	3	3.8	2.9	8	11	3	2.2	-2.4	4	6	4	2.8	-3.2
3	10	2	2.8	2.8	4	4	3	5.7	5.8	1	12	3	-1.5	-1.7	5	6	4	10.4	9.9
4	10	2	0.0	0.1	5	4	3	10.2	-10.1	2	12	3	4.0	-4.5	6	6	4	4.9	4.5
5	10	2	3.2	2.3	6	4	3	2.4	-2.8	3	12	3	0.0	-0.3	7	6	4	0.0	-0.3
6	10	2	5.0	-4.8	7	4	3	3.7	-3.4	4	12	3	-0.7	1.0	8	6	4	0.0	-1.1
7	10	2	1.8	1.4	8	4	3	8.1	8.3	5	12	3	0.0	0.3	9	6	4	-1.4	-1.2
8	10	2	0.0	0.0	9	4	3	2.8	-3.1	0	0	4	9.2	9.0	10	6	4	-1.1	1.1
9	10	2	2.1	-2.1	10	4	3	5.0	-5.7	1	0	4	10.0	-9.8	11	6	4	3.3	3.1
10	10	2	-1.9	0.7	11	4	3	3.3	-3.3	2	0	4	0.0	0.8	12	6	4	0.0	-0.1
11	10	2	-1.2	-0.7	12	4	3	8.5	-8.9	3	0	4	15.1	-15.1	1	7	4	-0.8	0.2
1	11	2	4.1	4.1	13	4	3	3.2	3.9	4	0	4	4.5	4.4	2	7	4	-1.7	1.6
2	11	2	-2.2	-2.2	14	4	3	3.3	-2.8	5	0	4	8.9	7.7	3	7	4	8.7	8.2
3	11	2	0.0	-0.4	0	5	3	8.6	7.7	6	0	4	-1.6	-0.7	4	7	4	5.7	5.0
4	11	2	-0.7	-0.7	1	5	3	3.0	-3.5	7	0	4	5.3	-5.4	5	7	4	5.6	5.6
5	11	2	0.0	1.1	2	5	3	4.5	5.0	8	0	4	11.2	11.9	6	7	4	3.9	-3.9
6	11	2	-1.3	-0.5	3	5	3	5.3	-5.8	9	0	4	13.0	-12.5	7	7	4	-1.5	1.8
7	11	2	4.4	-4.5	4	5	3	0.0	-0.2	10	0	4	6.7	6.7	8	7	4	-0.8	0.3
8	11	2	2.0	-0.3	5	5	3	1.6	1.9	11	0	4	6.4	6.8	9	7	4	4.3	4.5



**APPENDIX**

APPENDIXComputer Programmes

The extensive calculations necessary for the work described in this thesis were carried out primarily on the University of Cambridge I.B.M. 370/165 computer in conjunction with the N.U.M.A.C. I.B.M. 360/67 and Durham I.B.M. 1130 computers. I would like to thank the staff of the Computer unit, especially the computer operators for their help and advice.

The major programmes used in the structure determinations and refinements were written by F.R. Ahmed and his associates (N.R.C. Crystallographic Programs for the I.B.M. 360 System, World List of Crystallographic Programs, 2nd edn., Appendix p.52) and I am grateful for permission to use these programmes.

I have personally written and amended several smaller programmes as was necessary. These include a programme written in conjunction with Dr H.M.M. Shearer to translate diffractometer data from card images of paper tape, stored on disc into planes on cards.

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