Crystal structures of some complexes of group IB ethynyl compunds

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CRYSTAL STRUCTURES OF SOME COMPLEXES OF GROUP IB ETHYNYL COMPOUNDS.

A thesis submitted for the degree of doctor of of philosophy by P.W.R. Corfield, B.Sc. (University College).

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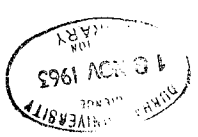

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ABSTRACT

Crystal Structures of Some Complexes of Group IB Ethynyl Compounds

Interest in these compounds centred on the bonding between the ethynyl groups and the metal atoms. The structures were determined by heavy atom techniques, and refined by the method of least squares, using three-dimensional data.

Phenylethynyl(trimethylphosphine)copper(I), $Me_3PCuC{\equiv}CPh$, is tetrameric. The centrosymmetric molecules are nearly flat, apart from the phosphine groups. The four copper atoms form a zig-zag chain, with Cu...Cu distances 2.45, 2.69, 2.45 Å. Two phosphine groups are attached to each terminal copper atom. Two of the ethynyl groups lie on a line through the two inner copper atoms, to which they are σ-bonded. The other two are each 'side-on' bonded to an inner copper atom, with the bond to the phenyl group distorted away from the copper atom. Their terminal carbon atoms each form a bridge bond with two further copper atoms in the chain. Neglecting any copper-copper interaction, the coordination around the inner copper atoms is approximately trigonal, and around the terminal copper atoms, tetrahedral.

Phenylethynyl(trimethylphosphine)silver(I), $Me_3PAgC{\equiv}CPh$, has silver atoms in infinite, almost straight, chains, with Ag...Ag = 3.03 Å. Alternate silver atoms lie on centres of symmetry, and are σ-bonded to two ethynyl groups. These are 'side-on' bonded to

adjacent silver atoms, which lie on two-fold axes, and which are bonded to two phosphine groups. The 'side-on' bonding is not symmetrical. (Ag-C = 2.55, 3.04 Å.) The silver atoms are alternately in linear, and approximately tetrahedral, coordination.

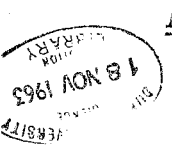
Phenylethynyl(isopropylamine)gold(I), $^{i}PrNH_2AuC{\equiv}CPh$, has gold atoms in infinite zig-zag chains, related in pairs by two-fold axes. Au...Au = 3.72 Å., along the chains, 3.27 Å. between chains. Each gold atom is linearly coordinated to an ethynyl carbon and an amine nitrogen atom, lying in the plane of the zig-zag. The arrangement excludes association through gold-ethynyl interaction, the shortest intermolecular distances being gold-gold or gold-nitrogen contacts.

INTRODUCTION

OLEFIN COMPLEXES OF THE TRANSITION METALS

Very stable complexes with olefins are formed by platinum and it is over a hundred years since the first one was reported by Zeise, (1827), $K[PtCl_3(C_2H_4)]$, prepared by the reaction of platinous chloride with ethylene and potassium chloride. Complexes with copper(I), silver(I), and palladium(II) have been prepared by similar methods, and olefin complexes with mercury(II) are reported to exist in solution. The olefin complexes of other transition metals are generally stable if the metal is in a low valency state and if a chelating diene is used. A variety of olefin complexes has been prepared in recent years (by e.g. Fischer and Frölich, 1959) by replacing one or more carbonyl groups with olefins in the zero-valent metal carbonyl compounds, or in cyclopentadienyl carbonyl compounds. Sometimes chelating dienes will react directly with the normal-valent halides to form complexes, as in the case of ruthenium and rhodium. (Abel, Bennet and Wilkinson, 1959). In the case of iron, more stable complexes are formed with conjugated dienes than with non-conjugated dienes. (Guy and Shaw, 1962, p. 86).

ACETYLENE COMPLEXES OF THE TRANSITION METALS



Until recently, only a few unstable acetylene complexes

of copper and silver were known. Now, a vast number of acetylene complexes have been prepared, usually by reaction of acetylenes with metal carbonyls. Acetylene complexes fall into two classes - those in which the acetylene is bonded only to the metal atom(s), and those in which the acetylene reacts to form new C-C bonds during complex formation. Compounds of the second class are usually formed by reactions of acetylenes with iron and cobalt carbonyls when the reaction conditions are at all energetic, and the polymerisation of acetylenes by chromium alkyls presumably occurs with such complexes as intermediates. Several structure determinations have been made of compounds in this class. (e.g. $Fe_2(CO)_6(C_6H_5C{\equiv}CH)_3$, King, 1962; and $Co_2(CO)_9HC{\equiv}CH$, Mills and Robinson, 1959).

Compounds of the first class, where no new ligand is formed, may be divided into three types:

i) Those where the acetylene combines with one metal atom, and still contains a recognisable carbon-carbon triple bond. Examples are the acetylene complexes of platinum described by Bukhovets and Molodova (1957), and by Chatt et al. (1961), and also the group IB acetylides, where it is presumed that metal-ethynyl coordination is responsible for the polymeric nature. (Blake, Calvin and Coates, 1959). The ethynyl stretching frequency, $\nu_{C{\equiv}C}$, for these compounds is not more than 200-300 cm^{-1}. different from the usual value for

disubstituted acetylenes (2200-2250 cm.$^{-1}$). Crystal structure determinations of two ethynyl copper(I) complexes of this type have been reported by Carter and Hughes, (1957), but no bond lengths were given. The copper atom is on the perpendicular bisector of the carbon-carbon triple bond.

ii) Those where the ethynyl group is effectively reduced to a double bond, and each carbon atom is joined to the metal atom by a σ-bond. This type of structure is suggested for the monomeric complexes $\left[ClRe(ac)_2(PPh_3)\right]$ and $\left[Pt(PPh_3)_2(ac)\right]$, (ac = acetylene) where the infra-red spectrum shows absorption bands around 1700cm^{-1}, in the region expected for C=C stretching frequencies. (Colton, Levitus and Wilkinson, 1960; Chatt, Rowe and Williams, 1957). Preliminary X-ray studies on the platinum compounds support the planar structure expected if two σ-bonds to the metal atom are formed. (Owston and Rowe, 1962). The structure of the cobalt complex $Co_4(CO)_{10}(C_2H_5C{\equiv}CC_2H_5)$ involves metal-carbon σ-bonds and reduction of the triple to a double bond, with an increase in the bond distance to 1.44Å, although the bonding here is complex. (Dahl and Smith, 1962).

iii) Those compounds where the acetylene is bonded to two metal atoms. Such structures are proposed for a few acetylene complexes with binuclear iron and cobalt carbonyls,

and for the dicyclopentadienyldinickelethynyl complexes, where chemical methods show that the acetylene is bonded only to the metal atoms. (e.g. Tilney-Basset, 1961). The crystal structure of $Co_2(CO)_6PhC{\equiv}CPh$ shows that the ethynyl group lies in a direction at right angles to the Co-Co axis with its midpoint above the midpoint of the Co-Co bond. (Sly, 1959). The C≡C length has increased to 1.46 Å, and the Ph-C≡C angle is 140°. The C≡C stretching frequency has disappeared altogether. The coordination around each carbon atom is tetrahedral, and it may be that both the ethynyl carbons form σ-bonds to each metal atom, in sp^3 hybridisation. However the view has been taken that the ethynyl group is joined to the metal atom by two $\sigma\pi$-bonds of the type described in the next section (Guy and Shaw, 1962, pp. 104-5. Bennet, 1962, p. 639).

THE NATURE OF THE METAL-OLEFIN OR METAL-ACETYLENE BOND

The theory now generally accepted for the bonding was first proposed by Dewar (1951), who used the molecular orbital theory to explain the structure of the silver-olefin complexes. The principle was adapted to the platinum-olefin complexes by Chatt and Duncanson, (1953). The structures are shown in Fig. 1.

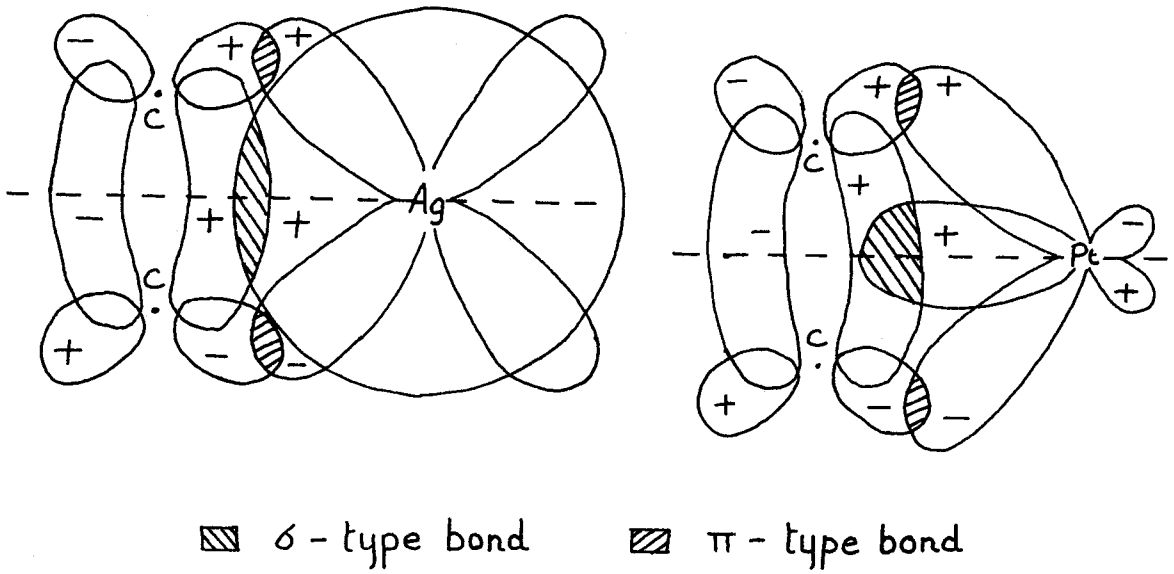


Fig. 1. Schematic structures for the silver-olefin and the platinum-olefin complexes.

The metal atom is assumed to lie on the perpendicular bisector of the carbon-carbon double bond. Overlap of the filled bonding $\pi_z 2_p$ molecular orbital of the olefin with the vacant 5s-orbital in the case of the silver complex, or with a vacant $5d6s6p^2$ hybrid orbital in the case of the platinum complex, forms a bond which has the symmetry of a σ-bond. The essential point in the structure is however the overlap of a filled 4d-orbital in the case of silver, or a filled 5d6p-hybrid orbital in the case of platinum, with the vacant antibonding π_z^* 2p molecular orbital of the olefin to form a π-type bond, so that the metal-olefin bond has both donor

and acceptor characteristics. Stable coordination complexes are not formed by olefins with acceptor molecules such as BF_3, where the boron atom has no d-electrons available to form the π-type bond. The bonding has been called $\sigma\pi$-bonding to emphasize the donor and acceptor characteristics of the bond. (Guy and Shaw, 1962, p. 80).

The bonding in metal-acetylene complexes is expected to be similar, except that in principle an acetylene could be involved in bonding to two metal atoms, since there are two sets of bonding and antibonding orbitals.

THE BOND ORDER IN OLEFIN AND ACETYLENE COMPLEXES

Both the σ-donation of bonding electrons to the metal atom, and the π-acceptance of d-electrons into antibonding orbitals would be expected to reduce the bond order in the olefin or acetylene. This is confirmed by the infra-red spectra of the compounds, which show that the double bond does still exist in the olefin complexes, but that the C=C stretching frequency is reduced by about 70 $cm.^{-1}$ in the case of the silver ion complexes, (Taufen, Murray and Cleveland, 1941) and by about 150 $cm.^{-1}$ in the case of the platinum complexes. (Chatt and Duncanson, 1953). Chatt et al. also reported that ($\nu_{C\equiv C}$) was lowered by about 200 $cm.^{-1}$ in the platinum-

alkyne complexes. (Chatt, Duncanson and Guy, 1961).

X-ray structure analyses have confirmed that the spatial arrangement in these complexes is such that the carbon-carbon double or triple bond is 'broadside' on to the metal atom, and that in general, the C=C or C≡C bond length is increased relative to the free olefin or acetylene, suggesting a decrease in bond order. The available X-ray evidence relevant to $\sigma\pi$-bonding in acetylene complexes is meagre and has already been summarised. Hence the discussion here is confined to the structures reported for olefin complexes.

The lengths of the carbon-carbon double bonds in the palladium dichloride norbornadiene complex are extended to 1.46 Å, and in the palladium dichloride styrene complex, the double bond is extended to 1.45 Å. (Baenziger, Doyle and Richards, 1961). The length of the double bond in the platinum ethylene complex studied by Alderman, Owston and Rowe, (1960) was 1.47 Å. and earlier work on platinum ethylene complexes had also indicated extension of the double bond to about 1.5 Å. (Bokii and Kukina, 1957; Mellor and Wunderlich, 1955). Recently, an increase of the C=C bond length to 1.44 $\pm$ 0.07 Å. has been reported for the 1,5-cyclooctadiene rhodium dichloride complex, (Ibers and

Snyder, 1962) and the C=C length in the acrylonitrile complex of iron tetracarbonyl is extended to 1.40 ± 0,02 Å. (Luxmoore and Truter, 1961).

In marked contrast to the palladium and platinum complexes, the two silver olefin complexes whose structures have been reported have C=C lengths normal for double bonds. Bond lengths of 1.36 and 1.34 Å. are quoted for the silver complex with cyclooctatetraene dimer, (Nyburg and Hilton, 1959) and of 1.33 and 1.37 Å. (± 0.04) for the 1:1 complex with cyclooctatetraene, (Matthews and Lipscomb, 1959) and in the latter complex the bond angles in the cyclooctatetraene part are the same as in the free molecule. Metal-carbon bond distances range from 2.4-2.8 Å, which is rather more than would be expected for a single covalent bond, whereas, in the platinum and palladium complexes, metal-carbon distances are about 2.2 Å, and in the iron acrylonitrile complex, the metal-carbon distance is 2.1 Å. The results for the silver-olefin complexes confirm the inference from the infra-red spectra, that the metal-olefin interaction is weaker in these complexes.

GROUP IB ACETYLIDES AND THEIR COMPLEXES

Aryl and alkyl acetylides of the group IB metals, (RC≡CM; M=Cu, Ag, Au) are prepared as yellow powders which

decompose without melting above 100-120°C, and which are insoluble in ordinary organic solvents. As already mentioned, they are regarded as coordination polymers, with the metal atoms linked to two or more ethynyl groups by σπ-bonding. The t-butylacetylides are exceptional in that they will dissolve in organic solvents. Molecular weight measurements on the solutions show that the copper compound is octameric, the gold compound tetrameric. t-Butylethynyl-silver is insufficiently soluble to determine its molecular weight accurately, but it is certainly at least tetrameric. It crystallises in very tiny needles, which tend to be fibrous and which turn black in the X-ray beam.

The ethynyl stretching frequencies for the phenyl and t-butyl acetylides are given in Table I.

TABLE I. Ethynyl Stretching Frequencies in RC≡CM. KBr Disc.

M:		½Hg		Cu	Ag	Au
R:	Ph	2149	2117	1933	2055	1973
	Me_3C	2180	2146	Abs.	2055	1950-2030

Shifts of about 200 $cm.^{-1}$ relative to frequencies observed in the mercury acetylides occur in the copper and gold compounds, and these are similar to the shifts of 200 $cm.^{-1}$

observed in the spectra of disubstituted acetylenes when they are $\sigma\pi$-bonded to platinum. One may compare the relatively small drop in frequency for the silver compound with the small effects on the ethenyl groups and the long silver-carbon distances in the silver-olefin complexes mentioned above. The strong coordination in the ethynyl gold compounds is remarkable, as neither olefinic nor acetylenic gold complexes have previously been reported.

For the di-ethynyl compounds, PhC≡CC≡CM, (M = Cu, Ag), the infra-red spectra indicate that one of the ethynyl groups absorbs at 2180-2190 cm^{-1} and it is assumed that this takes no part in the $\sigma\pi$-bonding.

Donor molecules where there are vacant d-orbitals available on the donor atom can break down the polymeric structures of the acetylides. Phosphine complexes $R'_3PMC{\equiv}CR$, M=Cu, Ag, Au and R' alkyl or aryl, have been prepared, and also some arsine and stibine complexes. The phosphine complexes can usually be crystallised as yellow needles. The degrees of association obtained from molecular weight determinations in solution for three typical phosphine complexes are given in Table II together with the ethynyl stretching frequencies. The data indicate that the degree of complexity in the phosphine complexes decreases in the order Cu-Ag-Au.

TABLE II. Degree of Association, (n), and Ethynyl Stretching Frequency, (v), in $R_3PMC{\equiv}CPh$.

Compound	n	v cm^{-1}
$Me_3PCuC{\equiv}CPh$	2.70	2019, 2045
$Me_3PAgC{\equiv}CPh$	2.00*	2075
$Et_3PAuC{\equiv}CPh$	1.3	2109

Spectra measured in KBr disc.
Molecular weights cryoscopically in benzene. *; ebullioscopically.

The gold acetylides will also form stable complexes with primary amines. In contrast to the phosphine complexes, the degree of association of the amine complexes of phenylethynyl gold is 3-4, varying with concentration. The dielectric constants of benzene solutions of the complexes indicate the presence of much less polar species in the amine complexes than in the phosphine complexes of phenylethynyl gold. The ethynyl stretching frequencies in the amine complexes (2120-2134 $cm.^{-1}$.) are however little removed from those found for the phosphine complexes (2109-2129 $cm.^{-1}$), or from those expected in disubstituted acetylenes containing ethynyl-metal σ-bonds.

THE SCOPE OF THE WORK PRESENTED

I have been concerned with the determination of structure

in the acetylides by X-ray methods with particular reference to the interaction between the ethynyl groups and the metal atoms. Only the phosphine or amine complexes of the acetylides have been studied as it is much easier to obtain crystals of these compounds appropriate for X-ray analysis than it is to obtain sui- table crystals of the highly insoluble parent acetylides. The t-butylacetylides present inconveniently large problems for X-ray analysis. I have carried out complete structure determinations in the case of the three complexes phenylethynyl(trimethylphosphine)-copper(I), $Me_3PCuC{\equiv}CPh$, phenylethynyl(trimethylphosphine)-silver(I), $Me_3PAgC{\equiv}CPh$, and phenylethynyl(isopropylamine)-gold(I), $^{i}PrNH_2AuC{\equiv}CPh$. The three structures are each expected to be representative of their particular class. For instance, all the phosphine complexes of phenylethynyl-copper(I) are expected to have structures similar to that of the trimethylphosphine complex.

During the course of the study, the unit cell dimensions and space groups of several of the phosphine and amine complexes of the ethynyl compounds were obtained, and it is convenient to list them at this point. (Table III). Some of the compounds will be referred to at a later stage.

Compound	Space Group	a	b	c	β	Z
$Me_3PCuC{\equiv}CPh$	Pbca	12.689	17.252	21.393		16
$Et_3PCuC{\equiv}CPh$	$P2_1/c$	15.6	17.3	24.0	95.7°	16
$Me_3PCuC{\equiv}CCMe_3$	$P2_1/c$	12.5	9.2	21.5	106.5°	8
$Me_3PCuC{\equiv}CC(CH_3)CH_2$	$P2_1/c$	8.9	17.5	14.5	109.2°	8
$Me_3PCuC{\equiv}CC{\equiv}CPh$	$P2_1/c$	11.3	23.7	24.3	90.4°	16
$[Et_3P]_3[CuC{\equiv}CC{\equiv}CPh]_2$	Pbca	14.85	20.82	26.77		8
$Me_3PAgC{\equiv}CPh$	$C2/c$	11.50	20.58	12.12	123.4°	8
$^{i}PrNH_2AuC{\equiv}CPh$	Pccn	17.924	17.149	7.222		8
$^{n}C_5H_{11}NH_2AuC{\equiv}CPh$	$P2_1/c$	22.00	16.99	7.18	98.0°	8
$^{n}C_9H_{19}NH_2AuC{\equiv}CPh$	Pccn	29.15	16.99	7.19		8

a,b,c in Å.
Z is the number of formula units in the unit cell

TABLE III. Space Groups and Unit Cell Dimensions of some Group IB Ethynyl Complexes.

THE DETERMINATION OF THE CRYSTAL STRUCTURE OF PHENYLETHYNYL(TRIMETHYLPHOSPHINE)COPPER(I)

INTRODUCTION

Phenylethynyl(trimethylphosphine)copper(I) was chosen for structure determination mainly on the grounds of stability. Crystals of this compound gave good reflections after several weeks exposure to air, whereas crystals of the corresponding t-butyl and isopropenyl compounds decomposed to powder after a few days and after a few hours respectively. The triethylphosphine complex of phenylethynylcopper(I) was not considered, as the asymmetric unit contained four formula units whereas in the trimethylphosphine complexes, the asymmetric unit contained two formula units.

EXPERIMENTAL

CRYSTALS

A sample of phenylethynyl(trimethylphosphine)copper(I) had been crystallised as yellow needles from toluene, and had been kept stored under nitrogen for some months previous to the investigation. The needles were reduced to crystals roughly cylindrical in shape, and 0.2-0.3 mm. in diameter, by rolling them around on a watch glass in benzene.

The benzene acted as a solvent, and also facilitated the removal of surface layers of decomposed material with which the original crystals had become coated. During the time in which the crystals were used each again became coated with a layer of decomposition product, but this appeared to protect the rest of the crystal, as there was no noticeable effect on the intensities of the X-ray reflections.

CRYSTAL DATA

Phenylethynyl(trimethylphosphine)copper(I)

$Me_3PCuC{\equiv}CPh$ M = 240.77

Orthorhombic: needles elongated in the direction of the 'a' axis.

a = 12.689; b = 17.252; c = 21.393 Å.

U = 4682 Å.^{3} Z = 16 formula units. D_m = 1.34;

D_x = 1.366 gm/cm.^{3} F(000) = 1984 electrons.

Absorption coefficient for MoKα radiation, μ = 20 cm.$^{-1}$

Reflections observed:

hkl	No conditions
hk0	h = 2n
0kl	k = 2n
h0l	l = 2n.

The space group is therefore uniquely determined as Pbca, (D_{2h}^{15}), no. 61 in the International Tables for Crystallography. The unit cell dimensions were obtained from three zero-layer precession photographs taken using MoKα radiation.

(λ = 0.7107Å.) The dimensions given are each the mean of two values obtained from different photographs, and the differences between the two values for 'a', 'b', and 'c' were 0.004, 0.010, and 0.015Å. respectively. The statistical standard deviations in the cell dimensions were 0.003-0.004Å., but if systematic errors are included, the uncertainty is probably of the order of 0.1%.

COLLECTION OF INTENSITIES

Partial three-dimensional data were recorded photographically using Zr-filtered molybdenum radiation. (MoKα, λ = 0.7107Å.) The precession method was used for layers with h = 0-2, k = 0-4, and l = 0, and the equi-inclination Weissenberg technique for layers with h = 3-7. A series of timed exposures was taken for each layer. The intensities were estimated visually, by comparison with a calibrated scale. On average, the intensity of each reflection was estimated on two films within each series.

The intensities on the upper layer Weissenberg photographs were corrected for spot extension using empirical length-$\S$ curves drawn separately for each layer. The intensities of the contracted spots were not estimated. The usual Lorentz and polarisation factors were applied, but no correction was

made for absorption. 1451 independent intensities were measured, 396 of them on two layers, 4 of them on three.

The structure factors were placed on the same relative scale using scale factors derived by a least squares method from the common reflections. An account of this method, and a comparison of the scale factors used with those obtained by two alternative least squares methods, are given in Appendix A.

STRUCTURE DETERMINATION

The atomic coordinates were found by heavy atom techniques, and refined by the method of least squares. The analysis was complicated by the disorder associated with one of the trimethylphosphine groups.

HEAVY ATOM POSITIONS.

The positions of the copper atoms were first found by inspection of the Patterson function in projection along the 'a' and the 'b' axes. The coordinates obtained were:

	x/a	y/b	z/c
Cu1	-0.013	0.053	0.049
Cu2	0.156	0.126	0.039

These coordinates imply that the two copper atoms and the two related by the centre of symmetry at the origin form a zig-zag chain. The copper-copper distances in the chain were very short, (2.5, 2.7, 2.5Å.) and the structure is therefore tetrameric.

The three-dimensional Patterson function was calculated with the intention of confirming the coordinates of the copper atoms and of locating the phosphorus atoms. The function evaluated was:

$$P(uvw) = \frac{8}{V}\sum_{0}^{h}\sum_{0}^{k}\sum_{0}^{l} \omega(hkl)\left|F(hkl)\right|^2 \cos 2\pi hu \cos 2\pi kv \cos 2\pi lw$$

and 'u' was calculated at intervals of 0.32Å., (a/40), 'v' at intervals of 0.22Å., (b/60), 'w' at intervals of 0.18Å, (c/120). The coefficients $\left|F(hkl)\right|^2$ were weighted with the function $w(hkl) = \exp(18\sin^2\theta)$, $= \exp(9.1\sin^2\theta/\lambda^2)$. The sum of the squares of the scattering factors of all the atoms in the structure falls off with $\sin\theta$ approximately as $\exp(-5\sin^2\theta/\lambda^2)$ and an analysis of the intensities of the (hk0) and (0kl) reflections by the method of Wilson (1942) gave an estimated overall temperature factor, B, of about 3Å.^{2} The weighted coefficients were intended to be intermediate between those that would be given by a set of stationary atoms, $w = \exp(6\sin^2\theta/\lambda^2)$ and those given by a set of stationary point atoms, $w = \exp(11\sin^2\theta/\lambda^2)$.

Inspection of the three Harker sections in the Patterson function due to the screw axes located the copper atoms, and their positions were determined more accurately by a least squares analysis of the coordinates of the peaks corresponding to the 22 independent copper-copper vectors in the unit cell. The two atoms shifted only 0.01 and 0.02Å. from these positions during the subsequent refinement. The coordinates of the phosphorus atoms were found by superposition methods. (Robertson, 1951). The Patterson function was set down with its origin in turn at each of the copper positions $\pm (x_{Cu2}, y_{Cu2}, z_{Cu2})$. A 'minimum' function was plotted by taking the lesser values of the super-imposed functions at every point. There were three peaks in the minimum function that could have arisen from phosphorus atoms. An unambiguous choice was made by carrying out a second superposition, using the coordinates of Cu1. The phosphorus positions were checked by locating each of the peaks corresponding to the 24 independent copper-phosphorus vectors in the original Patterson function. The heavy atom coordinates at this stage were:

	x/a	y/b	z/c	x(Å)	y(Å)	z(Å)
Cu1	-0.0065	0.0515	0.0465	-0.08	0.89	0.99
Cu2	0.1555	0.1272	0.0398	1.97	2.19	0.85
P1	0.2850	0.0683	0.0916	3.62	1.18	1.96
P2	0.1725	0.2433	-0.0042	2.19	4.20	-0.09

LIGHT ATOM POSITIONS

A first set of structure factors was calculated using the coordinates of the copper and phosphorus atoms. The value of the reliability index, $R = \frac{\Sigma||F_o|-|F_c||}{\Sigma|F_o|}$ for these atoms alone was 0.32. The observed structure factors were allotted signs based on the heavy atom contributions, and a three-dimensional Fourier synthesis was calculated on the same coordinate grid as the Patterson function. The function evaluated was:

$$\rho(xyz) = {}^{h+k=2n}\,4/V \sum_{0}^{h}\sum_{0}^{k}\sum_{-l}^{l} F(hkl)\cos 2\pi hx \cos 2\pi(ky+lz)$$

$$+ {}^{h+k=2n+1}\,4/V \sum_{0}^{h}\sum_{0}^{k}\sum_{-l}^{l} F(hkl)\sin 2\pi hx \sin 2\pi(ky+lz)$$

where $\rho(xyz)$ is the electron density at the point (xyz).

The electron density showed peaks at the positions of the copper and phosphorus atoms, with heights 45 and 18 e/Å.^{3} respectively. The positions of the phenylethynyl carbon atoms were clearly recognised, and all the peaks were resolved, except that the two representing the ethynyl carbon atoms C9 and C10 overlapped considerably. The peak heights ranged from 3.3-6.0 e/Å.^{3}, with an average height of 4.6 e/Å.^{3} There were eight peaks near the phosphorus atoms with

heights ranging from 3.0-4.5 e/Å.^{3}, and several other smaller ones. It was not possible to place the methyl carbon atoms with confidence.

A new set of structure factors was calculated on the basis of the heavy atoms and the phenylethynyl carbon atoms, except that coordinates were not assigned to the atoms C9 and C10. Agreement with the observed structure factors improved to R = 0.25. The signs were used to calculate a second Fourier synthesis. From this synthesis, coordinates could be obtained for the ethynyl carbon atoms C9 and C10, and the average height of the peaks corresponding to the phenylethynyl carbon atoms was now 5.8 e/Å.^{3} There were seven unassigned peaks with heights of more than 4 e/Å.^{3}, and six of these were designated as methyl carbon atoms. The average peak height for these atoms was 4.7 e/Å.^{3} The unassigned peak lay in a position which ruled out the possibility of it representing a carbon atom.

The coordinates of all the atoms except hydrogen had now been obtained, and they were refined through a cycle of least squares. The value of R for structure factors calculated during this cycle was 0.176. In the two previous structure factor calculations, the temperature factor U = 0.04 Å.^{2} had been used for all the atoms, where $U = B/8\pi^2$. In this case, the temperature factors used for the copper,

phosphorus, phenylethynyl carbon, and methyl carbon atoms were respectively 0.048, 0.040, 0.065, and 0.035$\mathring{A}^2$.

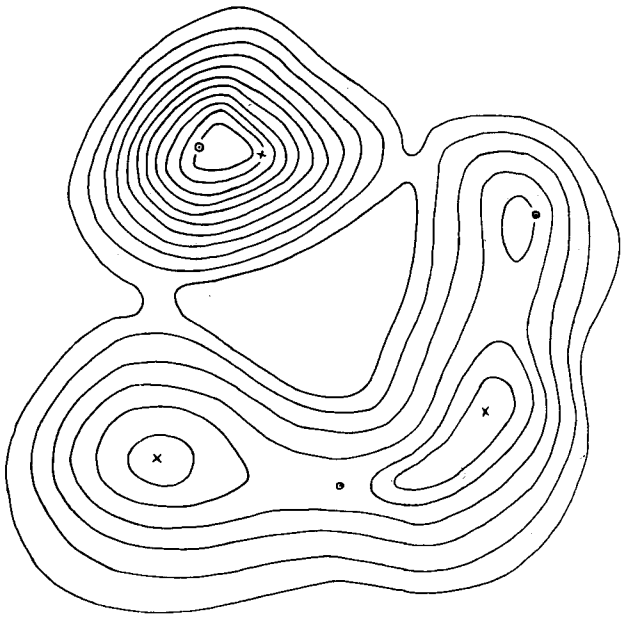
A third Fourier synthesis was calculated, and this showed features which suggested that the methyl groups attached to P2 were disordered. The peaks representing the carbon atoms of this phosphine group were more smeared out than the peaks due to the other methyl carbon atoms, and the peak heights were appreciably less. It was not really clear whether the disorder was due to free rotation about the copper-phosphorus bond, or whether it was due to two preferred orientations of the phosphine group.

REFINEMENT, AND TREATMENT OF THE DISORDERED PHOSPHINE GROUP

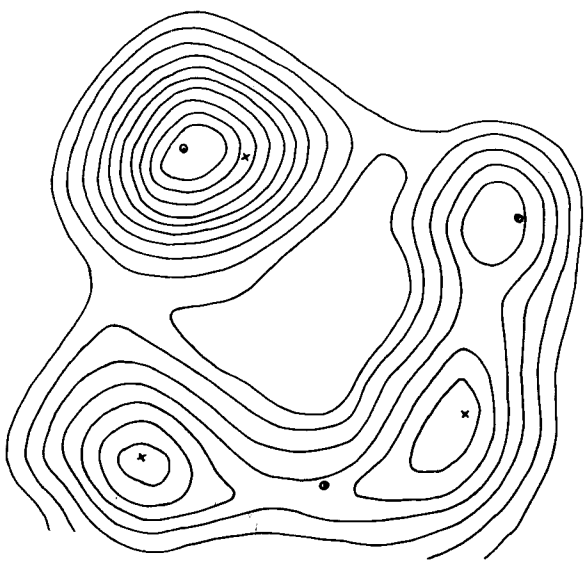
The refinement was at first continued isotropically, and the three disordered carbon atoms were replaced by six atoms with a statistical weight of a half. The half atoms were given positions consistent with the electron density distribution, corresponding roughly to two orientations of the phosphine group, related by a rotation of 40° about the copper-phosphorus bond. The coordinates and the temperature factors of the half atoms were refined through a cycle of least squares, with parameters for all the other atoms exactly

the same as in the previous cycle. The value of R dropped 0.007 to 0.169, so that there was at least some improvement in using six, rather than three, sites for the carbon atoms attached to P2. After a further cycle of refinement, two of the half atoms were only 0.7Å. apart, and they were only 0.6Å. apart after the next cycle, even though their coordinates had been altered so as to space them apart in between the two cycles. There was very little improvement in the value of R during the last cycle, although the mean coordinate shift of 0.028Å. was still large. The two half atoms were alarmingly close to one another while the other four were nearly equally spaced, and it was felt that the disorder should be investigated more fully before further refinement of the structure was undertaken.

An (F_o-F_c) synthesis was calculated, where the F_c's were based on all the atoms, except that the contributions from the disordered carbon atoms were omitted. The electron density in the plane of the disordered atoms is shown in Fig. 1a. The half atoms which had been very close to one another appear as a single peak of height 2.6 e/Å.^{3}, and the other four half atoms as small bulges on a semi-circular ridge in the electron density, at a height of 1.2-1.5 e/Å.^{3} One of the small peaks is just off the section and is not shown. The large peak is separated from the ridge by regions where the electron density is less than 0.5 e/Å.,^{3} and the discontinui-



a



b

Electron Density in the Plane of the Disordered Atoms

a First $(F_O - F_C)$ synthesis b Second $(F_O - F_C)$ synthesis

Contours at intervals of 0·2 e/A^3, starting at 0·4 e/A^3

× Final positions of atoms weighted three-fifths

⊙ " " " " " two-fifths

ties would appear to be significant, since the standard deviation in the electron density is estimated to be 0.25 e/Å^3. (Cruickshank 1949). The distribution of the electron density, and the positions of the maxima, are consistent with the results of the least squares refinement, and although the precise nature of the disorder is not clear, it does seem that it is not due to free rotation about the copper-phosphorus bond.

An attempt was made to represent the electron density distribution in the region of the disordered carbon atoms, by using only three atoms, with anisotropic temperature factors. After three cycles of refinement using anisotropic temperature factors for the copper, phosphorus, and all the methyl carbon atoms, the value of R was 0.089 and the mean coordinate shift, not including shifts in the methyl carbon atoms attached to P2, was 0.0060Å. The vibration amplitudes for the disordered atoms were very large however, and still increasing, and it appeared that the three atoms were not adequate to represent the electron density. The three atoms were replaced by six atoms in the positions obtained from the isotropic refinement. On the basis of the electron density distribution, and also of the temperature factors obtained during the isotropic refinement, three of the six atoms were given a weight of 2/3, and the other three a

weight of 1/3. (At a later stage, weights of 3/5 and 2/5 were used). After four more cycles during which all the atoms were given anisotropic temperature factors, the mean coordinate shift not including the methyl carbon atoms on P2 was 0.0026Å., and the value of R was 0.079,

It was later discovered that the scattering factors used for the phosphorus atoms were incorrect, as the values of $\sin\theta/\lambda$ had been taken as if they were expressed in reciprocal Ångström units, whereas the original authors of these scattering factors express $\sin\theta/\lambda$ in atomic units. (Tomiie and Stam, 1958). There is a factor of nearly two between the two units, and the main effect would be for the temperature factors for the phosphorus atoms to be calculated too small. Five further cycles of refinement using an alternative scattering-factor curve for the phosphorus atoms were required before shifts in all the atomic coordinates and temperature parameters became no longer significant. The value of R was now 0.074, and the mean coordinate shift for all the atoms except the methyl carbon atoms on P2 was 0.0016Å., with a maximum shift of 0.0076Å. No parameter shift was more than a half of the corresponding standard deviation. The introduction of the correct scattering curve for the phosphorus atoms increased their mean temperature factor, as expected, but also caused appreciable shifts in the coordinates of the light atoms.

Thirteen of the carbon atoms were moved by more than 0.01Å., and one by as much as 0.035Å.

During these last stages of refinement, part of a second (F_o-F_c) synthesis was calculated, where the F_c's were again structure factors with contributions from the disordered carbon atoms omitted. A section in the mean plane of the disordered atoms is reproduced in Fig. 1b. The electron density in this plane is almost identical with that calculated earlier, and this establishes that the previous electron density distribution had not been associated with the use of the incorrect scattering-factor curve for phosphorus. The standard deviation in the electron density was now calculated to be 0.15 $e/Å.^3$

The analysis of the structure is summarised in Table I. The second to the fifth columns in the table indicate whether isotropic or anisotropic temperature factors were assigned for the various groups of atoms in the structure factor/least squares refinement. The sixth column shows whether three or six atoms were used to represent the disordered carbon atoms, C20-22, and the seventh gives the factor R at each stage. The eighth column gives R', which is the quantity minimised in the least squares refinement, and is given by:

$$R' = \sum w||F_o| - |F_c||^2 \Big/ \sum w|F_o|^2$$

where w represents a weighting coefficient. The table also shows the points at which the various F_o and (F_o-F_c) syntheses were calculated.

The weighting schemes used in the refinement were:

for steps 3-4, constant weights,	w=0.0625	
5-6, and 8	w=0.03125	$K\|F_o\| < 24$
	w=0.0625	$24 \leq K\|F_o\| \leq 96$
	$w=0.0625 \times 96/K\|F_o\|$	$K\|F_o\| > 96$
9-17, and 19-20	w=0.024(0.012 in the final cycle)	$K\|F_o\| < 32$
	$w=1/A+B(K\|F_o\|)+C(K\|F_o\|)^2$	$KF_o \geq 32$

(A=15, B and C varied)

From step 13 onwards, these weights were halved for planes with $\sin\theta/\lambda$ less than 0.1. K is a factor introduced for scaling, and its value was always about 1.1. The values of the constants A, B, C, and K for the final cycle were A = 15, B = 1, C = 0.0085, and K = 1.113.

The mean overall value of $w \times \left||F_o| - |F_c|\right|^2 = w|\Delta|^2$ in the final cycle was 0.31. For the estimated standard deviations to be theoretically correct, $w|\Delta|^2$ should not vary systematically over the observed data. The variation of

TABLE I. Structure Determination and Refinement of $(Me_3PCuC{\equiv}CPh)_4$

Step No.	SF/LS Refinement (isotropic or anisotropic) Cu,P	Cl-16	C17-19	C20-22	No. atoms used for C20-22	R	R'	
1.(SF only)	Iso	-	-	-	-	0.32		Four.1.
2.(SF only)	Iso	Iso	-	-	-	0.25		Four.2.
3.	Iso	Iso	Iso	Iso	3	0.176	0.0309	Four.3.
4.	[a]Iso	[a]Iso	[a]Iso	Iso	6	0.169	0.0287	
5.	Iso	Iso	Iso	Iso	6	0.144	0.0267	
6.	Iso	Iso	Iso	Iso	6	0.140	0.0244	
7.(SF only)	Iso	Iso	Iso	-	-			$(F_o-F_c)1$
8.	Anis	Iso	Anis	Anis	3	0.128	0.0211	
9.	Anis	Iso	Anis	Anis	3	0.101	0.0131	
10.	Anis	Iso	Anis	Anis	3	0.089	0.0104	
11.	[a]Anis	[a]Iso	[a]Anis	Anis	6	0.086	0.0101	
12.	Anis	Anis	Anis	Anis	6	0.086	0.0099	
13.	Anis	Anis	Anis	Anis	6	0.081	0.0080	
14.	Anis	Anis	Anis	Anis	6	0.079	0.0076	
Introduction of correct phosphorus scattering curve								
15.	Anis	[a]Anis	Anis	Anis	6	0.152	0.0311	
16.	Anis	Anis	Anis	Anis	6	0.086	0.0150	
17.	Anis	Anis	Anis	Anis	6	0.076	0.0091	
18.(SFonly)	Anis	Anis	Anis	-	-			$(F_o-F_c)2.$
19.	Anis	Anis	Anis	Anis	6	0.074	0.0086	
20.	Anis	Anis	Anis	Anis	6	0.074	0.0084	

a: these atoms not refined.

$w|\Delta|^2$ with $|F_o|$, and with $\sin\theta/\lambda$ is given in Table II. The values of $w|\Delta|^2$, increase slightly for low values of $\sin\theta/\lambda$, and for large values of $|F_o|$, but it was not felt that this was important.

TABLE II. Weighting Analysis after the Final Cycle.

$K\|F_o\|$	Mean $w\|\Delta\|^2$	No. of Planes
8-16	0.45	6
16-32	0.30	373
32-64	0.30	615
64-128	0.26	334
128-	0.46	123

$\sin\theta/\lambda$	Mean $w\|\Delta\|^2$	No. of Planes
0-0.1	0.78	17
0.1-0.2	0.61	114
0.2-0.3	0.31	307
0.3-0.4	0.22	470
0.4-0.5	0.29	384
0.5-0.6	0.33	151
0.6-	0.04	8

During the final cycle, structure factors were calculated for the unobserved planes, and it was found that for only 73

out of 1020 were the calculated structure factors greater than the maximum expected value, F_{min}, and for only 27 of these were they greater than $1.2F_{min}$. The parameter shifts calculated by including the unobserved planes greater than F_{min} in the last cycle of the refinement differed from the shifts due to the observed planes only, by less than 0.001Å. for the coordinate shifts, and by less than 0.003Å.^{2} for the shifts in the vibration parameters. Since their effect was so slight, the unobserved planes were not included in the refinement, as it is difficult to decide how these planes should be weighted. The final parameters are based on the observed planes only.

The shifts in the coordinates in the final cycle are listed in Table III, and the shifts in the anisotropic thermal parameters in Table IV. The parameters $U_{11}...U_{13}$ are defined by the expression:

$$f = f_o \exp.-2\pi^2\left[h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+hka^*b^*U_{12}+klb^*c^*U_{23}+hla^*c^*U_{13}\right]$$

where f_o is the atomic scattering factor, for an atom at rest. The final values of the atomic coordinates and their estimated standard deviations are given in Table V, and the anisotropic temperature parameters and their standard deviations in Table VI. In these, and in all subsequent tables, C20a, C21a, and C22a refer to the carbon atoms with weights 3/5, and C20b, C21b,

and C22b refer to the carbon atoms with weights 2/5. Table V also gives the root mean square value of the standard deviation for each atom. The structure factors calculated during the final cycle are given in Table VII.

The sources for the scattering factors used were:

for carbon, Berghuis et al. (1955),

for copper(O), Berghuis et al./Thomas and Umeda, (1957), as given in the library of 'f' curves issued by by the Leeds group,

for phosphorus, Freeman and Watson, (1961).

TABLE III. Shifts in the Atomic Coordinates during the Final Cycle.

(in Å)

Atom	x	y	z
Cu1	0.0001	0.0000	0.0002
Cu2	0.0003	0.0001	0.0001
P1	-0.0003	0.0001	-0.0001
P2	0.0000	0.0012	-0.0001
C1	0.0006	0.0010	0.0014
C2	0.0034	-0.0005	-0.0005
C3	0.0025	0.0000	-0.0009
C4	0.0012	0.0013	-0.0013
C5	0.0038	0.0005	0.0028
C6	-0.0025	-0.0013	-0.0029
C7	0.0041	0.0010	-0.0015
C8	-0.0003	-0.0013	-0.0002
C9	0.0020	0.0007	-0.0017
C10	0.0017	-0.0002	-0.0039
C11	0.0016	-0.0002	-0.0017
C12	0.0026	-0.0041	-0.0009
C13	-0.0003	-0.0030	0.0005
C14	0.0023	0.0002	-0.0027
C15	-0.0013	0.0076	0.0063
C16	-0.0011	0.0022	-0.0021
C17	0.0002	-0.0065	0.0010
C18	0.0018	0.0044	-0.0019
C19	-0.0016	-0.0023	0.0010
C20a	-0.0065	0.0106	-0.0032
C21a	0.0022	-0.0069	-0.0047
C22a	-0.0054	-0.0160	0.0004
C20b	0.0160	-0.0024	0.0013
C21b	0.0119	-0.0061	0.0026
C22b	0.0195	0.0000	0.0209

Only half of the above shifts were applied for the last six atoms.

TABLE IV. Shifts in Anisotropic Temperature Parameters During the Final Cycle (in $A.^2$)

Atom						
Cu1	-0.0002	-0.0001	0.0000	-0.0000	-0.0002	-0.0002
Cu2	-0.0001	-0.0000	-0.0001	0.0001	-0.0001	-0.0003
P1	0.0004	0.0004	0.0007	0.0001	0.0003	-0.0002
P2	0.0005	0.0006	0.0001	0.0008	-0.0008	-0.0008
C1	-0.0017	0.0007	0.0012	0.0017	0.0003	0.0000
C2	-0.0026	-0.0000	0.0007	0.0012	-0.0009	0.0004
C3	0.0007	0.0009	-0.0009	0.0041	-0.0000	0.0000
C4	-0.0000	0.0004	-0.0015	0.0024	-0.0053	0.0012
C5	0.0027	-0.0019	0.0003	0.0019	-0.0025	0.0001
C6	-0.0015	0.0002	0.0017	0.0004	0.0001	0.0002
C7	0.0026	0.0019	-0.0002	-0.0010	-0.0038	0.0005
C8	0.0010	-0.0021	-0.0001	-0.0004	-0.0001	-0.0020
C9	-0.0000	-0.0013	0.0001	-0.0002	-0.0000	-0.0006
C10	0.0007	-0.0003	-0.0015	0.0031	0.0000	0.0008
C11	-0.0019	0.0014	-0.0005	0.0013	-0.0018	0.0015
C12	-0.0022	-0.0022	0.0016	0.0015	-0.0011	0.0011
C13	-0.0012	-0.0001	-0.0002	0.0030	-0.0020	0.0021
C14	0.0006	0.0093	-0.0026	0.0022	0.0044	0.0002
C15	0.0032	-0.0046	0.0005	-0.0010	-0.0035	0.0001
C16	0.0023	-0.0011	-0.0018	-0.0041	0.0041	0.0021
C17	0.0015	0.0007	-0.0020	-0.0018	0.0048	-0.0041
C18	0.0026	-0.0033	0.0008	-0.0021	-0.0023	0.0055
C19	0.0013	0.0003	0.0003	0.0009	-0.0038	-0.0003
C20a	-0.0008	-0.0014	0.0047	0.0041	-0.0060	-0.0037
C21a	0.0301	0.0005	-0.0054	-0.0218	0.0084	-0.0108
C22a	-0.0031	0.0074	-0.0122	-0.0001	-0.0050	-0.0029
C20b	0.0213	0.0113	0.0107	0.0300	-0.0068	-0.0082
C21b	0.0005	0.0010	-0.0023	0.0036	-0.0048	-0.0028
C22b	-0.0197	-0.0080	0.0071	0.0175	- 0.0073	-0.0053

Only half of the above shifts were applied for the last six atoms.

TABLE V. $(Me_3PCuC{\equiv}CPh)_4$: Final Values of the Atomic Coordinates (in Å.) and Standard Deviations (in 10^3 Å.)

Atom	x	y	z	Mean (e.s.d.)
Cu1	-0.093 (2)	0.888 (2)	1.008 (2)	0.002
Cu2	1.972 (2)	2.199 (2)	0.857 (2)	0.002
P1	3.594 (4)	1.167 (4)	2.003 (5)	0.004
P2	2.222 (6)	4.174 (5)	-0.130 (6)	0.005
C1	0.281 (17)	2.315 (15)	2.295 (17)	0.016
C2	0.361 (15)	3.165 (15)	3.163 (17)	0.016
C3	0.429 (16)	4.185 (13)	4.189 (15)	0.015
C4	-0.727 (17)	4.488 (15)	4.927 (16)	0.016
C5	-0.638 (20)	5.471 (19)	5.928 (18)	0.019
C6	0.522 (20)	6.118 (16)	6.161 (18)	0.018
C7	1.668 (18)	5.845 (16)	5.421 (17)	0.017
C8	1.627 (15)	4.861 (17)	4.451 (17)	0.016
C9	1.347 (15)	0.688 (13)	-0.470 (15)	0.015
C10	1.839 (16)	0.114 (14)	-1.449 (17)	0.016
C11	2.872 (15)	-0.091 (16)	-2.474 (14)	0.015
C12	2.811 (18)	-1.187 (20)	-3.334 (17)	0.019
C13	3.904 (20)	-1.311 (25)	-4.288 (18)	0.021
C14	4.918 (19)	-0.413 (25)	-4.317 (18)	0.021
C15	4.934 (21)	0.679 (25)	-3.458 (18)	0.021
C16	3.946 (19)	0.824 (20)	-2.500 (17)	0.019
P1 C17	3.020 (28)	-0.313 (19)	2.895 (21)	0.023
P1 C18	4.963 (21)	0.503 (23)	1.007 (24)	0.023
P1 C19	4.494 (20)	2.100 (23)	3.313 (19)	0.021
P2 C20a	1.010 (44)	5.460 (28)	0.734 (45)	0.039
P2 C21a	1.579 (57)	4.269 (34)	-1.073 (38)	0.044
P2 C22a	3.647 (29)	5.221 (35)	0.093 (47)	0.038
P2 C20b	0.897 (58)	5.051 (44)	-0.787 (78)	0.061
P2 C21b	3.274 (51)	4.123 (41)	-1.968 (38)	0.044
P2 C22b	3.664 (83)	5.163 (44)	0.692 (61)	0.065

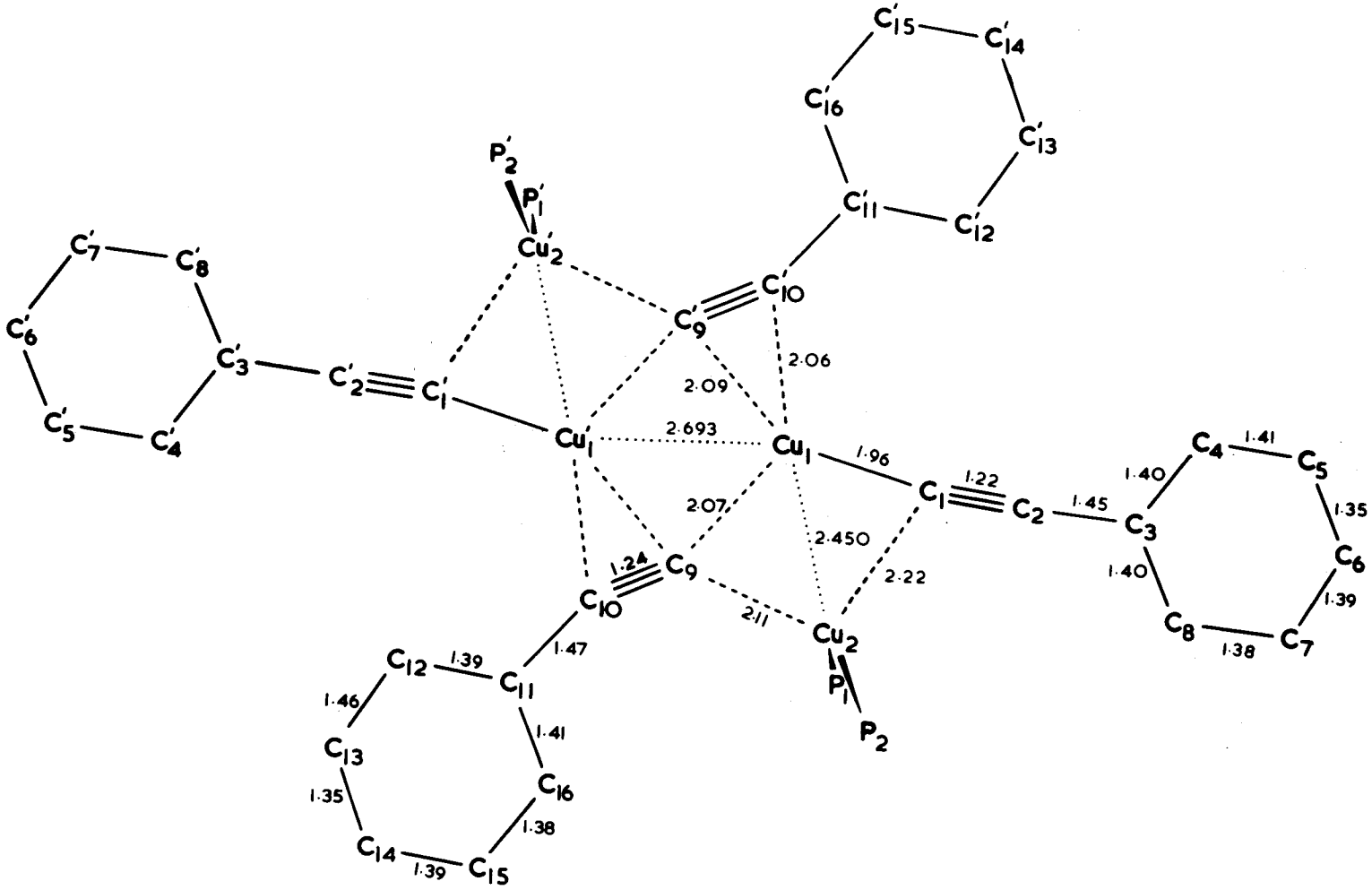
TABLE VI. $(Me_3PCuC{\equiv}CPh)_4$: Final Values of the Anisotropic Temperature Parameters, (in Å^2), and their Standard Deviations. (in 10^3 Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Cu1	0.052(1)	0.040(1)	0.071(1)	-0.004(2)	-0.031(2)	-0.007(2)
Cu2	0.059(1)	0.038(1)	0.087(1)	-0.011(2)	-0.007(2)	-0.013(3)
P1	0.061(3)	0.051(2)	0.066(3)	0.019(5)	-0.003(5)	0.011(5)
P2	0.097(4)	0.044(2)	0.107(4)	-0.028(6)	0.019(5)	-0.070(7)
C1	0.075(12)	0.052(9)	0.087(12)	0.032(19)	-0.037(18)	-0.031(21)
C2	0.041(10)	0.060(9)	0.095(13)	0.001(17)	-0.028(19)	-0.008(19)
C3	0.089(12)	0.033(7)	0.062(10)	0.009(17)	-0.044(14)	-0.023(18)
C4	0.082(12)	0.059(10)	0.073(12)	0.010(21)	-0.043(17)	0.027(21)
C5	0.109(16)	0.093(13)	0.074(12)	-0.045(27)	-0.064(21)	0.072(24)
C6	0.110(17)	0.053(10)	0.087(13)	-0.040(22)	-0.014(18)	-0.021(24)
C7	0.087(13)	0.075(10)	0.061(10)	-0.042(21)	-0.025(19)	-0.022(21)
C8	0.050(10)	0.072(11)	0.082(12)	-0.021(18)	-0.050(19)	-0.057(19)
C9	0.056(10)	0.041(8)	0.066(10)	-0.021(16)	-0.013(15)	-0.002(16)
C10	0.061(10)	0.048(9)	0.078(12)	-0.005(17)	0.002(16)	-0.026(19)
C11	0.055(11)	0.081(11)	0.043(9)	0.045(19)	0.031(17)	0.001(16)
C12	0.079(14)	0.100(14)	0.080(13)	0.036(25)	-0.054(23)	0.012(21)
C13	0.075(13)	0.164(21)	0.072(13)	0.011(31)	0.012(27)	-0.008(22)
C14	0.065(12)	0.191(22)	0.064(12)	-0.005(29)	0.110(27)	0.000(21)
C15	0.101(15)	0.155(21)	0.060(11)	-0.009(31)	0.064(26)	-0.021(23)
C16	0.077(12)	0.114(15)	0.070(12)	-0.035(26)	0.046(24)	0.019(20)
C17	0.175(23)	0.072(13)	0.100(15)	0.019(29)	0.017(24)	0.112(33)
C18	0.096(15)	0.128(18)	0.127(18)	0.114(29)	-0.063(30)	0.077(29)
C19	0.085(14)	0.131(17)	0.093(14)	0.018(28)	-0.087(27)	-0.015(25)
C20a	0.164(40)	0.033(15)	0.209(44)	0.066(41)	-0.013(44)	0.056(72)
C21a	0.382(71)	0.064(21)	0.085(25)	-0.112(69)	0.041(39)	-0.103(76)
C22a	0.040(18)	0.107(26)	0.242(47)	-0.068(38)	0.158(60)	-0.129(51)
C20b	0.132(48)	0.052(27)	0.330(94)	0.144(65)	0.186(87)	-0.201(115)
C21b	0.143(43)	0.065(27)	0.045(24)	-0.042(60)	0.020(44)	0.054(58)
C22b	0.282(91)	0.044(26)	0.159(55)	-0.203(86)	0.056(63)	-0.062(113)

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The complex occurs in the crystal as discrete tetramers, $(Me_3PCuC{\equiv}CPh)_4$. These are centrosymmetric, and nearly flat, apart from the phosphine groups. A diagram of the molecule projected onto the mean plane through the copper atoms and the phenylethynyl carbon atoms is given in Fig. 2. The four copper atoms are arranged in a zig-zag chain, with the centre of symmetry between Cu1 and Cu1' Two phosphine groups are bound to the terminal copper atom Cu2, one of them above, and one below the mean plane of the molecule, and the inner copper atom, Cu1, is not bonded to a phosphorus atom. Cu1 is bonded to the ethynyl carbon atom C1, with the ethynyl group in the 'end-on' position, and is $\sigma\pi$-bonded to the atoms C9' and C10', where the ethynyl group is 'side-on' to the copper atom. C9' also comes very close to the copper atoms Cu1' and Cu2', and it appears that the ethynyl groups (C9, C10) and (C9', C10') are each bonded to three copper atoms.

Around Cu1, the four atoms C1, Cu2, C9, and Cu1', together with the point mid-way between C9' and C10', (which will be written as C9,10') are situated at five vertices of a distorted hexagon. The four angles subtended at Cu1 are respectively 59°, 55°, 50° and 67°, and none of the atoms is more than 0.06Å. from the mean plane of the hexagon. The



$(Me_3PCuC{\equiv}CPh)_4$

fig 2 36a

four atoms Cu1, C1, Cu2, and C9 are more accurately coplanar, however, and the equation of the mean plane through these atoms is:

$$0.4666\ x - 0.6724\ y + 0.5747\ z = -0.0840$$

where x, y, and z are in Å., and are referred to the crystal axes. The distances of the atoms Cu1, C1, Cu2, and C9 from this plane are respectively 0.023, -0.021, 0.018, and -0.020Å. Cu1' and the point C9,10' are at distances of 0.145 and 0.162 Å. from the plane, and so do not lie in the plane through the other four atoms. The atoms C1 and C9, with the point C9,10' are arranged approximately trigonally around Cu1, with angles C1-Cu1-C9, C9-Cu1-C9,10' and C9,10'-Cu1-C1 of 114, 117, and 130° respectively. Cu1 lies at a distance of 0.02Å. from the plane through C1, C9, and C9,10', and the atoms are coplanar within experimental error.

Around Cu2, the atoms P1, P2, and Cu1 are arranged approximately trigonally, the angles P1-Cu2-P2, P2-Cu2-Cu1, and Cu1-Cu2-P1 being respectively 124, 127, and 109°. Cu2 lies at a distance of 0.04Å. from the plane through the other three atoms. However the four atoms P1, P2, C1, and C9 are in a distorted tetrahedral arrangement about Cu2, with the angles P1-Cu2-P2 and C1-Cu2-C9 equal to 124° and 103°, the one considerably greater than, and the other rather less than,

the tetrahedral angle of 109°. The plane of P1, P2, and Cu2 is very nearly at right angles to the plane through the atoms C1, C9, and Cu2, but the positions of the phosphorus atoms are such that the P-Cu-C angles are a little less for P1 than for P2.

The copper-copper distances are very short, with Cu1-Cu2 = 2.450Å., and Cu1-Cu1' = 2.693 Å. One of these distances is less than the Cu-Cu separation in the metal, 2.556Å., and such short distances would suggest bonding between the copper atoms. However the coordination of the copper atoms is difficult to describe if copper-copper bonding is included. Apart from any copper-copper bonding, Cu1 is trigonally coordinated to the atoms C1 and C9, and to the ethynyl group (C9'-C10'), while Cu2 is tetrahedrally coordinated to P1, P2, C1, and C9. This does, of course assume that there is bonding between the atom Cu2 and the ethynyl carbon atoms C1 and C9, and between Cu1 and C9, and this point will be discussed at a later stage. The tetrahedral arrangement is the usual one for copper(I), but trigonal coordination occurs in the $Cu(CN)_2^-$ ion, (Cromer, 1957) and is thought to occur in some complexes of the type $(R_3P)_2CuI$, (Cass, Coates, and Hayter, 1954).

There are other compounds of copper(I) where the coordina-

tion is simple to describe, but where there are in addition short copper-copper distances which may imply bonding. In the tetrameric triethylarsine complex of copper(I) iodide, $\left[(C_2H_5)_3AsCuI\right]_4$, each copper atom is described as tetrahedrally coordinated to an arsenic atom and three iodine atoms, but there are in addition three Cu...Cu contacts of 2.60Å. (Wells, 1936) Also, in the structure of the methylisocyanide complex of copper(I) iodide, there are chains of copper atoms tetrahedrally coordinated to iodine atoms, and neighbouring copper atoms are 2.89Å. apart. (Fisher, Taylor, and Harding, 1960). In the crystal structure of diazoaminobenzene copper(I), (Brown and Dunitz, 1961) each copper atom is linearly coordinated to two nitrogen atoms, but there is also a Cu...Cu contact of 2.45Å. in a direction perpendicular to the direction of the bonds to the nitrogen atoms. Short metal-metal distances are reported in the crystal structures of some polymeric thiocarbamates of the coinage metals. (Hesse, 1961). In some of these cases, metal-metal bonding is assumed to occur, and in others, the close proximity of the metal atoms is said to be due to steric factors, as the atoms are bound to common groups. The situation is quite different in the case of copper(II) acetate dihydrate, (Niekerk and Schoening, 1953) where weak copper-copper bonding is known to occur. (Cu-Cu = 2.64Å.) Here the 3d-orbitals are not completely filled. Each copper

atom in the dimer is octahedrally coordinated, with the other copper atom occupying one of the octahedral positions.

The ethynyl carbon atoms C1 and C2 are coplanar with the phenyl carbon atoms C3-C8, and the equation of the mean plane through these eight atoms is

$$0.2524\,x - 0.6965\,y + 0.6717\,z = 0.0062$$

The distances of the atoms C1-C8 from the plane are respectively -0.004, 0.004, 0.001, -0.006, 0.004, 0.003, -0.012, and 0.010Å., and the mean distance is 0.006Å. The copper atoms Cu1 and Cu2 lie at distances 0.029 and -0.464Å. from the plane. The bond Cu1-C1 is therefore very nearly in the plane of the phenylethynyl group.

The ethynyl carbon atom C9 is not in the plane of the phenyl carbon atoms C11-C16. The equation of the mean plane through the phenyl carbon atoms is:

$$0.5138\,x - 0.5515\,y + 0.6572\,z = -0.0912$$

The distances of the atoms C11-C16 from the plane are respectively -0.008, -0.003, 0.003, 0.010, -0.021, and 0.021Å., while the atoms C9 and C10 are at distances 0.095 and 0.021Å. from the plane. The bond C11-C10 is therefore in the plane of the phenyl group, but C10-C9 is tilted out of

the plane by about 3°. Since Cu1' is at a distance of only -0.034Å. from the plane, the system C9, C10, Cu1' is approximately coplanar with the phenyl group.

The equation of the best plane through the four copper atoms and all the phenylethynyl carbon atoms is:

$$0.4730\,x - 0.6457\,y + 0.5994\,z = 0$$

None of these atoms is displaced more than 0.3Å. from the plane, and the mean displacement is 0.11Å. The phenyl group (C3-C8) is inclined at about 14°, and the phenyl group (C11-C16) at about 7° to the mean plane.

The bond lengths and angles calculated from the final coordinates are given in Tables VIII and IX. The standard deviations in the bond lengths were calculated using the formula:

$$\sigma^2(l_1) = \left(\sigma^2(x_1) + \sigma^2(x_2)\right) l^2 + \left(\sigma^2(y_1) + \sigma^2(y_2)\right) m^2 + \left(\sigma^2(z_1) + \sigma^2(z_2)\right) n^2$$

where l, m, and n are the direction cosines for the bond 1-2, with respect to the crystal axes a, b, c, and l_1 is the bond distance 1-2. The formula used to calculate the standard deviations for the bond angles was:

$$\sigma^2(\theta) = \frac{\sigma_1^2}{l_1^2} + \frac{l_{13}^2}{l_1^2 l_3^2} \cdot \sigma_2^2 + \frac{\sigma_3^2}{l_3^2}$$

(Darlow 1960)

TABLE VIII. BOND LENGTHS IN $(Me_3PCuC{\equiv}CPh)_4$

	Bond Length	e.s.d.
Cu1-Cu2	2.450	0.003
Cu1-Cu'1	2.693	0.004
Cu1-Cu'2	4.067	0.003
Cu2-P1	2.238	0.005
Cu2-P2	2.222	0.005
Cu1-C1	1.957	0.016
Cu1-C'9	2.085	0.014
Cu1-C'10	2.061	0.016
Cu1-C9	2.073	0.015
Cu2-C9	2.105	0.015
Cu2-C1	2.223	0.017
Cu2-C2	2.975	0.017
P1-C17	1.821	0.021
P1-C18	1.818	0.023
P1-C19	1.843	0.022
P2-C20a	1.97	
P2-C21a	1.70	
P2-C22a	1.78	
P2-C20b	1.72	
P2-C21b	2.12	
P2-C22b	1.93	
C1-C2	1.218	0.023
C9-C10	1.237	0.022
C2-C3	1.449	0.021
C10-C11	1.470	0.022
C3-C4	1.404	0.023
C4-C5	1.406	0.024
C5-C6	1.348	0.027
C6-C7	1.391	0.026
C7-C8	1.382	0.023
C8-C3	1.401	0.022
C11-C12	1.394	0.024
C12-C13	1.457	0.026
C13-C14	1.354	0.031
C14-C15	1.389	0.032
C15-C16	1.384	0.027
C16-C11	1.411	0.025

TABLE IX. Bond Angles in $(Me_3PCuC{\equiv}CPh)_4$.

	Angle	e.s.d.
Cu2-Cu1-Cu1'	104.4	0.1
Cu1-Cu2-P1	109.4	0.2
Cu1-Cu2-P2	126.7	0.2
C1-Cu1-C9	114.0	0.6
C1-Cu1-C9,10'	129	
C9-Cu1-C9,10'	117	
P1-Cu2-P2	123.8	0.2
P1-Cu2-C1	104.1	0.4
P1-Cu2-C9	101.9	0.4
P2-Cu2-C1	109.0	0.4
P2-Cu2-C9	113.0	0.4
C1-Cu2-C9	102.7	0.6
Cu1-C9-Cu2	71.8	0.5
Cu1-Cu2-C9	53.5	0.4
Cu2-Cu1-C9	54.7	0.4
Cu1-C1-Cu2	71.5	0.5
Cu1-Cu2-C1	49.2	0.4
Cu2-Cu1-C1	59.2	0.4
[illegible]	[illegible]	[illegible]
Cu1-Cu1'-C9'	49.8	0.4
Cu'1-Cu1-C1	163.7	0.5
Cu1-C1-C2	172.0	1.4
Cu2-C1-C2	116.6	1.4
C1-C2-C3	178.9	1.7
C9-C10-C11	153.7	1.5
Cu1-C9-C10	152.3	1.3
Cu2-C9-C10	135.6	1.2
Cu1-C'9-C'10	71.6	1.0
Cu1-C'10-C'9	73.7	1.0
Cu2-P1-C17	113.4	0.7
Cu2-P1-C18	115.7	0.7
Cu2-P1-C19	119.0	0.7
Cu2-P2-C20a	108.5	
Cu2-P2-C21a	114.7	
Cu2-P2-C22a	123.8	
Cu2-P2-C20b	122.5	
Cu2-P2-C21b	114.8	
Cu2-P2-C22b	110.5	
C17-P1-C18	102.1	1.0
C18-P1-C19	101.0	1.0
C19-P1-C17	102.5	1.0

	Angle	e.s.d.
C2-C3-C4	119.1	1.4
C2-C3-C8	120.8	1.4
C3-C4-C5	118.2	1.5
C4-C5-C6	120.9	1.7
C5-C6-C7	121.5	1.7
C6-C7-C8	119.3	1.6
C7-C8-C3	120.0	1.5
C8-C3-C4	120.1	1.4
C10-C11-C12	120.6	1.4
C10-C11-C16	117.2	1.4
C11-C12-C13	116.0	1.6
C12-C13-C14	121.3	1.9
C13-C14-C15	121.1	2.0
C14-C15-C16	120.1	1.9
C15-C16-C11	119.2	1.7
C16-C11-C12	122.1	1.5
Mean Cu-P-C (P1)	116.1	
Mean Cu-P-C (P2)	115.8	
Mean C-P-C (P1)	102.2	
Mean C-C-C(phenyl)	120.0	

where θ is the angle 1-2-3, and 1_1, 1_3, and 1_{13} are the distances 1-2, 2-3, and 1-3. The σ's are the root mean square standard deviations for the atoms 1,2,3. In this compound the values of the standard deviations in different directions are roughly the same for any one atom, so that the error in the e.s.d.'s for the bond angles will be very small.

The C≡C distances are 1.218 ± 0.023 Å. for C1-C2, and 1.237 ± 0.022 Å. for C9-C10. The average C≡C distances found for triple bondsis 1.205Å., and the values of $t = \frac{l - \bar{x}}{\sigma}$ for the two ethynyl groups are 0.5 for C1-C2, and 1.5 for C9-C10. The two bond lengths are therefore not significantly different from the value of 1.205Å. The angle Cu1-C1-C2 is 172.0 ± 1.4°, a value significantly different from 180°. The distortion of the angle at C1 is such as to increase the distance between the copper atoms Cu1 and Cu2. The angle C1-C2-C3 is 178.9 ± 1.7°, close to 180°, but the angle C9-C10-C11 is 153.7 ± 1.5°. The distortion of the linear (sp) arrangement at C10 is such as to bend the bond to the phenyl group away from Cu1'. There is a similar deformation in the ethynyl-copper complexes described by Carter and Hughes, (1957) where the ethynyl group is reported to adopt a 'cis'-configuration when it is $\sigma\pi$-bonded to the copper atom.

The bond distance Cu1-C1 is 1.957 ± 0.016Å. This is

slightly greater than the copper-carbon distances in the trigonally-coordinated cuprous cyanide complexes, 1.92Å. in $KCu(CN)_2$, 1.89 and 1.87Å. in $KCu_2(CN)_3$. (Cromer, 1959; Cromer and Larson, 1962). The mean of the two- and four-covalent radii for copper(I), (Pauling, 1960, p.253), is 1.27Å. Hence the length expected for Cu-C bonds with the carbon atom in sp hybridisation would be 1.97Å., and some bond-shortening due to 'end-on' π-bonding in the cyanide complexes is possible. In the present case, this effect may also occur. The three-covalent radius of the copper atom seems inappropriate because of the close proximity of Cu2 and Cu1', and a larger value might be expected. The bonding between Cu1-and C9'-C10' is clearly of the $\sigma\pi$-type discussed in the introduction. The distances Cu1-C9', Cu1-C10' are 2.09 and 2.06Å., equal within experimental error. There are two other types of copper-carbon distances, Cu1-C9 and Cu2-C9, (2.07, 2.11Å.) and Cu2-C1 and Cu2-C2 (2.22 and 2.98Å.). The interaction in these cases is considered in the Discussion. (p. 106). The angles at C9 are Cu2-C9-C10 = 136°, and Cu1-C9-C10 = 152°.

The mean carbon-carbon length in the phenyl groups is 1.393Å. and the mean bond angle is 120.0°. If the individual values of the bond lengths in the phenyl groups are assumed to be estimates of the same quantity, a statistical standard deviation in the bond length of 0.028Å. may be deduced, and a standard deviation in the bond angles of 1.7° is

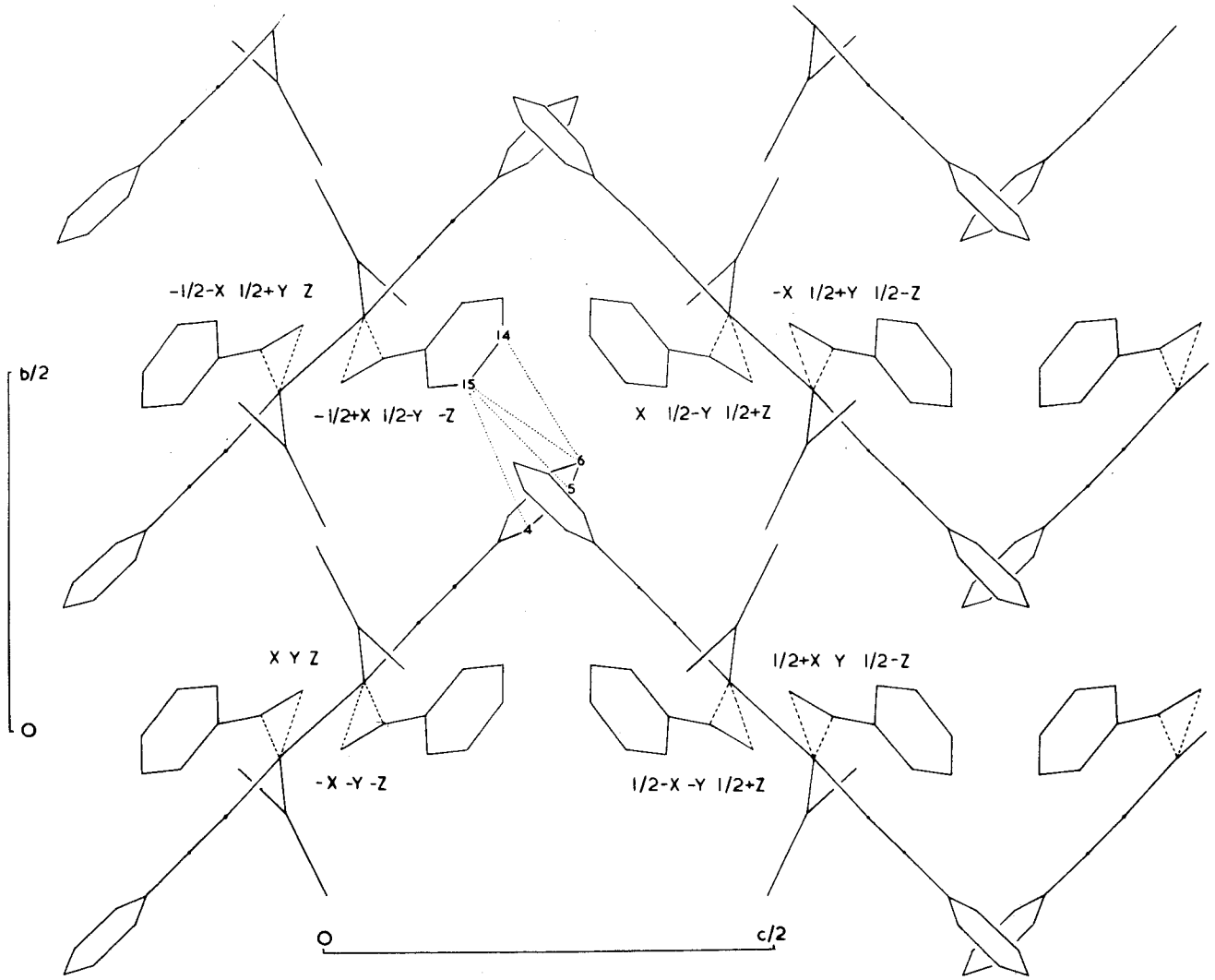
obtained by similar means. These values are very similar to the average values of 0.026Å. and 1.6° obtained from the least squares estimates of the coordinate standard deviations. The carbon-carbon single bonds C2-C3 and C10-C11 are contracted to 1.45 and 1.47Å. respectively. These values are in reasonable agreement with an estimated value of about 1.45Å. for a carbon-carbon single bond adjacent to both an ethynyl group and a phenyl group. The difference between the two bond lengths C2-C3 and C10-C11 is not significant.

The values of the phosphorus-carbon bond lengths for P1 are all the same within experimental error, and the mean distance is 1.83Å. This is 0.04Å. less than the sum of the covalent radii for phosphorus and carbon, (1.87Å.) but the difference is only possibly significant. The phosphorus-carbon bond lengths in trimethylphosphine and in the dimethylphosphinoborine trimer, $(Me_2P.BH_2)_3$, are 1.87 and 1.84Å. respectively. (Springall and Brockway, 1938; Hamilton, 1955). The Cu-P-C angles at P1 are 113.4, 115.7, and 119.0°, all ± 0.7°. Considering the angles in pairs, the values of $t \left(= \frac{\text{Angle 1-Angle 2}}{\sqrt{(\sigma_1^2 + \sigma_2^2)}}\right)$ are respectively 2.1, 3.3, and 5.4, and the differences are therefore significant. The angles are all greater than the tetrahedral value of 109°, and the average value is 116°. The phosphorus-carbon bond lengths and the Cu-P-C angles for P2 vary greatly, which is not

surprising, since the partial atoms C20a-C22b may represent only small maxima in the electron density distribution. The average values of 1.87Å. and 116° for the P-C bond lengths and the P-C angles agree quite well with the corresponding values for P1.

The Cu-P distances of 2.22 and 2.24Å. are rather less than would be expected for a single covalent bond, for which a value of 2.45Å. is estimated, using a tetrahedral covalent radius of 1.35Å. for copper(I), (Kleinberg et al. 1960). The contraction suggests some double bond character in the Cu-P bond, presumably arising from $4d\pi - 3d\pi$ bonding. The mean Cu-P-C angle of 116°, and the mean C-P-C angle of 102° are consistent with this view, for it would be expected that the extra electron density in the copper phosphorus bond would repel the single bond pairs more than the latter repel each other. A similar distortion of tetrahedral angles is observed in many phosphorus compounds where there is double bonding, for instance in PCl_3O, where the Cl-P-Cl angle is 103.5°. (Badgley and Livingston, 1954).

The packing in the crystal is illustrated in Fig. 3, where the structure is projected along the 'a' axis. Only six of the approach distances are less than 3.7Å., and they are all greater than 3.5Å., so that there does not appear to



$(Me_3PCuC{\equiv}CPh)_4$: The Structure in the (100) Projection.

fig 3 47a

be any significant interaction between the molecules. The intermolecular contacts less than 4.0Å. are listed in Table X. There is only one pair of phenyl groups with approach distances of less than 4.0Å., and these contacts are the ones indicated in Fig. 3. The contacts are between the atoms C4, C5, C6 at (x, y, z) and C14, C15 at ($-\frac{1}{2}+x$, $\frac{1}{2}-y$, $-z$), and are all greater than 3.7Å. except C5-C15 which is 3.58Å. Three contacts between phenyl and methyl carbon atoms are 3.5-3.6Å., the others are all greater than 3.8Å. Of the methyl-methyl contacts, there is one of 3.56Å., which represents the shortest contact between tetramers repeated by the translation 'a'. Within the tetramer itself, the shortest contacts are C2-C22a = 3.40Å., and C16-C21b = 3.41Å.

The temperature parameters are generally larger for atoms at the outer parts of the molecule, such as the methyl carbon atoms C17-C19, and the atoms C5-C7 and C13-C15. Possibly, there is an overall vibration of the phenyl groups and the trimethylphosphine groups about the bonds linking them to the centre of the molecule. No attempt has been made to allow for any effect on the atomic coordinates. The magnitudes and directions of the vibration ellipsoids for some of the atoms are given in table XI. The values given indicate that the phosphorus atoms are vibrating mainly in

TABLE X. $(Me_3PCuC{\equiv}CPh)_4$ Non-Bonding Contacts < 4 Å.

Intramolecular (excluding contacts between atoms bound to a common atom)

Cu1-C17	3.83	C1-C11'	3.86	C9-C17	3.89
Cu1-C12'	3.59	C1-C12'	3.45	C9-C18	3.91
P1-C2	3.97	C2-C12'	3.74	C1-C17	3.84
P2-C2	3.91	C1-C20a	3.59	C16-C18	3.67
		C2-C20a	3.40	C16-C21b	3.41
		C3-C20a	3.73		
		C8-C20a	3.82		
		C9-C21a	3.79		

Intermolecular

1-x -y -z		$\frac{1}{2}$-x $\frac{1}{2}$+y z		x $\frac{1}{2}$-y $\frac{1}{2}$+z	
C14-C19	3.82	C7-C17	3.90	C5-C21a	3.94
C15-C18	3.90			C6-C21a	3.50
				C7-C21a	3.87
C18-C18	3.56	$\frac{1}{2}$-x -$\frac{1}{2}$+y z		C7-C21b	3.92
		C10-C22a	3.94		
-$\frac{1}{2}$+x $\frac{1}{2}$-y -z		C12-C21b	3.59		
C4-C15	3.82	C17-C22b	3.86		
C5-C14	3.99	C18-C20a	3.70		
C5-C15	3.58				
C6-C14	3.97	-$\frac{1}{2}$+x y $\frac{1}{2}$-z			
C6-C15	3.79	C4-C19	3.61		
		C5-C19	3.87		
Cu1-C22a	3.79				
C1-C22a	3.97	$\frac{1}{2}$-x -y -$\frac{1}{2}$+z			
C2-C21b	3.87	C13-C17	3.91		
C4-C15	3.77	C13-C19	3.80		
		C14-C17	3.90		
C20b-C22b	3.92				
$\frac{1}{2}$+x $\frac{1}{2}$-y -z					
C18-C20a	3.98				
C18-C20b	3.83				

The first atom in each pair is taken to be at (x, y, z)

TABLE XI. The Magnitudes and Directions of the Principal Axes of the Vibration Ellipsoids for Some Atoms.

Atom		U	$10^4 g_{i1}$	$10^4 g_{i2}$	$10^4 g_{i3}$
Cu1	i=1	0.0778	0958	3735	-9226
	i=2	0.0524	9794	-2015	0196
	i=3	0.0332	1768	9055	3851
Cu2	i=1	0.0885	2129	0417	-9767
	i=2	0.0592	9416	-2774	1934
	i=3	0.0359	2620	9601	0984
P1	i=1	0.0721	5770	2230	7859
	i=2	0.0613	6518	4543	-6075
	i=3	0.0452	-5319	8444	0608
P2	i=1	0.1403	-6537	1615	7396
	i=2	0.0680	7139	-1832	6761
	i=3	0.0401	2253	9741	-0223
C1	i=1	0.1085	5371	3969	-7440
	i=2	0.0637	7764	0666	6262
	i=3	0.0419	-3303	9152	2306
C2	i=1	0.0996	0637	3234	-9443
	i=2	0.0553	-0491	9435	3278
	i=3	0.0401	9919	0884	0916
C9	i=1	0.0678	1527	-2764	9488
	i=2	0.0607	-8765	3737	3101
	i=3	0.0343	4260	8860	1842
C10	i=1	0.0855	-4746	0523	8783
	i=2	0.0547	8398	-2762	4680
	i=3	0.0473	2805	9552	0935

'g_{ij}' is the direction cosine of the principal axis 'i' with respect to the cell axis 'j'.

'U' is the magnitude of the axis of the vibration ellipsoid in $Å^2$.

directions perpendicular to the copper-phosphorus bonds, as might be expected. The major axes of the vibration ellipsoids of the copper atoms and the ethynyl carbon atoms are not perpendicular to the plane of the molecule, but are all pointing in roughly the same direction, at an angle of about 45° to the normal of the mean molecular plane. This group of atoms possibly vibrates mainly as a rigid body.

TABLE VII. Observed and Calculated Structure Factors.

Successive columns give values of k, l, $|F_o|$, F_c
h = 0

0	0	---	1984	4	8	40	36	8	5	97	-91	12	8	91	89
0	2	422	383	4	9	29	25	8	6	59	55	12	9	<20	12
0	4	222	208	4	10	127	119	8	7	79	-76	12	10	132	120
0	6	<16	-5	4	11	15	-14	8	8	37	35	12	11	<20	8
0	8	112	-101	4	12	68	66	8	9	<18	-10	12	12	129	117
0	10	117	-116	4	13	31	32	8	10	27	29	12	13	<21	3
0	12	179	-174	4	14	97	88	8	11	<19	-9	12	14	57	57
0	14	84	-84	4	15	39	36	8	12	<20	-8	12	15	<22	-23
0	16	67	-65	4	16	77	72	8	13	44	43	12	16	27	27
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0	20	75	71	4	18	21	24	8	15	26	31	12	18	<22	-16
0	22	29	26	4	19	46	47	8	16	36	32	12	19	27	-30
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2	0	193	179	4	22	<21	-8	8	19	<21	4	14	1	71	65
2	1	129	-125	4	23	<21	-16	8	20	<21	-19	14	2	<20	-12
2	2	154	166									14	3	130	119
2	3	432	-413	6	0	102	-104	10	0	253	-242	14	4	44	-46
2	4	277	-259	6	1	32	27	10	1	<17	10	14	5	151	139
2	5	163	-162	6	2	94	-98	10	2	136	-128	14	6	42	-44
2	6	75	-87	6	3	27	14	10	3	34	-33	14	7	106	95
2	7	260	-233	6	4	49	-46	10	4	107	-98	14	8	<21	-10
2	8	149	-144	6	5	33	-21	10	5	114	-111	14	9	79	77
2	9	91	-83	6	6	27	-24	10	6	<18	18	14	10	21	18
2	10	152	-135	6	7	38	34	10	7	96	-93	14	11	<21	4
2	11	20	-21	6	8	23	23	10	8	39	34	14	12	<21	-13
2	12	102	-104	6	9	100	95	10	9	70	-66	14	13	<21	-13
2	13	20	24	6	10	74	-73	10	10	41	37	14	14	22	-22
2	14	81	-79	6	11	71	67	10	11	<20	-7	14	15	41	-36
2	15	64	61	6	12	39	-36	10	12	35	30	14	16	34	-31
2	16	<18	-12	6	13	48	49	10	13	41	38	14	17	44	-43
2	17	93	90	6	14	<20	1	10	14	45	37	14	18	<22	-12
2	18	22	21	6	15	29	31	10	15	62	60	14	19	26	-26
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2	21	<21	16	6	18	<21	1	10	18	<21	-14	16	1	<21	4
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2	23	<21	-7	6	20	27	-26	10	20	34	-33	16	3	<21	10
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4	3	78	-83	8	0	53	52	12	3	112	112	16	8	25	-18
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4	6	22	33	8	3	74	-70	12	6	<19	-1	16	11	31	-24
4	7	106	-91	8	4	90	72	12	7	48	46	16	12	31	-27

TABLE VII. -continued.

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18 2	<22	9	
18 3	<22	-22	
18 4	<22	-7	
18 5	<22	-8	
18 6	22	-26	
18 7	<22	-12	
18 8	28	-26	
18 9	<22	-8	
18 10	35	-33	
20 0	<22	8	
22 0	<21	16	

h = 1

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0 6	105	-98	
0 8	102	-80	
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0 14	<16	2	
0 16	41	36	
0 18	70	65	
0 20	53	53	
0 22	<19	9	
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1 2	126	-132	
1 3	231	234	
1 4	74	-74	
1 5	<11	21	
1 6	86	-90	
1 7	84	-83	
1 8	95	-94	
1 9	117	-115	
1 10	33	-35	
1 11	164	-163	
1 12	<21	2	
1 13	91	-88	
1 14	52	49	
1 15	40	-34	
1 16	42	43	
1 17	<19	17	
1 18	33	31	
1 19	21	22	
1 20	24	19	
1 21	23	25	
2 1	219	-245	
2 2	34	55	
2 3	102	-112	
2 4	123	-113	
2 5	67	66	
2 6	49	49	
2 7	23	23	
2 8	28	32	
2 9	39	43	
2 10	<14	18	
2 11	39	39	
2 12	<17	-8	
2 13	53	50	
2 14	51	-54	
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2 17	19	24	
2 18	<20	4	
2 19	<20	-3	
2 20	<19	26	
3 1	<15	-7	
3 2	79	-84	
3 3	130	131	
3 4	281	-283	
3 5	44	-45	
3 6	89	-102	
3 7	<14	-8	
3 8	175	-168	
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3 10	22	-27	
3 11	19	-12	
3 12	28	27	
3 13	<18	-5	
3 14	57	57	
3 15	<19	20	
3 16	77	78	
3 17	19	23	
3 18	41	35	
3 19	<19	5	
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4 2	165	174	
4 3	51	-53	
4 4	197	194	
4 5	62	82	
4 6	110	118	
4 7	34	33	
4 8	90	96	
4 9	34	-38	
4 10	54	51	
4 11	46	-48	
4 12	34	36	
4 13	<18	0	
4 14	<19	10	
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5 2	56	-54	
5 3	72	-70	
5 4	45	42	
5 5	24	-34	
5 6	118	-116	
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5 9	30	33	
5 10	<17	-2	
5 11	33	37	
5 12	75	78	
5 13	61	61	
5 14	56	55	
5 15	20	26	
5 16	52	52	
5 17	<21	7	
5 18	<21	18	
5 19	<21	-1	
6 1	110	103	
6 2	<12	11	
6 3	42	52	
6 4	24	25	
6 5	96	101	
6 6	36	-38	
6 7	21	-20	
6 8	91	-87	
6 9	82	-84	
6 10	36	-41	
6 11	114	-111	
6 12	<18	22	
6 13	68	-63	
6 14	<19	0	
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7 3	44	-43	
7 4	82	-80	
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7 6	15	18	
7 7	27	-33	
7 8	81	-78	
7 9	56	61	
7 10	43	46	
7 11	18	21	
7 12	37	41	
7 13	<19	10	
7 14	37	29	
7 15	<20	-11	
7 16	29	24	
7 17	<21	-9	
7 18	<22	16	
8 1	<17	-12	
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8 4	<15	-6	
8 5	26	-29	
8 6	90	-95	
8 7	<16	12	
8 8	152	-148	
8 9	17	22	
8 10	49	-50	
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8 13	<19	15	
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8 15	<20	5	
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9 2	48	-50	
9 3	28	-25	
9 4	52	-58	
9 5	34	-33	
9 6	66	-60	
9 7	44	50	
9 8	<17	-9	
9 9	59	62	

TABLE VII. -continued.

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9	17	<22	-11
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10	2	<16	3
10	3	108	-108
10	4	16	27
10	5	94	-94
10	6	<17	-14
10	7	<17	-20
10	8	25	-24
10	9	65	62
10	10	<19	-16
10	11	69	64
10	12	<19	8
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10	14	<20	-10
10	15	29	18
10	16	<21	-10
10	17	<23	-2
11	1	163	-161
11	2	<17	4
11	3	132	-128
11	4	<17	-1
11	5	30	-33
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11	13	75	76
11	14	<21	-11
11	15	21	16
11	16	<21	-8
12	1	74	74
12	2	43	43
12	3	33	22
12	4	62	58
12	5	<18	-14
12	6	80	75
12	7	<19	4
12	8	55	54
12	9	43	44
12	10	34	32
12	11	20	23
12	12	<20	0
12	13	<21	-2
12	14	<21	-14
12	15	<21	-12
12	16	<21	-13
13	1	54	-56
13	2	59	58
13	3	36	-32
13	4	108	111
13	5	<19	10
13	6	98	90
13	7	27	30
13	8	63	63
13	9	40	39
13	10	29	30
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13	12	<20	-9
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14	3	<19	7
14	4	33	-30
14	5	<19	-16
14	6	<19	-5
14	7	<20	-13
14	8	<20	13
14	9	20	-28
14	10	<20	-5
14	11	39	-40
14	12	<21	-21
14	13	37	-36
14	14	<21	-21
14	15	<22	-21
14	16	<22	-6
15	1	36	33
15	2	61	60
15	3	<20	19
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15	5	<20	3
15	6	82	78
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15	8	51	50
15	9	<20	-19
15	10	<21	10
15	11	45	-37
15	12	<19	-19
15	13	22	-25
15	14	42	-40
15	15	27	-24
15	16	32	-31
16	1	<20	7
16	2	35	-34
16	3	<20	3
16	4	50	-46
16	5	<20	23
16	6	36	-36
16	7	30	29
16	8	<21	-22
16	9	<21	17
17	1	60	55
17	2	<21	4
17	3	36	36
17	4	<21	14
17	5	<21	17
17	6	<21	7
17	7	<22	-7
17	8	<21	-12
18	1	58	-62
18	2	<21	7
18	3	34	-37
18	4	<21	11
18	5	<23	-6
19	1	<22	9
19	2	<22	4
19	3	<22	14
19	4	<22	-1
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20	2	39	26
20	3	<23	15
20	4	23	31

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0	12	116	-114
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0	18	29	36
0	20	<19	15
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1	1	<23	-27
1	2	195	-163
1	3	39	32
1	4	208	-192
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1	6	38	-47
1	7	72	-83
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1	9	17	-29
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1	18	<21	14
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1	20	<22	-17
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2	3	104	-84
2	4	253	216
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2	8	85	-84
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TABLE VII. -continued.

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3	2	--	-4	5	9	35	49	8	2	182	-184				
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3	4	123	-110	5	11	<17	28	8	4	110	-107	11	1	<20	17
3	5	211	180	5	12	54	-63	8	5	38	-43	11	2	35	-36
3	6	45	48	5	13	<19	-18	8	6	45	-49	11	3	62	66
3	7	113	110	5	14	86	-89	8	7	16	-17	11	4	<17	9
3	8	48	52	5	15	20	-30	8	8	37	39	11	5	54	59
3	9	56	68	5	16	34	-36	8	9	<17	-10	11	6	31	36
3	10	78	74	5	17	<21	-6	8	10	136	136	11	7	40	41
3	11	<16	21					8	11	18	30	11	8	43	45
3	12	94	93	6	0	41	42	8	12	95	94	11	9	25	26
3	13	<18	-12	6	1	57	-58	8	13	28	32	11	10	36	33
3	14	47	48	6	2	14	-11	8	14	20	23	11	11	<20	0
3	15	18	-20	6	3	139	-137	8	15	21	32	11	12	35	44
3	16	<19	18	6	4	28	-34	8	16	<21	-5	11	13	<21	-6
3	17	33	-33	6	5	189	-178					11	14	26	28
3	18	<21	17	6	6	<17	5	9	0	164	-159	11	15	<22	-27
3	19	<22	-9	6	7	205	-191	9	1	<15	-15				
3	20	<23	12	6	8	27	34	9	2	131	-131	12	0	72	-72
3	21	28	-21	6	9	108	-110	9	3	45	-47	12	1	19	-13
				6	10	79	86	9	4	98	-98	12	2	63	-64
4	0	22	20	6	11	<17	-2	9	5	98	-95	12	3	<17	20
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4	3	34	-34	6	14	34	36	9	8	<17	5	12	6	20	29
4	4	93	94	6	15	63	67	9	9	42	-45	12	7	62	62
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4	7	118	-127					9	12	<19	17	12	10	<20	10
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4	10	95	-100	7	2	141	141	9	15	21	27	12	13	<21	-20
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4	12	45	-49	7	4	39	46					12	15	32	-35
4	13	99	102	7	5	74	-83	10	0	115	-113				
4	14	33	-33	7	6	21	27	10	1	28	-31	13	0	20	22
4	15	82	86	7	7	90	-92	10	2	51	-51	13	1	20	31
4	16	<21	-15	7	8	<19	-20	10	3	16	-19	13	2	<18	15
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TABLE VII. -continued.

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13 15	<22	-4	
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14 4	31	27	
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14 13	22	-28	
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16 3	46	46	
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16 5	51	50	
16 6	<21	11	
16 7	40	39	
16 8	<22	-7	
16 9	<22	6	
17 0	50	-49	
17 1	<21	-7	
17 2	59	-55	
17 3	<21	5	
17 4	28	-28	
17 5	<22	-13	
17 6	<21	-17	
18 0	32	30	
18 1	<22	11	
18 2	46	46	
18 3	38	37	
18 4	22	28	
18 5	32	37	
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19 2	<23	0	
19 3	<23	13	
19 4	<23	-2	
19 5	33	28	
20 0	47	47	
20 1	<23	7	
20 2	23	29	
21 0	24	22	
22 0	27	27	

h = 3

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0 8	52	-51	
0 10	37	-35	
0 12	<15	-3	
0 14	34	38	
0 16	<17	12	
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1 2	53	-59	
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1 4	27	26	
1 5	15	-23	
1 6	76	75	
1 7	84	-83	
1 8	31	31	
1 9	17	-20	
1 10	28	35	
1 11	<17	-19	
1 12	<17	-6	
1 13	23	-25	
1 14	<19	-22	
1 15	<19	-1	
1 16	<20	-17	
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1 22	24	-23	
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2 20	<21	-7	
2 21	<23	7	
3 1	185	196	
3 2	52	-53	
3 3	245	227	
3 4	50	-55	
3 5	66	60	
3 6	32	-29	
3 7	37	-43	
3 8	52	50	
3 9	110	-116	
3 10	33	39	
3 11	95	-95	
3 12	<17	20	
3 13	100	-92	
3 14	30	32	
3 15	44	-47	
3 16	20	22	
3 17	<21	4	
3 18	27	32	
3 19	<22	13	
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3 21	28	31	
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4 2	39	38	
4 3	<13	8	
4 4	<14	16	
4 5	89	-86	
4 6	22	30	
4 7	41	-48	
4 8	47	53	
4 9	31	30	
4 10	<17	0	
4 11	25	29	
4 12	33	-33	
4 13	<19	-10	
4 14	<18	3	
4 15	<20	-10	
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4 18	<21	-4	
4 19	<22	5	
4 20	<23	-9	
5 1	16	19	
5 2	145	-153	
5 3	18	23	
5 4	243	-257	
5 5	53	59	
5 6	299	-330	
5 7	16	-24	
5 8	109	-119	
5 9	66	-71	
5 10	58	-68	
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5 14	50	59	
5 15	<20	-10	
5 16	47	51	
5 17	<21	-14	
5 18	47	53	
5 19	<23	5	
5 20	28	33	
6 1	42	47	
6 2	22	-24	

TABLE VII -continued-

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6	5	22	-22
6	6	21	25
6	7	70	-77
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6	9	10	18
6	10	<18	-6
6	11	<19	-5
6	12	<19	3
6	13	22	-24
6	14	25	-20
6	15	<20	-10
6	16	21	27
6	17	<22	-10
6	18	<22	9
6	19	<23	15
6	20	<23	8
7	1	191	-200
7	2	84	-79
7	3	91	-101
7	4	189	-191
7	5	<17	6
7	6	147	-163
7	7	90	101
7	8	117	-123
7	9	85	91
7	10	27	-30
7	11	84	94
7	12	34	40
7	13	84	94
7	14	49	58
7	15	37	43
7	16	43	52
7	17	<22	20
7	18	39	45
7	19	<23	-12
7	20	29	23
8	1	47	-56
8	2	46	-51
8	3	<17	-7
8	4	95	-92
8	5	<17	2
8	6	<17	-10
8	7	<18	-10
8	8	<18	-1
8	9	<19	-3
8	10	<19	-1
8	11	<19	-2
8	12	48	-49
8	13	<20	0
8	14	<21	-7
8	15	<21	11
9	1	222	-245
9	2	17	22
9	3	130	-145
9	4	40	45
9	5	<18	-6
9	6	29	33
9	7	46	52
9	8	41	43
9	9	73	79
9	10	24	31
9	11	84	90
9	12	20	16
9	13	54	63
9	14	<21	5
9	15	29	35
10	1	60	-66
10	2	18	-23
10	3	18	-14
10	4	<19	-7
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10	6	<19	-10
10	7	19	24
10	8	19	25
10	9	<20	-5
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10	11	<20	6
11	1	<19	-4
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11	3	36	37
11	4	76	82
11	5	41	49
11	6	82	89
11	7	53	58
11	8	35	36
11	9	25	25
11	10	30	32
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11	12	<21	26
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12	3	<20	-10
12	4	<20	14
12	5	38	40
12	6	<20	3
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12	9	<21	-2
12	10	<21	-5
12	11	<21	-17
13	1	20	-10
13	2	<20	2
13	3	<20	0
13	4	<20	26
13	5	<21	3
13	6	<21	-21
13	7	<21	-15
13	8	<21	-13
13	9	<22	10
13	10	<24	-12
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14	3	<21	21
14	4	<21	7
14	5	<21	14
14	6	<22	-2
14	7	<22	18
14	8	<22	-18
14	9	<22	-7
14	10	<23	-12
14	11	<22	3
15	1	<22	-16
15	2	<22	25
15	3	22	-18
15	4	<22	10
15	5	<22	-9
15	6	27	30
15	7	<22	21
15	8	<23	17
15	9	40	47
15	10	<22	1
15	11	29	38
16	1	<22	-13
16	2	<22	-1
16	3	<23	-10
16	4	<23	12
16	5	<23	-1
16	6	<23	-10
16	7	<23	-5
16	8	<23	-21
17	1	<23	-1
17	2	<23	15
17	3	<23	-11
17	4	47	54
17	5	<23	-12
17	6	58	65
17	7	<24	-9
17	8	42	53
18	1	<24	6
18	2	<24	9
18	3	<24	8
19	1	50	65
19	2	<24	9
19	3	52	59

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0	10	<15	6
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0	14	19	-15
0	16	<17	-4
0	18	21	22
0	20	27	23
0	22	27	26
1	0	65	75
1	1	<14	-17
1	2	64	79
1	3	29	22
1	4	169	168
1	5	118	119
1	6	16	20
1	7	131	121
1	8	15	14
1	9	67	74
1	10	36	-35
1	11	45	46
1	12	24	-24
1	13	44	-47
1	14	18	-9
1	15	41	-43
1	16	<20	5
1	17	<20	-5
1	18	<21	13
1	19	<21	-6
1	20	<22	-1
1	21	<22	-8

TABLE VII. -continued.

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2	4	<12	2
2	5	<13	9
2	6	60	-62
2	7	64	67
2	8	<15	-6
2	9	32	27
2	10	52	-56
2	11	36	32
2	12	49	-48
2	13	20	-18
2	14	30	-28
2	15	<19	9
2	16	<24	5
2	17	<20	2
2	18	<21	24
2	19	<21	7
2	20	30	26
2	21	<23	-14
2	22	28	25
3	0	37	-38
3	1	<10	8
3	2	41	35
3	3	48	-52
3	4	56	49
3	5	69	-65
3	6	17	15
3	7	56	-62
3	8	132	-126
3	9	<16	-3
3	10	108	-102
3	11	17	-19
3	12	97	-92
3	13	<18	-8
3	14	40	-35
3	15	<19	8
3	16	<20	5
3	17	20	16
3	18	<21	-15
3	19	<21	15
3	20	<22	3
3	21	<23	8
3	22	<23	-1
4	0	93	97
4	1	42	-44
4	2	77	80
4	3	203	-190
4	4	<21	22
4	5	146	-138
4	6	<15	-11
4	7	109	-111
4	8	22	-25
4	9	36	-33
4	10	120	-116
4	11	<17	3
4	12	78	-72
4	13	<18	7
4	14	63	-62
4	15	29	30
4	16	<20	-9
4	17	57	54
4	18	<21	-4
4	19	<22	21
5	0	28	-24
5	1	55	-53
5	2	31	-28
5	3	<14	3
5	4	61	63
5	5	79	-74
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5	7	74	-71
5	8	33	27
5	9	42	-39
5	10	17	16
5	11	25	-27
5	12	38	33
5	13	<19	24
5	14	58	55
5	15	<20	14
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5	17	<21	7
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6	2	43	-39
6	3	187	-179
6	4	34	-31
6	5	191	-183
6	6	64	58
6	7	192	-191
6	8	73	68
6	9	86	-81
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6	11	<18	3
6	12	<18	12
6	13	36	36
6	14	45	43
6	15	43	41
6	16	<21	13
6	17	64	61
6	18	<22	19
6	19	32	34
7	0	118	-123
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7	2	106	-104
7	3	31	36
7	4	66	-61
7	5	57	51
7	6	50	-47
7	7	32	30
7	8	57	-57
7	9	18	18
7	10	18	-14
7	11	18	20
7	12	<19	11
7	13	<19	18
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7	15	20	22
7	16	<21	6
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7	18	<22	1
7	19	<22	-17
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8	1	<16	-7
8	2	201	-200
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8	4	78	-76
8	5	64	-54
8	6	<17	11
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8	9	22	-31
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8	15	36	32
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8	20	31	-29
8	21	<24	-7
8	22	34	-30
9	0	109	114
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9	2	130	127
9	3	17	22
9	4	61	57
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9	8	<18	11
9	9	<19	6
9	10	<19	-27
9	11	<19	-12
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9	13	<20	17
9	14	<21	-14
9	15	<21	5
9	16	<22	-16
9	17	<22	-16
9	18	<23	3
9	19	<23	-19
10	0	84	-82
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10	2	56	-52
10	3	76	74
10	4	<18	-1
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10	6	51	49
10	7	55	54
10	8	98	97
10	9	50	52
10	10	46	43
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11	1	23	-26
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11	5	62	-51
11	6	44	-41
11	7	37	-37

TABLE VII. -continued

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11	15	<22	18
11	16	<22	-25
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12	2	<19	-10
12	3	48	44
12	4	<19	-7
12	5	48	44
12	6	28	29
12	7	25	18
12	8	<20	9
12	9	<20	2
12	10	<21	14
12	11	<21	8
12	12	<21	-14
12	13	<22	-2
12	14	<22	-16
12	15	<23	-12
12	16	40	-32
13	0	<19	-3
13	1	28	-26
13	2	<20	-21
13	3	65	-58
13	4	<20	-4
13	5	56	-50
13	6	<20	-9
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13	8	36	44
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13	11	<22	-16
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14	6	<21	4
14	7	<21	6
14	8	37	34
14	9	<22	-2
14	10	41	34
15	0	52	-53
15	1	<21	6
15	2	43	-37
15	3	<21	-8
15	4	37	-34
15	5	40	39
15	6	<22	2
15	7	47	48
15	8	<22	-4
15	9	27	35
16	0	<21	13
16	1	22	20
16	2	<22	-20
16	3	31	29
16	4	<22	-16
16	5	50	51
16	6	<22	-9
16	7	55	52
16	8	<23	8
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17	2	<23	26
17	3	<23	15
17	4	33	37
17	5	<23	12
17	6	<23	19
17	7	<23	19
17	8	<23	6
17	9	<23	12
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18	9	30	25
19	0	<22	7
19	1	<24	7
19	2	<24	2
20	0	40	40
20	1	<24	-6
20	2	30	32

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0	6	159	161
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0	10	76	71
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0	14	44	-42
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0	18	36	-36
0	20	<19	-11
0	22	19	-14
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1	2	38	-41
1	3	58	62
1	4	47	-46
1	5	59	63
1	6	17	-17
1	7	19	-23
1	8	53	-56
1	9	134	-132
1	10	<18	-5
1	11	133	-127
1	12	22	26
1	13	59	-60
1	14	36	32
1	15	<21	-5
1	16	32	30
1	17	<21	22
1	18	22	10
1	19	26	33
2	1	165	164
2	2	<15	-15
2	3	137	135
2	4	<13	0
2	5	61	67
2	6	<15	5
2	7	<16	14
2	8	51	51
2	9	103	-103
2	10	<17	11
2	11	111	-107
2	12	<18	3
2	13	54	-53
2	14	<19	-18
2	15	42	-40
2	16	20	-16
2	17	<21	1
2	18	<21	2
3	1	<15	10
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3	5	<15	-7
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3	8	139	-137
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3	15	<21	1
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3	17	29	27
3	18	<22	7
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4	4	73	-79
4	5	<15	8
4	6	131	-124
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4	8	111	-117
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4	10	28	-25
4	11	41	-36
4	12	<19	-1
4	13	<20	-11
4	14	24	23
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4	16	<21	1
4	17	<22	5
4	18	29	24
5	1	52	51
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5	3	35	-32
5	4	89	-99
5	5	<17	4
5	6	131	-127

TABLE VII. -continued.

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5 15	22	16
5 16	44	39
5 17	<24	-2
5 18	<24	17
6 1	76	-77
6 2	<17	-11
6 3	46	-45
6 4	<17	11
6 5	29	-25
6 6	<17	-7
6 7	26	25
6 8	<19	-17
6 9	45	44
6 10	<20	-5
6 11	38	38
6 12	48	46
6 13	45	42
6 14	<22	-8
6 15	34	31
6 16	<24	6
6 17	32	29
6 18	<25	-6
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7 2	56	-56
7 3	78	-75
7 4	77	-76
7 5	77	-81
7 6	92	-84
7 7	<19	-10
7 8	53	-49
7 9	73	68
7 10	31	-34
7 11	69	71
7 12	22	22
7 13	<22	2
7 14	<23	28
7 15	<23	-7
7 16	<24	21
7 17	<24	-11
7 18	<25	4
8 1	32	30
8 2	70	68
8 3	<18	3
8 4	70	67
8 5	<19	0
8 6	72	67
8 7	20	-19
8 8	35	36
8 9	<21	-12
8 10	58	58
8 11	<22	-25
8 12	<22	2
8 13	<22	-12
8 14	<23	16
8 15	<24	-5
8 16	34	-28
8 17	<25	-1
8 18	31	-28
9 1	24	-27
9 2	61	-58
9 3	44	-45
9 4	56	-58
9 5	<20	-13
9 6	39	-38
9 7	23	25
9 8	<21	21
9 9	107	105
9 10	<22	3
9 11	67	73
9 12	<22	-12
9 13	<23	23
10 1	117	113
10 2	<20	-8
10 3	76	70
10 4	21	-21
10 5	<21	-3
10 6	45	-45
10 7	<21	14
10 8	27	-26
10 9	55	-50
10 10	<22	-15
10 11	28	-28
10 12	33	34
10 13	29	-28
11 1	86	-83
11 2	<21	-17
11 3	54	-55
11 4	<21	-15
11 5	27	-27
11 6	33	23
11 7	44	43
11 8	<22	32
11 9	38	43
11 10	<23	3
11 11	<24	44
12 1	<22	-3
12 2	56	-52
12 3	38	-35
12 4	67	-63
12 5	<22	-12
12 6	92	-87
12 7	38	-33
12 8	59	-56
12 9	31	30
12 10	<24	-12
12 11	<24	11
13 1	44	-43
13 2	22	18
13 3	<22	-8
13 4	59	56
13 5	37	28
13 6	59	53
13 7	44	40
13 8	61	60
13 9	34	37
13 10	24	28
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14 1	57	-55
14 2	<24	8
14 3	46	-38
14 4	<24	-15
14 5	27	-31
14 6	<24	24
14 7	32	28
14 8	<24	22
14 9	46	37
14 10	<25	23
14 11	46	48
15 1	<24	-3
15 2	42	40
15 3	<24	6
15 4	46	46
15 5	<25	14
15 6	50	49
15 7	<25	11
15 8	25	28
16 1	<25	0
16 2	<25	8
16 3	<25	-4
16 4	38	37
16 5	<25	2
16 6	36	33
16 7	<26	-1
16 8	39	43
17 1	34	38
17 2	<26	21
17 3	32	33
17 4	34	36
17 5	26	25
17 6	26	25
18 1	33	34
18 2	<27	3
18 3	27	34

h = 6

0 0	270	266
0 2	240	237
0 4	128	132
0 6	29	31
0 8	93	-85
0 10	116	-111
0 12	106	-106
0 14	57	-53
0 16	<18	6
0 18	<19	19
0 20	36	37
1 0	72	81
1 1	25	32
1 2	26	27
1 3	70	72
1 4	51	53
1 5	26	30
1 6	72	-68
1 7	24	24
1 8	<18	-6
1 9	20	-20
1 10	23	-25
1 11	<20	1
1 12	<20	-13
1 13	<21	9

TABLE VII. -continued.

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2	1	67	-71
2	2	36	41
2	3	127	-130
2	4	25	19
2	5	154	-157
2	6	81	-85
2	7	167	-162
2	8	94	-93
2	9	102	-105
2	10	91	-93
2	11	18	-25
2	12	65	-67
2	13	28	29
2	14	33	-33
2	15	44	44
2	16	<21	-5
2	17	49	49
2	18	<22	16
2	19	29	26
3	0	109	109
3	1	67	71
3	2	108	111
3	3	35	-33
3	4	24	-23
3	5	47	-48
3	6	17	-20
3	7	49	-50
3	8	<18	-15
3	9	<18	-18
3	10	<19	-7
3	11	19	-13
3	12	<20	-9
3	13	<20	11
3	14	28	-33
3	15	<21	7
3	16	<22	-9
3	17	<17	-8
4	0	81	-87
4	1	<15	-10
4	2	16	-18
4	3	53	-55
4	4	<17	11
4	5	101	-98
4	6	<18	11
4	7	104	-102
4	8	19	23
4	9	42	-43
4	10	53	56
4	11	<22	4
4	12	59	60
4	13	34	33
4	14	54	55
4	15	45	45
4	16	41	40
4	17	32	20
5	0	71	68
5	1	50	-50
5	2	<17	0
5	3	36	-40
5	4	70	-70
5	5	59	-60
5	6	51	-50
5	7	<19	-15
5	8	<20	8
5	9	<21	-11
5	10	34	32
5	11	<22	5
5	12	<23	5
5	13	<23	9
6	0	73	-69
6	1	<18	10
6	2	58	-56
6	3	18	14
6	4	56	-55
6	5	<19	-10
6	6	52	-48
6	7	<25	-10
6	8	<21	-13
6	9	<21	8
6	10	<22	-10
6	11	30	31
6	12	<23	23
6	13	35	32
7	0	44	48
7	1	<19	2
7	2	<19	5
7	3	65	-62
7	4	<20	14
7	5	<20	3
7	6	<21	-2
7	7	45	43
7	8	<21	7
7	9	<23	8
7	10	27	29
7	11	31	40
7	12	<23	-7
7	13	34	-36
8	0	67	68
8	1	<20	-15
8	2	62	65
8	3	50	-51
8	4	41	45
8	5	51	-49
8	6	40	38
8	7	53	-50
8	8	27	24
8	9	23	-30
8	10	33	29
8	11	<23	4
8	12	24	21
9	0	<19	-4
9	1	18	-24
9	2	18	19
9	3	24	-25
9	4	21	23
9	5	<22	-8
9	6	<22	0
9	7	<23	5
9	8	<23	-4
9	9	42	41
9	10	50	-48
9	11	<24	11
9	12	<25	-24
10	0	107	-103
10	1	22	-24
10	2	93	-94
10	3	53	-53
10	4	55	-51
10	5	44	-46
10	6	<23	-14
10	7	31	-31
10	8	23	17
10	9	30	-28
10	10	32	34
10	11	<25	-4
10	12	44	46
11	0	<19	-12
11	1	<23	-10
11	2	<23	-1
11	3	28	-29
11	4	35	29
11	5	41	-44
11	6	35	39
11	7	42	-46
11	8	<25	-11
11	9	27	-21
11	10	<25	10
11	11	25	15
11	12	<26	-30
12	0	94	-91
12	1	<24	6
12	2	67	-64
12	3	24	23
12	4	<24	-12
12	5	51	50
12	6	33	32
12	7	34	37
12	8	55	52
12	9	22	20
12	10	68	71
12	11	<26	6
12	12	66	67
13	0	54	-52
13	1	<25	3
13	2	35	-43
13	3	21	18
13	4	<25	-9
13	5	<25	-21
13	6	<25	-5
13	7	<25	-12
13	8	<26	27
13	9	<26	2
14	0	<20	-12
14	1	25	23
14	2	<25	-6
14	3	69	73
14	4	<26	6
14	5	89	91
14	6	<26	-3
14	7	82	84
14	8	<26	-7
14	9	48	53
15	0	<21	-11

TABLE VII. -continued.

15	1	26	26
15	2	<26	-18
15	3	35	20
15	4	<26	-15
15	5	33	26
15	6	<27	11
15	7	<27	3
16	0	64	64
16	1	<27	12
16	2	54	57
16	3	<27	22
16	4	36	40
16	5	34	30
16	6	<27	19
16	7	27	23
17	0	<22	13
17	1	<28	-1
17	2	<28	17
17	3	31	25

h = 7

0	2	<25	-30
0	4	19	18
0	6	<16	3
0	8	36	-33
0	10	<17	-6
0	12	28	-20
0	14	19	-13
0	16	<18	5
1	1	219	201
1	2	78	-78
1	3	122	128
1	4	96	-99
1	5	19	-23
1	6	98	-103
1	7	102	-102
1	8	42	-44
1	9	86	-84
1	10	38	-36
1	11	64	-63
1	12	<21	-19
1	13	60	-63
1	14	<22	20
1	15	38	-34
1	16	22	18
2	1	55	-49
2	2	27	32
2	3	<14	-5
2	4	34	33
2	5	<17	-5
2	6	<18	-1
2	7	<18	-12
2	8	<19	-4
2	9	<19	-4
2	10	<20	-20
2	11	22	18
2	12	20	-23
2	13	20	20
2	14	29	-31
2	15	<21	11
2	16	<26	-13
3	1	<14	3
3	2	99	-100
3	3	<15	-4
3	4	170	-166
3	5	<17	-9
3	6	123	-114
3	7	41	-39
3	8	34	-32
3	9	18	-13
3	10	21	-19
3	11	<21	9
3	12	<21	-2
3	13	26	26
3	14	<22	25
3	15	<22	17
3	16	52	51
3	17	<27	7
3	18	41	40
3	19	<28	9
3	20	34	30
4	1	72	72
4	2	24	30
4	3	32	27
4	4	90	82
4	5	26	26
4	6	35	38
4	7	<20	-9
4	8	46	51
4	9	27	-31
4	10	45	38
4	11	<21	-15
4	12	<21	-8
4	13	<22	-7
4	14	<22	7
4	15	<23	-3
5	1	81	-79
5	2	41	-46
5	3	36	-36
5	4	62	-60
5	5	<20	-7
5	6	33	-28
5	7	23	20
5	8	21	7
5	9	22	-17
5	10	28	23
5	11	<23	13
5	12	<24	2
5	13	43	49
5	14	<25	14
5	15	26	24
6	1	92	89
6	2	19	-20
6	3	72	69
6	4	<19	-8
6	5	<20	11
6	6	21	-12
6	7	28	-27
6	8	<22	-7
6	9	45	-47
6	10	<23	-24
6	11	34	-35
6	12	<24	-5
6	13	33	-35
6	14	<26	-10
6	15	29	-33
7	1	17	-21
7	2	20	-23
7	3	20	22
7	4	<21	-15
7	5	45	49
7	6	21	-15
7	7	27	22
7	8	<23	0
7	9	<23	-20
7	10	<24	15
7	11	<24	-12
7	12	<25	30
7	13	<25	4
8	1	34	27
8	2	43	-40
8	3	29	32
8	4	65	-62
8	5	<22	18
8	6	53	-50
8	7	<23	-1
8	8	23	-19
8	9	<24	-8
8	10	<24	-5
8	11	<25	-5
8	12	<25	-23
8	13	<26	8
9	1	55	-58
9	2	<22	-14
9	3	<23	-9
9	4	49	-51
9	5	23	21
9	6	59	-60
9	7	<24	21
9	8	58	-62
9	9	<25	12
9	10	<25	-21
9	11	<25	19
9	12	<26	11
9	13	27	24
10	1	49	-43
10	2	<23	-16
10	3	33	-23
10	4	26	-23
10	5	38	-31
10	6	<24	-13
10	7	24	15
10	8	<28	-6
10	9	<28	-12
10	10	<29	-11
10	11	<29	18
10	12	<30	8
10	13	<30	15
11	1	99	-101
11	2	<24	21
11	3	61	-65
11	4	24	20
11	5	<25	-6
11	6	<25	-6
11	7	34	30
11	8	<26	-18
11	9	45	46
11	10	<26	-5
11	11	64	60

TABLE VII. -continued.

11	12	<27	16
11	13	44	48
12	1	<25	-2
12	2	<23	1
12	3	<25	3
12	4	29	21
12	5	<26	20
12	6	<26	21
12	7	<26	1
12	8	32	31
12	9	27	28
12	10	<27	21
12	11	<28	12
13	1	34	-34
13	2	64	60
13	3	26	-26
13	4	84	84
13	5	<26	-15
13	6	69	72
13	7	<27	7
13	8	31	35
13	9	34	34
13	10	<28	21
13	11	47	42
14	1	<27	-2
14	2	<27	5
14	3	<27	-1
14	4	<27	-18
14	5	<27	-11
14	6	<27	9
14	7	<28	1
14	8	<28	-5
15	1	44	52
15	2	28	32
15	3	<28	26
15	4	52	55
15	5	<28	-5
15	6	45	47
15	7	<29	-14
15	8	35	39
16	1	<29	-4
16	2	<29	-13
17	1	36	41

h = 8

0	0	97	104
0	2	61	60
0	4	<17	3
0	6	24	-28
0	8	81	-81
0	10	93	-94
0	12	51	-56
0	14	26	-26
0	16	<19	-3
0	18	<19	5
0	20	24	24
1	0	128	-129
1	1	29	-25
1	2	70	-70
1	3	73	-74
1	4	<20	-25
1	5	<21	-28
1	6	<21	-20
1	7	<21	5
1	8	<21	-2
1	9	<21	-21
1	10	<21	-5
1	11	31	-34
1	12	<22	9
1	13	38	-36
1	14	<22	15
1	15	<24	-8
1	16	<26	9
2	0	130	128
2	1	<19	-15
2	2	88	97
2	3	56	-55
2	4	55	64
2	5	43	-44
2	6	20	17
2	7	39	-38
2	8	25	-27
2	9	<20	-24
2	10	50	-50
2	11	<21	2
2	12	26	-24
2	13	26	26
2	14	<21	-7
2	15	22	21
2	16	<22	3
3	0	54	-50
3	1	19	25
3	2	19	-27
3	3	49	51
3	4	32	35
3	5	70	64
3	6	58	53
3	7	72	72
3	8	<21	11
3	9	26	36
3	10	<21	15
3	11	<22	1
3	12	<22	9
3	13	22	-26
3	14	36	33
3	15	<22	-16
3	16	40	37
4	0	21	19
4	1	<20	-21
4	2	<20	1
4	3	59	-59
4	4	20	-15
4	5	67	-75
4	6	26	-17
4	7	50	-49
4	8	43	-46
4	9	30	-27
4	10	<22	-12
4	11	<22	3
4	12	<23	-28
4	13	28	28
4	14	<23	0
4	15	33	40
5	0	55	47
6	0	32	33
7	0	67	70
8	0	51	-50
9	0	50	-53
10	0	47	-47
11	0	<20	-2
12	0	51	-54
13	0	<21	23
14	0	<21	3
15	0	<21	8
16	0	<22	7
17	0	61	-58
18	0	24	25

h = 9

0	2	37	-35
0	4	<17	28
0	6	<18	-20
0	8	34	-34
0	10	36	-36
0	12	22	-21
0	14	<19	-2
0	16	17	-15
1	1	<21	14
1	2	<21	12
1	3	<21	22
1	4	21	31
1	5	<21	5
1	6	<21	14
1	7	<22	18
1	8	<22	8
1	9	22	-27
1	10	<22	8
1	11	42	-40
1	12	<22	18
1	13	<22	-18
1	14	<23	7
2	1	38	-32
2	2	43	39
2	3	<20	-2
2	4	20	29
2	5	<21	-19
2	6	44	43
2	7	<21	-6
2	8	<21	12
2	9	21	15
2	10	<21	2
2	11	21	19
2	12	<22	-4
2	13	<22	7
2	14	<23	-8
3	1	76	77
3	2	<21	5
3	3	57	55
3	4	<21	16
3	5	21	19
3	6	<22	-13
3	7	<22	-14
3	8	34	-33

TABLE VII. -continued.

3	9	22	-28
3	10	<22	9
3	11	55	-58
3	12	36	37
3	13	40	-39
3	14	37	28
4	1	53	56
4	2	37	31
4	3	27	18
4	4	51	54
4	5	22	-21
4	6	22	21

h = 10

0	0	19	17
0	2	<18	24
0	4	<18	-15
0	6	<18	-8
0	8	<18	-12
0	10	<18	8
1	0	26	29
1	1	35	34
1	2	65	67
1	3	59	59
1	4	<22	22
1	5	48	49
1	6	<22	16
1	7	22	13
1	8	<22	3
1	9	<22	10
1	10	<23	1
2	0	84	90
2	1	<21	-10
2	2	31	27
2	3	<21	14
2	4	21	22
2	5	<21	5
2	6	<21	-8
2	7	27	30
2	8	<22	-26
2	9	27	32
2	10	22	-18
2	11	<22	5
3	0	62	58
3	1	<22	8
3	2	<22	6
3	3	45	43
3	4	<22	-15
3	5	<22	-4
3	6	28	-25
3	7	<23	-7
3	8	33	-37
3	9	<23	0
3	10	29	-22
4	0	67	69
4	1	23	-20
4	2	61	62
4	3	54	-60
4	4	37	36
4	5	50	-53
4	6	<23	10
4	7	47	-39
4	8	29	-27
4	9	<24	-9
4	10	42	-46
4	11	<24	-1
4	12	39	-39
5	0	56	55
6	0	46	-44
7	0	<20	-4
8	0	107	-118
9	0	<19	1
10	0	39	-38
11	0	<21	-18
12	0	<21	-7
13	0	<21	-22
14	0	<21	-9
15	0	<21	-24
16	0	20	-16

h = 11

0	2	22	23
0	4	52	45
0	6	76	76
0	8	72	71
0	10	33	26
0	12	<19	-2
0	14	24	-21
1	1	39	35
1	2	<23	-3
1	3	23	34
1	4	<23	-15
1	5	<23	-2
1	6	<23	6
1	7	<23	-17
1	8	<23	4
1	9	<23	-22
1	10	<24	3
1	11	<24	-8
2	1	42	46
2	2	<22	19
2	3	47	47
2	4	<22	-11
2	5	35	34
2	6	<22	24
2	7	<22	-14
2	8	<22	14
2	9	32	-38
2	10	<23	9
2	11	33	-39
3	1	29	31
3	2	41	-38
3	3	<24	30
3	4	34	-35
3	5	<24	9
3	6	24	-25
3	7	24	-19
3	8	<24	-1
3	9	<24	-22
3	10	<24	-5
3	11	30	-22
4	1	<24	6
4	2	<24	-16
4	3	<24	1
4	4	34	-26
4	5	<24	9
4	6	46	-43

h = 12

0	0	27	25
0	2	76	71
0	4	40	37
0	6	<19	11
0	8	23	-22
0	10	52	-47
0	12	33	-29
1	1	<24	-14
1	2	<24	23
1	3	<24	15
1	4	<24	13
1	5	50	50
1	6	<24	-5
1	7	41	45
1	8	<24	-20
1	9	<24	30
1	10	24	-20
2	0	<20	21
2	1	<23	-9
2	2	<23	6
2	3	<23	-16
2	4	<23	16
2	5	43	-48
2	6	<23	-5
2	7	40	-44
2	8	<23	-21
2	9	<25	-31
2	10	23	-28
3	0	34	29
3	1	<24	-7
3	2	34	32
3	3	<24	-11
3	4	30	26
3	5	<25	-13
3	6	<25	1
3	7	<25	-3
3	8	<25	-11
3	9	<25	1
3	10	25	-31
4	0	<21	-13
5	0	<21	-13
6	0	<21	-12
7	0	<21	1
8	0	<21	15
9	0	<21	21
10	0	<21	-29
11	0	<21	14
12	0	29	-33
13	0	23	-24

TABLE VII. -continued.

h = 13

0	2	19	16
0	4	31	22
0	6	19	17
0	8	<19	-4
0	10	<19	-2
0	12	<20	6
1	1	51	50
1	2	<24	-9
1	3	24	24
1	4	24	-26
1	5	<24	10
1	6	24	-32
1	7	<24	-16
1	8	<24	-22
1	9	24	-27
1	10	<24	-13
1	11	34	-34
1	12	<25	-3
1	13	29	-28
2	1	<23	7
2	2	<23	15
2	3	<24	3
2	4	<25	16
2	5	<25	-14
2	6	<26	7
2	7	<26	-16
2	8	<26	3
3	1	<23	4
3	2	<23	-19
3	3	<24	-17
3	4	25	-26
3	5	<24	-6
3	6	51	-46
3	7	<25	-2
3	8	25	-28

h = 14

0	0	39	36
0	2	35	31
0	4	<19	1
0	6	27	-20
0	8	19	-19
0	10	22	-19
1	0	<20	-11
1	1	<21	7
1	2	<22	-13
1	3	<22	7
2	0	23	25
2	1	<23	-11
2	2	<23	19
2	3	24	-26
3	0	<20	5
3	1	<23	17
3	2	<23	-1
3	3	<23	22
4	0	<20	-11
4	1	<27	-16
4	2	<27	-6
4	3	27	-27
5	0	29	32
6	0	<21	-9
7	0	25	25

THE DETERMINATION OF THE CRYSTAL STRUCTURE OF PHENYLETHNYL-(TRIMETHYLPHOSPHINE)SILVER(I)

INTRODUCTION

This compound was investigated after the structure analyses of the copper and gold complexes had been completed. The rather complicated bonding in the copper compound, and the apparent lack of metal-ethynyl interaction of the 'side-on' $\sigma\pi$-type in the gold compound made the structure of a silver complex of especial interest. The most readily available silver compound was the trimethylphosphine complex of phenylethynylsilver(I).

EXPERIMENTAL

CRYSTALS

The compound was recrystallised from acetone as white needles, which turn black on exposure to light, or to the X-ray beam, and which decompose to powder with evolution of phosphine after about a day. The crystals used in this work were coated with shellac, applied in several thin layers, and this slowed down the decomposition. They gave good reflections even after abou t a fortnight's exposure to X-radiation, although there were powder lines visible on the X-ray photographs after this period.

CRYSTAL DATA

Phenylethynyl(trimethylphosphine)silver(I)

$Me_3PAgC{\equiv}CPh$ M = 285.1

Monoclinic; needles extended in the direction of 'c'.

a = 11.50	b = 20.58	c = 12.12 Å.
β = 123° 25'	U = 2394 Å^3	Z = 8 formula units
D_x = 1.582	D_m = 1.57-1.58 gm/cm^3	F(000) = 1136 e.

Absorption coefficient for MoKα radiation, μ = 17.3 cm^{-1}

Reflections observed:

hkl	h + k = 2n	
h0l	l = 2n	(h = 2n)
0k0	(k = 2n)	

The space group is either C2/c, (C_{2h}^6), no. 15 in the International Tables for Crystallography, or Cc, (C_s^4), no. 9. The centrosymmetric space group was chosen on the basis of the Patterson function, and confirmed by the subsequent refinement.

The unit cell dimensions were estimated from photographs obtained by the precession method, using MoKα radiation. (λ = 0.7107 Å.) The uncertainty in the cell dimensions is probably of the order of 0.1-0.2% for the lengths, and 5' for β.

COLLECTION OF INTENSITIES

Three-dimensional data were collected photographically using Zr-filtered MoKα radiation, (λ = 0.7107 Å.). In some

cases, unfiltered radiation was used, in order to avoid over-long exposures. The Weissenberg technique was used for the layers (hk0)-(hk8), and the layers (h0l)-(h3l), (0kl), and ($hk\bar{2}\bar{h}$) were obtained by the precession method. The sizes of the crystals used for the photographs are given in table I.

TABLE I Crystals used for Data Collection in $Me_3PAgC{\equiv}CPh$

	Layers	Cross-section, mm.	
Weissenberg:	hk1, hk2	0.06 x 0.10	
	hk3-hk5	0.16 x 0.23	(Two parts of the same crystal)
	hk0, hk6-hk8	0.20 x 0.28	(Two parts of the same crystal)
Precession:	h0l-h3l 0kl, $hk\bar{2}h$	0.25 x 0.37	

The multiple film technique was used for the Weissenberg photographs, with the films interleaved by 0.0008 inch nickel foil, and the method of multiple time exposures was used for the precession photographs. The intensities of the $K\alpha$ reflections were estimated visually, by comparison with a calibrated intensity scale. On average, the intensity of each reflection was estimated on two films for each layer. The film ratios for the films separated by the nickel foil were found to have values ranging from 3.0-4.2, much higher than expected. A value of 2.65 is quoted by Abrahams and

Sime, (1960) for normal-beam exposures. The cause of the difference was not known, but much better agreement between structure factors for reflections common to both Weissenberg and precession photographs was obtained using a film ratio of 2.65, and so this value was adopted. In view of the uncertainty, no account was taken of the small effect on the film ratio of varying the equi-inclination angle.

On the upper layer Weissenberg photographs, the intensities of both extended and contracted reflections were estimated. Empirical estimates of the lengths of the reflections were obtained by finding an analytical expression that would give approximately the observed variation of the lengths on each layer with $\sin^2\theta$. Corrections to the intensities for the lengths of the reflections could then be applied at the same time as the Lorentz and polarisation corrections. The expression

$$l = \frac{A + B \sin^2\theta + C \sin^4\theta}{D + \sin^2\theta}$$

was found convenient. The term in $\sin^4\theta$ was included for the contracted reflections only, in order to allow for the increase in length of low-order reflections on the uppermost layers. Values of the coefficients A-D could be chosen so that 'R' never differed by more than 3% from the smoothed length-$\sin^2\theta$ curves for the extended reflections, or by more

than 10% from the curve for the contracted reflections, each of the empirical curves being drawn on the basis of a dozen or so reflections. The procedure was followed only for reflections on the fourth and eighth layers, as reflections with **l** $\neq$ 4n were very weak, and it was difficult to estimate their lengths, These were calculated using values of A-D linearly interpolated from layers with l = 0, 4, 8. For the low-order planes on these layers, the interpolation was not very successful, and the lengths were obtained by direct measurement.

The common reflections were used to place the structure factors on the same relative scale, using the least squares method due to Rollet and Sparks. (1960; see appendix A)

No correction was applied for absorption.

There were 1171 independent reflections observed, 264 of them occurring on two layers, and 16 of them on three.

STRUCTURE DETERMINATION

Reflections with **l** = 4n are all strongly marked, while those with **l** $\neq$ 4n are nearly all very weak. The silver atoms will make the main contribution to the structure factors, implying that the cell axis 'c' is quartered for these atoms,

and hence that they form a nearly straight chain with repeat distance c/4. The final results show that the silver atoms are in the special positions (0,0,0); $(0,0,\frac{1}{2})$ and $(0,y,\frac{1}{4})$; $(0,\bar{y},\frac{3}{4})$, with y small, but the analysis was first attempted assuming the atoms to be in general positions.

PATTERSON FUNCTION

The arrangement of the silver atoms in chains was confirmed by inspection of the Patterson function in projection along the crystal axes. The projections showed silver-silver vectors almost perfectly aligned with the 'c' axis, with lengths c/4, c/2, 3c/4, etc., consistent with silver coordinates very near (0,0,0.125), for space group C^2/c. It was possible to identify the peaks due to the silver-phosphorus vectors, and a centrosymmetrical structure was indicated by the number of these peaks observed, and by their heights. Coordinates of (0.224, -0.069, 0.278) for the phosphorus atom accounted satisfactorily for the silver-phosphorus vectors, and implied one phosphorus atom attached to each silver atom. These coordinates for the heavy atoms appeared to be a reasonable interpretation of the main features of the Patterson function. However, confirmatory evidence from peaks due to phosphorus-phosphorus vectors

was lacking, as these peaks are submerged in the general background.

Part of the three-dimensional Patterson function was calculated, in order to determine the coordinates of the silver atom more precisely. The function was evaluated at intervals (a/40, b/80, c/50), that is, at intervals of 0.29, 0.26, and 0.24Å. Sections were calculated in the regions where peaks due to the silver-silver and silver-phosphorus vectors were expected to occur. The intensities were weighted with the function $w = \exp(20\sin^2\theta) = \exp(10.1\ \sin^2\theta/\lambda)$, by analogy with the copper compound. An analysis of the positions of the four peaks due to the silver-phosphorus vectors gave the coordinates of the silver and the phosphorus atoms listed in table II.

TABLE II. Preliminary Coordinates of the Silver and Phosphorus Atoms.

	Patterson			Refinement		
	x/a	y/b	z/c	x/a	y/b	z/c
Ag	0.0018	-0.0028	0.1248	0.0008	-0.0015	0.1251
P	0.229	-0.070	0.269	0.223	-0.069	0.273

As a check on these coordinates, and on the signs of the x- and y- coordinates of the silver atom, the coordinates obtained from the two-dimensional projections of the Patterson

function were refined through two cycles of structure factor/least squares refinement. The value of R for structure factors calculated during the second cycle was 0.29, and the coordinates obtained are also given in table II. They are similar to the coordinates obtained from the three-dimensional Patterson function. The y-coordinate of the silver atom has the same sign as that of the phosphorus atom, while the z-coordinate is almost exactly $\frac{1}{8}$. The x-coordinate of the silver atom is very small.

ATTEMPTED SOLUTION

SILVER ATOMS IN GENERAL POSITIONS

An (F_o-F_c) synthesis was calculated, at the same intervals as in the Patterson function. The F_c were structure factors based on the coordinates of the silver and phosphorus atoms obtained from the least squares refinement. There were peaks corresponding to not one, but two, phenylethynyl groups in the asymmetric unit, each well resolved. The peak heights ranged from 1.4-3.4 e/Å.^{3} (mean 2.8 e/Å.^{3}), for peaks in the first group, and from 2.0-3.7 e/Å.^{3}, (mean 3.1 e/Å.^{3}) for peaks in the second group. Each silver atom was apparently bonded 'end-on' to two ethynyl groups, arranged so that there was almost a centre of symmetry at the silver atom. In addition, there were small peaks related by translations of c/4 to the

positions of the two pairs of ethynyl carbon atoms. Including these peaks, each silver atom appeared to be bonded to four ethynyl groups. There were other peaks in the electron density with heights of 2-3 $e/\text{Å}^3$, and some were near the position of the phosphorus atom, but it was not possible to assign positions for the methyl carbon atoms.

If the appearance of more than one set of light atoms were due to false symmetry imposed on the electron density because of the arrangement of the silver atoms, one of the two well-marked phenylethynyl groups would be the true one. The positions of atoms in the first phenylethynyl group were plausible, but phenyl carbon atoms of the second group came too close to the phosphorus atom, and would also interfere with phenyl carbon atoms of adjacent chains. Sets of structure factors were calculated based on the heavy atoms in the same positions as before, and on eight carbon atoms placed in positions corresponding to the first phenylethynyl group. As a check structure factors were also calculated with carbon atoms in the second set of positions. The R factors obtained were:

	Ag,P	Ag,P,8C(1)	Ag,P,8C(2)
R: Overall	0.274	0.245	0.251
ℓ = 1,2,3, only	0.554	0.508	0.507

There was a slight improvement in the agreement on including the contributions from the light atoms, but the R factors were very high for the planes with $l \neq 4n$, where the contributions from the silver atoms were much smaller. The agreement was equally bad for each of the positions assumed for the phenyl ethynyl groups, and it seemed unlikely that either position could be correct.

CORRECT SOLUTION

SILVER ATOMS IN SPECIAL POSITIONS

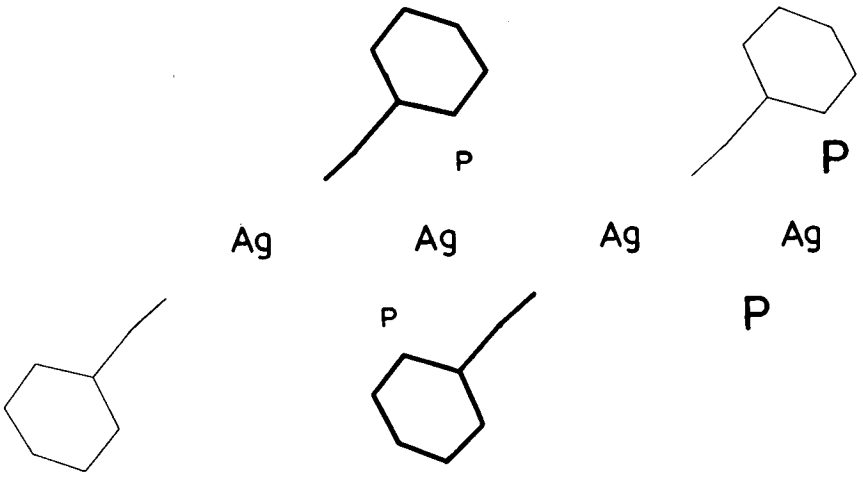
A re-examination of the Patterson function showed that it was equally consistent with a centrosymmetric structure involving silver atoms in the special positions 4a, (0,0,0); $(0,0,\frac{1}{2})$ and 4e, $(0, y, \frac{1}{4})$; $(0,\bar{y},\frac{3}{4})$, with two phosphorus atoms bound to the silver at $(0,y,\frac{1}{4})$. (The difference between the 'x' components of the silver-phosphorus vectors were small, and could be ignored.) With this arrangement alternate silver atoms are bonded 'end-on' to two ethynyl groups, and around the others are two ethynyl groups 'side-on', and two phosphorus atoms, in a tetrahedral arrangement, which seemed plausible. An arrangement with two phosphorus atoms bound to the silver atom at (0,0,0) did not fit the Patterson vectors exactly, nor could the structure pack well.

A set of structure factors was calculated, based on the

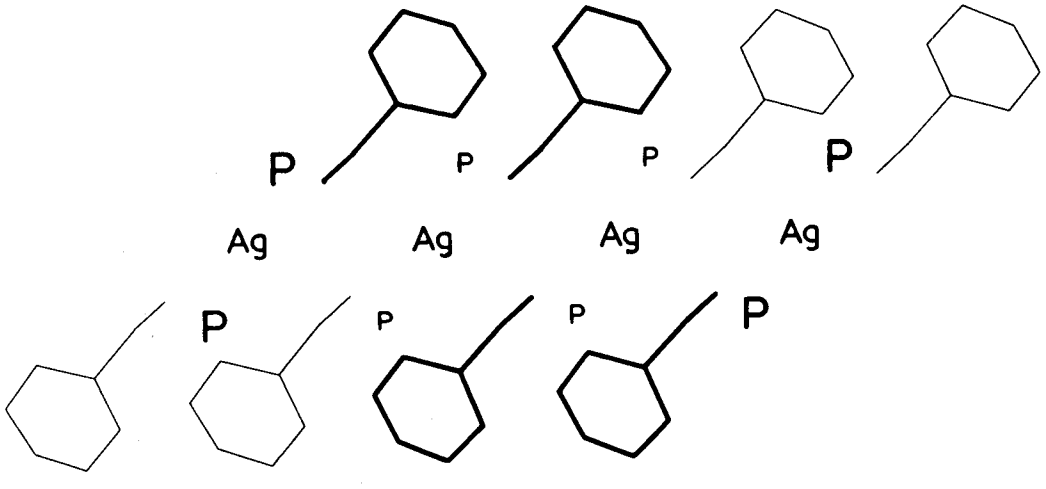
coordinates (0,0,0) and (0,-0.0024, 0.250) for silver atoms Ag1 and Ag2 and (0.223,-0.069,0.398) for the phosphorus atom, and the value of R was 0.248 compared with the previous value of 0.274. For structure factors based on the silver atoms as above, but with the phosphorus atoms joined to the silver atom at (0,0,0), the R factor was 0.268, confirming that this arrangement was incorrect. The value of R for structure factors calculated including terms due to the eight phenylethynyl carbon atoms was 0.172.

These calculations confirmed that the silver atoms were in the special positions. The earlier coordinates for the heavy atoms had z coordinates differing by $\frac{1}{8}$ from the correct ones. Assigning the silver atoms to general positions meant that there were no longer two kinds of silver atom, and the space group symmetry would repeat the phenylethynyl and phosphine groups so that each silver atom was attached both to two phosphorus atoms and to two ethynyl groups. (See fig. 1). This explains the occurrence of an extra set of phenylethynyl carbons in the (F_o-F_c) synthesis.

A second (F_o-F_c) synthesis was now obtained, where the F_c's were based on the silver, phosphorus, and phenylethynyl carbon atoms. There were three peaks in the electron density clearly corresponding to methyl carbon atoms, and their heights were 2.9, 3.8, and 4.1 $e.Å^{-2}$. Apart from the regions near



True Arrangement: silver atoms in special positions



False Arrangement: silver atoms in general positions

Fig 1. Showing the effect of misplacing the silver atoms

the silver atom, the electron density over the rest of the unit cell varied from -1.7 to 1.6 e/Å.^{2}, although it lay usually between 0 to 0.5 e/Å.^{2}.

The analysis of the structure is summarised schematically in fig. 2.

REFINEMENT

The atomic parameters were refined through two cycles of least squares refinement, in which the heavy atoms were given anisotropic temperature factors, and then four further cycles with anisotropic thermal parameters for all the atoms. The mean shifts in the coordinates fell to 0.0009Å. in the final cycle, with a maximum shift of 0.0026Å., and no shift in any parameter was more than 0.36 times the corresponding estimated standard deviation. Details of the refinement are given in table III. The final value of R was 0.066.

The weighting used in the refinement was of the form $w = {}^1/A+K|F_o| +B(K|F_o|)^2$, with A = 12, and values of B and K near B = 0.005 and K = 0.8. The values of $w|\Delta|$ tended to be high at low values of $\sin\theta/\lambda$, and this was probably due to the large number of weak planes at low $\sin\theta/\lambda$, since the intensities of these planes would be less accurately known. A not-very-successful attempt to improve the weighting was made during

Schematic Outline of the Determination of the Structure

Values of the reliability index R at each stage are given in brackets.

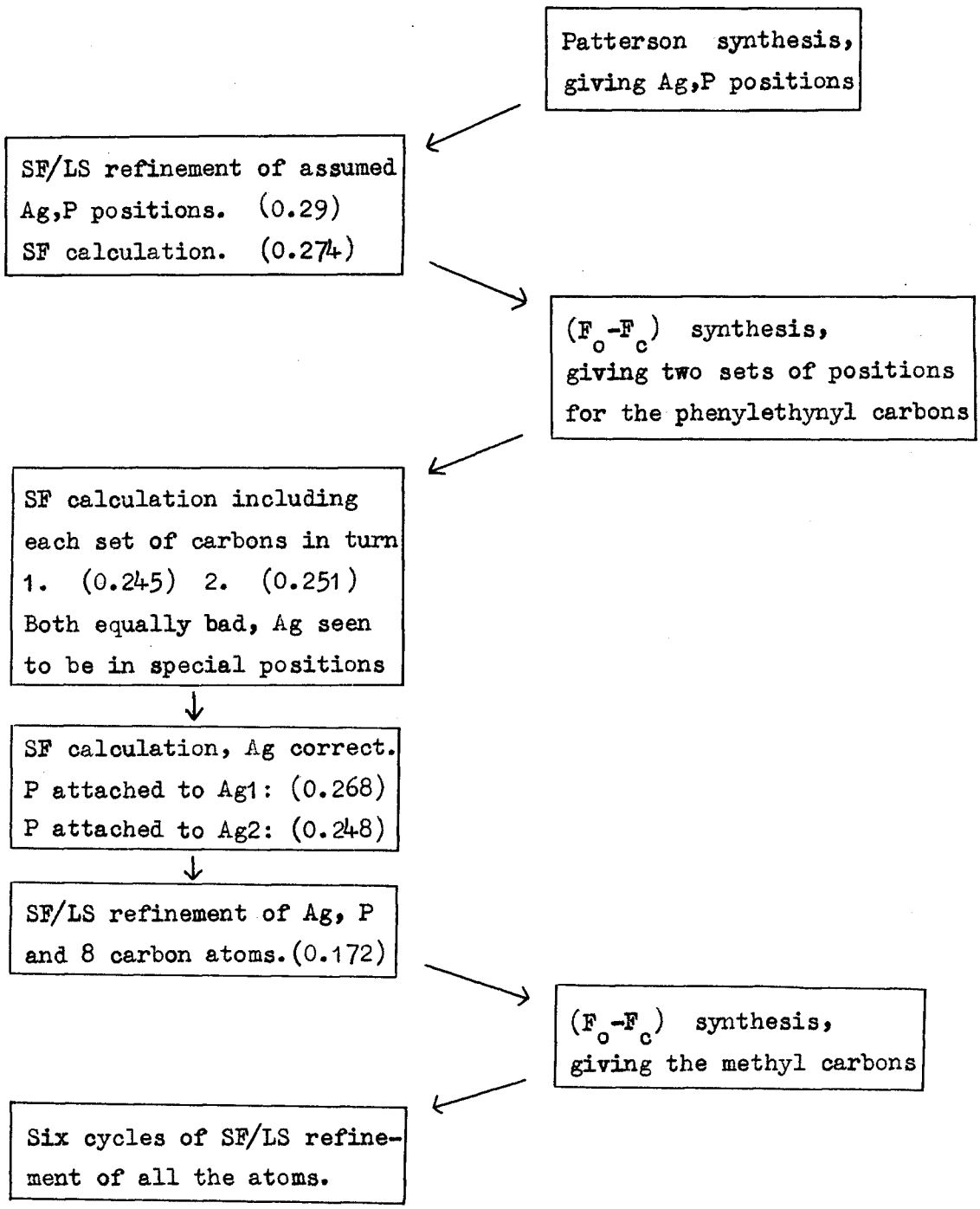


TABLE III. Refinement of the Structure of $Me_3PAgC{\equiv}CPh$.

Cycle No.	Mean shift in coords.	Max. shift of coords.	R	R'	
1.	0.0537	0.158	0.172	0.0317	(All atoms isotropic, no methyls)
2.	0.0313	0.157	0.127	0.0144	(Ag,P anisotropic)
3.	0.0251	0.084	0.080	0.0141	"
4.	0.0052	0.021	0.072	0.0114	(All atoms anisotropic)
5.	0.0037	0.013	0.067	0.0089	"
6.	0.0033	0.008	0.066	0.0089	"
7.	0.0009	0.003	0.066	0.0088	"

$$R = \frac{\Sigma||F_o| - |F_c||}{\Sigma|F_o|} \qquad R' = \frac{\Sigma||F_o| - |F_c||^2.w}{\Sigma|F_o|^2.w}$$

the last two cycles, when the weights used were given by:

$$w = \frac{1}{A + K|F_o| + B(K|F_o|)^2} \times \frac{1}{(2\sin\theta/\lambda - 0.9)^4 + 0.2}$$

with A = 12, B = 0.01, and K = 0.82. The function in $\sin\theta/\lambda$ was designed to vary slowly with $\sin\theta/\lambda$ except for $\sin\theta/\lambda < 0.2$, and $\sin\theta/\lambda > 0.7$, when it rapidly becomes smaller. The weighting analysis after the final cycle is given in table IV. The values of $w|\Delta|^2$ are not particularly even, and this may

effect the estimated standard deviations.

The shifts in the coordinates in the final cycle are listed in table V, and the shifts in the anisotropic temperature parameters in table VI.

TABLE IV. $Me_3PAgC{\equiv}CPh$: Weighting Analysis after the Final Cycle.

$K\|F_o\|$	Mean $w\|\Delta\|^2$	No. of planes
8 - 16	1.38	91
16 - 32	1.86	499
32 - 64	1.02	309
64 - 128	1.30	180
128 -	1.41	92

$\sin\theta/\lambda$	Mean $w\|\Delta\|^2$	No. of planes
0 - 0.1	0.96	4
0.1 - 0.2	3.25	65
0.2 - 0.3	1.16	167
0.3 - 0.4	1.18	283
0.4 - 0.5	1.04	286
0.5 - 0.6	1.27	243
0.6 - 0.7	2.88	110
0.7 - 0.8	4.96	13

Overall mean $w|\Delta|^2$ is 1.48.

The structure factors calculated during the final cycle are given in table VII. They include 494 unobserved planes, only 2 of which calculated more than the maximum value expected, F_{min}. The unobserved planes were not included in the refinement. The final values of the atomic coordinates, together with the appropriate estimated standard deviations, and also the coordinates referred to orthogonal axes parallel to 'a*', 'b', and 'c', are given in table VIII. The final values of the anisotropic temperature factors are given in table IX.

The scattering curve used for silver was that due to Thomas and Umeda, (1957), based on the Thomas-Fermi-Dirac model. No correction was made for dispersion, although $\Delta f'$ for MoKα radiation is -1.0 electrons for silver atoms. Neglect of dispersion is expected to affect mainly the individual temperature factors. (Dauben and Templeton, 1958). The scattering curves for phosphorus and carbon were the same as were used in the copper compound. (See p. 31).

TABLE V. Shifts in the Atomic Coordinates in the Final Cycle. (in Ångströms)

	x	y	z
Ag1	0	0	0
Ag2	0	-0.0005	0
P	0.0000	-0.0005	0.0003
C1	0.0006	0.0000	0.0012
C2	0.0026	-0.0013	0.0023
C3	0.0009	0.0016	0.0026
C4	0.0015	-0.0005	-0.0002
C5	0.0008	-0.0002	0.0012
C6	0.0025	-0.0014	-0.0008
C7	-0.0005	-0.0024	-0.0003
C8	-0.0009	-0.0006	-0.0009
C9	0.0011	-0.0010	0.0026
C10	-0.0005	-0.0015	0.0003
C11	-0.0005	-0.0003	0.0002

TABLE VI. Shifts in the Anisotropic Temperature Parameters in the Final Cycle. (Å.^{2}).

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Ag1	0.0000	-0.0001	0.0003	-0.0000	-0.0000	0.0002
Ag2	0.0001	-0.0000	-0.0001	0	0	-0.0000
P	-0.0000	0.0001	0.0002	-0.0003	-0.0005	0.0002
C1	0.0012	-0.0001	0.0008	-0.0004	-0.0007	0.0024
C2	-0.0004	0.0004	-0.0000	0.0001	-0.0001	-0.0009
C3	-0.0010	-0.0002	-0.0002	0.0008	0.0000	-0.0016
C4	-0.0014	0.0024	-0.0009	-0.0005	0.0004	-0.0007
C5	0.0001	-0.0003	-0.0006	0.0003	-0.0026	-0.0017
C6	-0.0014	0.0008	-0.0012	0.0030	0.0014	-0.0027
C7	0.0005	0.0006	-0.0003	-0.0005	-0.0024	-0.0004
C8	-0.0004	0.0007	0.0001	-0.0015	-0.0023	0.0001
C9	-0.0006	0.0017	0.0001	-0.0003	0.0005	-0.0003
C10	0.0002	-0.0008	0.0005	-0.0025	-0.0013	0.0005
C11	-0.0007	-0.0008	0.0010	0.0011	-0.0003	0.0004

TABLE VIII. $Me_3PAgC{\equiv}CPh$: Final Values of the Atomic Coordinates, (in Å.), and their Standard Deviations. (10^3 Å.)

The last three columns give the root mean square e.s.d., and the x- and z-coordinates referred to axes parallel to a* and c.

Atom	x	y	z	σ(r)	x'	z'
Ag1	0	0	0		0	0
Ag2	0	-0.133 (1)	3.030		0	3.030
P	2.534 (4)	-1.409 (3)	4.738 (4)	0.004	2.115	3.343
C1	1.102 (14)	1.378 (12)	1.798 (14)	0.013	0.920	1.191
C2	1.905 (13)	2.160 (12)	2.871 (13)	0.013	1.590	1.822
C3	2.977 (14)	3.064 (11)	4.160 (14)	0.013	2.485	2.521
C4	3.852 (18)	4.022 (16)	3.925 (17)	0.017	3.215	1,804
C5	4.917 (18)	4.873 (15)	5.217 (20)	0.018	4.105	2.509
C6	5.064 (16)	4.793 (15)	6.640 (18)	0.016	4.227	3.852
C7	4.201 (15)	3.847 (15)	6.911 (16)	0.015	3.507	4.597
C8	3.124 (15)	3.008 (12)	5.606 (15)	0.014	2.608	3.886
C9	3.487 (19)	-1.672 (19)	3.641 (19)	0.019	2.910	1.721
C10	4.189 (18)	-0.778 (18)	6.692 (18)	0.018	3.497	4.385
C11	2.364 (20)	-3.127 (15)	5.288 (19)	0.018	1.973	3.987

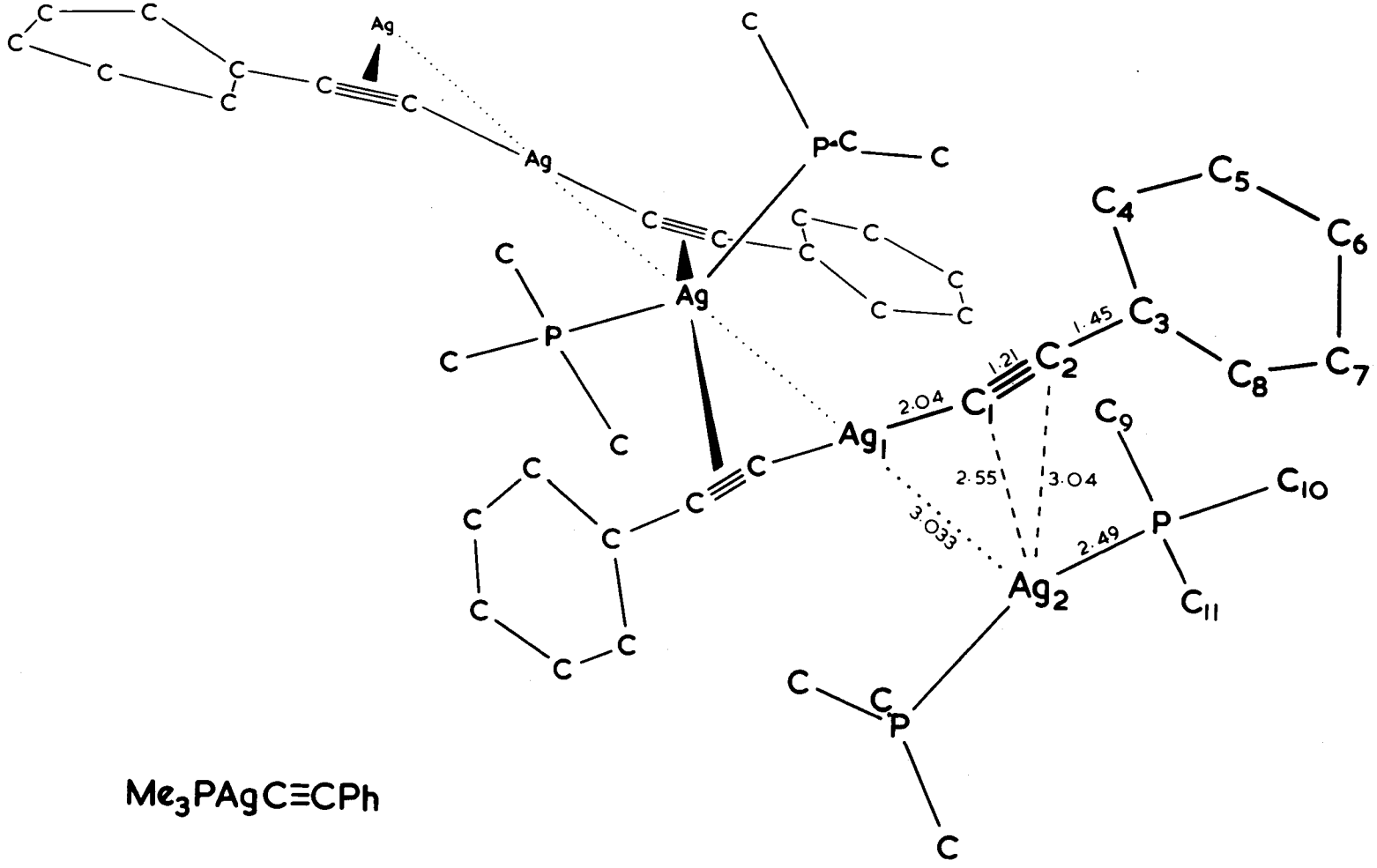
TABLE IX. $Me_3PAgC{\equiv}CPh$: Final Values of the Anisotropic Temperature Parameters, (in $Å^2$), and their Standard Deviations. (in 10^3 $Å^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Ag1	0.0497(.7)	0.0705(.8)	0.0663(.7)	-0.0127(1.2)	-0.0189(1.3)	0.0719(1.2)
Ag2	0.0499(.7)	0.0826(.9)	0.0510(.6)	0	0	0.0624(1.1)
P	0.053(2)	0.070(2)	0.045(1)	0.012(3)	0.008(3)	0.060(3)
C1	0.055(7)	0.065(8)	0.064(7)	-0.022(11)	-0.040(12)	0.077(12)
C2	0.042(6)	0.065(7)	0.054(6)	0.007(11)	-0.005(11)	0.061(11)
C3	0.049(7)	0.054(7)	0.055(6)	0.008(11)	0.013(11)	0.041(11)
C4	0.071(9)	0.094(11)	0.080(9)	-0.007(16)	-0.056(17)	0.073(16)
C5	0.098(11)	0.073(10)	0.077(10)	0.015(16)	-0.029(16)	0.074(18)
C6	0.085(11)	0.077(9)	0.061(8)	-0.030(16)	-0.013(15)	0.050(15)
C7	0.067(9)	0.083(10)	0.056(8)	-0.023(14)	0.000(14)	0.030(13)
C8	0.055(7)	0.057(7)	0.059(7)	-0.006(11)	-0.015(12)	0.045(11)
C9	0.082(11)	0.144(15)	0.092(11)	0.034(21)	0.063(21)	0.128(20)
C10	0.074(10)	0.106(13)	0.069(9)	-0.034(18)	-0.031(17)	0.033(15)
C11	0.093(12)	0.070(9)	0.099(11)	0.032(16)	-0.004(17)	0.100(20)

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

A perspective diagram of the structure is given in fig. 3. The silver atoms are arranged in infinite, almost straight, chains, lying in the direction of the 'c' axis, with silver-silver distances of 3.033 Å., and angles of 175°. Two chains, related by the C centering, pass through each unit cell. The silver atoms are situated alternately at centres of symmetry, (Ag1), and on two-fold axes, (Ag2). Ag1 is σ-bonded to two ethynyl groups in linear coordination. Ag2 is bonded to two phosphorus atoms, and is also bound 'side-on' to two ethynyl groups, the four ligands being in a distorted tetrahedral arrangement. The ethynyl groups thus act as bridging units linking together adjacent silver atoms along the chain. Formally, the structure is built up of $\left[PhC{\equiv}C\text{-}Ag\text{-}C{\equiv}CPh\right]^-$ and $\left[(Me_3P)_2Ag\right]^+$ ions.

Because of the special positions of the silver atoms, the coordination at Ag1 must be truly linear, and the coordination at Ag2 must at least have symmetry 2. However, the angle P-Ag2-P" is increased to 118°, and the plane through Ag2, P, and P" makes an angle of 72° with the plane through Ag2 and the carbon atoms C1 and C1", (writing a double prime for atoms related by the two-fold axis). If the mid-points



$Me_3PAgC{\equiv}CPh$

fig 3 84a

of the ethynyl groups are taken instead of C1, the planes are inclined at 59°. An angle of 90° is required for true tetrahedral symmetry. The distortion results in the angles P-Ag2-C1 and P-Ag2-C1" being 95° and 121° respectively, and presumably prevents the methyl carbons coming too close to phenylethynyl carbon atoms related to atoms C1-C8 by the glide plane. As in the case of the copper compound, the metal-metal distances are short, (3.033 Å.), and are comparable with those in the free element. (in silver, 2.889 Å.) The distances may imply some bonding between the silver atoms, but it is difficult to include any such bonding in a description of the coordination.

The 'side-on' bonding of the ethynyl groups to Ag2 is of interest, as the metal atom does not lie on the perpendicular bisector of the triple bond. The distances Ag2-C1 and Ag2-C2 are 2.55 and 3.04 Å., and the angle between the direction of the triple bond and the line joining Ag2 to the mid-point of the ethynyl group is 66°. The 'oblique' bonding brings the silver atoms closer together, for if the 'side-on' bonding were symmetrical the silver-silver distance would be 3.5 Å, and this could be due to silver-silver bonding.

The ethynyl carbon atom C1 is not coplanar with the phenyl carbon atoms. The equation of the mean plane through the phenyl carbon atoms is:

$$-0.7374\ x' + 0.6660\ y + 0.1127\ z' = 0.5044$$

where coordinates are expressed in Å., and are referred to axes parallel to 'a', 'b', and 'c'. The distances of the atoms C3-C8 from the plane are respectively 0.012, -0.007, 0.003, -0.004, 0.009, and -0.013 Å., with a mean distance of 0.008 Å., while the atoms C1 and C2 are at distances 0.131 and 0.033 Å. from the plane. The bond C3-C2 is therefore not significantly out of the plane of the phenyl group, but C2-C1 is tilted out of the plane by about 5°. The distances of the silver atoms from the plane are 0.504 Å. for Ag1, and 0.252 Å. for Ag2, so that the bonding to the silver atoms is appreciably out of the plane of the phenyl group. However the ethynyl carbon atoms C1 and C2 are coplanar with the silver atoms to 0.05 Å., the plane

$$-0.8254\,x' + 0.5643\,y + 0.0248\,z' = 0$$

passing through the two silver atoms Ag1 and Ag2, with C1 and C2 at distances $\pm$0.048 Å. The equation of the best plane through the silver atoms and the atoms of the two phenylethynyl groups attached to Ag1 is

$$-0.7788\,x' + 0.6259\,y + 0.0426\,z' = 0$$

None of these atoms is more than 0.2 Å. from the plane, and the mean distance is 0.09 Å. The phenyl group is inclined at 5° to the plane.

The bond lengths and angles are tabulated in table X. Standard deviations were calculated as in the copper compound. For angles where the coordinate error for Ag2 made a significant contribution to the error in the bond angle, the full formula for standard deviations of bond angles was used, because $\sigma(x)$ and $\sigma(z)$ for this atom are zero, but not $\sigma(y)$.

The C≡C distance in the ethynyl group is 1.208 $\pm$ 0.018Å., very close to the mean distance for triple bonds. (1.205Å.) The bonding is not quite linear, as the angles Ag1-C1-C2 and C1-C2-C3 are 172.9 $\pm$ 1.2° and 175.5 $\pm$ 1.4° respectively. On the basis of the calculated standard deviations the probabilities that the quoted angles are 180° are 0.001% and 0.1% respectively, so that both angles are significantly different from 180°. The ethynyl group adopts a cis configuration, and the distortion increases the distance between the silver atoms by 0.1 Å. The four atoms Ag1, C1, C2, and C3, are coplanar to better than 0.01Å., and their mean plane makes an angle of about 58° with the plane of the phenyl group, so that the distortion of the ethynyl group is out of the plane of the phenyl group. This is in contrast to the copper compound, where the 8° distortion from 180° of the angle C2-C1-Cu1 is in the plane of the phenyl group, (C3-C8).

TABLE X. $Me_3PAgC{\equiv}CPh$: Bond Lengths and Bond Angles.

	Length (Å.)	e.s.d.		Angle (Degrees)	e.s.d.
Ag1-Ag2	3.033	0.001	Ag1-Ag2-Ag1"	175.0	0.1
Ag2-P	2.490	0.004	Ag1-Ag2-P	98.5	0.1
			Ag1-Ag2-P"	84.1	0.1
Ag1-C1	2.040	0.013			
			P-Ag2-P"	118.4	0.2
Ag2-C1	2.552	0.014	C1-Ag2-C1"	107.4	0.6
			P-Ag2-C1	95.0	0.3
Ag2-C2	3.040	0.012	P-Ag2-C1"	121.3	0.3
C1-C2	1.208	0.018	Ag2-Ag1-C1	56.4	0.4
			Ag1-C1-Ag2	81.9	0.5
C2-C3	1.452	0.018	Ag1-C1-C2	172.9	1.2
			Ag2-C1-C2	101.9	0.7
C3-C4	1.402	0.021			
			C1-C2-C3	175.5	1.4
C4-C5	1.419	0.024			
			C2-C3-C4	120.1	1.2
C5-C6	1.350	0.024	C2-C3-C8	120.6	1.2
C6-C7	1.404	0.022	C3-C4-C5	118.8	1.5
			C4-C5-C6	121.1	1.6
C7-C8	1.421	0.021	C5-C6-C7	121.4	1.5
			C6-C7-C8	117.2	1.4
C8-C3	1.372	0.022	C7-C8-C3	122.1	1.3
			C8-C3-C4	119.4	1.3
P-C9	1.825	0.019			
			Ag2-P-C9	109.4	0.6
P-C10	1.842	0.019	Ag2-P-C10	122.2	0.6
			Ag2-P-C11	117.2	0.6
P-C11	1.841	0.016			
			C9-P-C10	103.0	0.8
			C10-P-C11	100.4	0.8
			C11-P-C9	102.2	0.8

The double prime refers to the atom at $-x, y, \frac{1}{2}-z$, i.e. to the atom related by the two-fold axis.

The silver-carbon distance for the 'end-on' bonded ethynyl group is 2.040 ± 0.013Å., shorter than the value of 2.13Å. found in $KAg(CN)_2$.(Hoard, 1933). The distance is only 0.08Å. greater than the distance Cu1-C1 in the copper compound, whereas the difference between the tetrahedral covalent radii of silver and copper is 0.18Å. There may be rather more 'end-on' π-bonding in the silver compound, but much of the shortening of the metal-carbon bond relative to the copper compound will be because Ag1 is linearly coordinated, while Cu1 is trigonally coordinated. The silver-carbon distances of 2.55 and 3.04Å. for the 'side-on' bonding are long, suggesting only a weak interaction between the metal atom and the ethynyl group. Similar silver-carbon distances are observed in the complexes of silver nitrate with cyclooctatetraene, and with its dimer, and also in the silver perchlorate benzene complex. (Matthews and Lipscomb, 1959; Nyburg and Hilton, 1959; Smith and Rundle, 1958).

The mean carbon-carbon bond length in the phenyl ring is 1.395Å. and the mean bond angle is 120.0°, and these values are the same as are found in other compounds. None of the individual values differs significantly from the mean. Assuming that the phenyl ring is a regular hexagon, a standard deviation in the bond lengths of 0.028Å. may

be deduced, and in the bond angles, 1.9°. The standard deviations quoted in table X and in the text were obtained from the least squares estimates of the coordinate errors, and the mean values for bond lengths and angles in the phenyl ring are 0.022Å. and 1.4°, rather less than the above values. Standard deviations obtained by the least squares method are sometimes optimistic, and the errors quoted ought probably to be increased by about a third.

The single bond C2-C3 is contracted to 1.45Å., a value in good agreement with the corresponding lengths in the copper compound.

The phosphorus-carbon bond distances are 1.83, 1.84, and 1.84Å., with the mean value of 1.836Å. very similar to the mean phosphorus-carbon distance in the copper compound. The carbon-phosphorus-carbon angles do not differ significantly from one another but the angles Ag2-P-C9, Ag2-P-C10, Ag2-P-C11 are respectively 109.4, 122.2, and 117.2°, all with e.s.d.'s of 0.6°. As in the copper compound, these values are significantly different from one another, although the range is even greater in this case. Probably the angles are distorted in order to improve the packing. The three methyl groups lie in between the phenyl group, and a parallel phenyl group from the chain related by the translation a. The plane through the methyl carbons makes an angle of 11° with the

planes of the phenyl groups, whereas the angle would be 18° if the angles at the phosphorus atom were regular. The distortion brings C9 within 3.54Å. of Ag2.

The silver-phosphorus distance of 2.490Å. is nearer the sum of the covalent radii of the atoms, (2.6Å.), than is the case in the copper compound. However the slight contraction does suggest some $d\pi-d\pi$ bonding. This is supported by the valence angles at the phosphorus atom, where the mean values of the Ag-P-C and the C-P-C angles are 116° and 102°.

The non-bonding contacts in the crystal of less than 4Å, are tabulated in table XI. Contacts between groups attached to the silver atoms in any one chain are all greater than 3.7Å. Distances between atoms in adjacent chains are all greater than 3.7Å., except for contacts between phenyl carbon atoms related by the centre of symmetry at $(\frac{1}{4},\frac{1}{4},0)$. The planes of the two rings are parallel, and are only 3.3Å. apart, and there are three independent contacts of 3.41, 3.42, 3.44Å. between atoms C6, C7, C8, and the symmetry related atoms.

The magnitudes and directions of the principal axes of the thermal vibration ellipsoids for the silver and the phosphorus atoms are given in table XII. The U_{ij}'s, which are referred to monoclinic axes, were first transformed to

TABLE XI. $Me_3AgC{\equiv}CPh$: Non-bonding Distances less than 4Å.

1. Atoms in the same chain.

x, y, z		-x, y, $\frac{1}{2}$-z		x, -y, $\frac{1}{2}$+z	
Ag1-C9	3.77	Ag1-P	3.72	C9-C7	3.90
C1-C9	3.68	C10-Ag1	3.95	C10-C1	3.90
C8-C10	3.92	C2-C2	3.99	C11-C1	3.85

2. Atoms in chains related by the C centering.

$\frac{1}{2}$+x, $\frac{1}{2}$+y z		$\frac{1}{2}$-x, $\frac{1}{2}$-y, 1-z	
C5-C11	3.90	C5-C7	3.72
		C6-C6	3.93
		C6-C7	3.41
		C6-C8	3.44
		C7-C7	3.42
		C7-C8	3.71

3. Atoms in chains related by the translation a.

1-x, -y, 1-z		1-x, y, 3/2-z	
C5-C11	3.99	C6-C7	3.99
C6-C9	3.98	C7-C7	3.70
C7-C9	3.89		

The first atom is always in the standard position, (x,y,z)

parameters U'_{ij}, referred to orthogonal axes parallel to a*, b, and c. (Rollett and Davies, 1955). The equations for this transformation are given in appendix C. An analysis of the anisotropic thermal motion of the carbon atoms was

TABLE XII. The Magnitudes and Directions of the Principal Axes of the Vibration Ellipsoids for the Silver and Phosphorus Atoms.

Atom		U	$10^4 g_{i1}$	$10^4 g_{i2}$	$10^4 g_{i3}$
Ag1	i=1	0.0430	8662	0714	-4948
	i=2	0.0593	4028	6440	6510
	i=3	0.0781	3462	-7883	5084
Ag2	i=1	0.0428	-5318	0000	8467
	i=2	0.0527	8466	0000	5316
	i=3	0.0826	0000	10000	0000
P	i=1	0.0409	0762	0069	-9970
	i=2	0.0511	9518	-2916	0925
	i=3	0.0722	2901	9562	0367

'g_{ij}' is the direction cosine of the principal axis 'i' with respect to the cell axis 'j'.

'U' is the magnitude of the axis of the vibration ellipsoid in $\mathring{A}^2$.

not undertaken, as the U_{ij}'s for these atoms are not reliable.

The major axis for Ag1 is perpendicular to the two σ-bonds to the ethynyl groups, and the major axis for Ag2 lies along the b axis, a direction which involves least distortion of the tetrahedrally arranged bonds. As might be expected, the major axis for the phosphorus atom is approximately perpendicular to the silver-phosphorus bond.

The vibration amplitudes for the light atoms are large, as they are in each of the complexes studied. The average temperature factors for the phenyl and the methyl carbon atoms correspond to B values of about 6 and 8 Å^2. respectively. The temperature factors are generally larger for atoms furthest from the silver-silver chain.

TABLE VII Observed and Calculated Structure Factors

Successive columns give values of h, k, $|F_o|$, F_c

l = 0

0	0	---	1136	1	5	196	193	4	10	103	99	2	16	74	76
2	0	120	118	3	5	348	314	6	10	136	138	4	16	66	58
4	0	270	262	5	5	167	169	8	10	51	52	6	16	37	41
6	0	137	130	7	5	122	118	10	10	37	33	8	16	30	32
8	0	102	101	9	5	60	65	12	10	26	20	10	16	26	21
10	0	55	52	11	5	33	43								
12	0	27	24	13	5	21	13	1	11	196	184	1	17	69	66
								3	11	166	153	3	17	49	47
1	1	---	364	0	6	213	200	5	11	116	104	5	17	62	58
3	1	302	275	2	6	242	238	7	11	53	58	7	17	27	28
5	1	236	228	4	6	182	189	9	11	32	39	9	17	25	29
7	1	89	90	6	6	158	154	11	11	25	22				
9	1	98	93	8	6	106	104					0	18	55	52
11	1	39	36	10	6	37	37	0	12	194	183	2	18	62	64
13	1	29	24	12	6	26	27	2	12	121	121	4	18	46	45
								4	12	128	130	6	18	33	34
0	2	---	346	1	7	298	271	6	12	60	63	8	18	19	21
2	2	254	245	3	7	213	226	8	12	42	44				
4	2	259	251	5	7	143	130	10	12	34	33	1	19	60	61
6	2	159	159	7	7	135	133					3	19	34	38
8	2	109	108	9	7	24	27	1	13	143	133	5	19	28	29
10	2	65	65	11	7	42	44	3	13	82	80	7	19	34	28
12	2	30	24					5	13	97	92				
				0	8	159	158	7	13	58	55	0	20	45	45
1	3	---	383	2	8	285	272	9	13	47	46	2	20	32	31
3	3	248	252	4	8	180	174					4	20	35	33
5	3	197	195	6	8	120	117	0	14	161	157	6	20	28	26
7	3	104	106	8	8	65	62	2	14	59	58	8	20	20	19
9	3	80	83	10	8	33	33	4	14	136	131				
11	3	31	29	12	8	31	28	6	14	31	36	1	21	24	22
13	3	25	23					8	14	38	40	3	21	39	38
				1	9	200	180	10	14	27	29	5	21	24	21
0	4	284	262	3	9	174	167					7	21	28	26
2	4	469	435	5	9	136	118	1	15	117	115				
4	4	170	170	7	9	129	123	3	15	83	84	0	22	25	17
6	4	153	147	9	9	39	38	5	15	66	63	2	22	41	38
8	4	78	82	11	9	35	32	7	15	22	21	4	22	<26	17
10	4	46	50					9	15	38	38				
12	4	30	25	0	10	127	122					1	23	23	22
				2	10	222	208	0	16	104	98	3	23	30	26

TABLE VII -continued

l = 0

0	24	<26	1
2	24	26	27
1	25	<27	12
3	25	20	15
0	26	27	20

l = 1

-13	1	<33	3
-11	1	<27	5
- 9	1	<24	3
- 7	1	18	-13
- 5	1	<19	9
- 3	1	85	-71
- 1	1	---	-41
+ 1	1	34	+40
3	1	46	+47
5	1	36	+36
7	1	20	-12
9	1	<28	+16
11	1	<33	-10
-12	2	24	-19
-10	2	28	29
- 8	2	33	-32
- 6	2	39	42
- 4	2	<20	-1
- 2	2	79	81
0	2	---	-12
+ 2	2	94	-81
4	2	80	+78
6	2	27	-31
8	2	28	+26
10	2	<26	-3
-13	3	<24	-3
-11	3	<23	-10
- 9	3	20	19
- 7	3	19	-18
- 5	3	57	58
- 3	3	106	82
- 1	3	---	130
+1	3	226	-163
3	3	<21	+13
5	3	<17	+9
7	3	<19	-4
9	3	25	+28
11	3	<24	-11
-8	4	26	-26
-6	4	34	32
-4	4	87	81
-2	4	188	-136
0	4	110	89
2	4	<20	-10
4	4	83	+79
6	4	24	-18
8	4	34	+31
-7	5	25	-25
-5	5	29	31
-3	5	51	-54
-1	5	141	124
+1	5	83	-73
3	5	94	+84
5	5	27	+28
7	5	33	+31
-8	6	<34	5
-6	6	25	20
-4	6	78	73
-2	6	18	13
0	6	68	+63
2	6	19	-26
4	6	33	+40
6	6	<31	+3
-7	7	<32	12
-5	7	59	64
-3	7	<23	13
-1	7	94	70
+1	7	33	+39
3	7	22	-21
5	7	26	+28
7	7	<34	+18
-8	8	<35	-5
-6	8	43	40
-4	8	31	-33
-2	8	29	31
0	8	24	+23
2	8	91	+86
4	8	27	+28
6	8	33	+34
-7	9	29	28
-5	9	47	-46
-3	9	53	53
-1	9	20	18
+1	9	96	+87
3	9	<27	+6
5	9	63	+61
7	9	<36	+15
-8	10	29	26
-6	10	<32	15
-4	10	38	38
-2	10	58	57
0	10	<24	-5
2	10	110	+100
4	10	21	-17
6	10	21	+24
-7	11	32	30
-5	11	<31	-8
-3	11	76	71
-1	11	<26	1
+1	11	79	+71
3	11	27	+26
5	11	<33	+8
7	11	34	+31
-8	12	40	44
-6	12	44	-38
-4	12	25	26
-2	12	26	28
0	12	<26	15
2	12	93	+82
4	12	<32	+19
6	12	40	+40
-5	13	<33	-8
-3	13	42	39
-1	13	<29	13
+1	13	51	+48
3	13	51	+51
5	13	<35	+13
-6	14	28	30
-4	14	27	26
-2	14	35	34
0	14	32	+33
2	14	33	+31
4	14	<34	+8
6	14	26	+19
-5	15	<35	13
-3	15	30	24
-1	15	32	32
+1	15	29	+29
3	15	<31	+12
5	15	34	+36
-6	16	30	24
-4	16	<31	-4
-2	16	20	19
0	16	40	+35
2	16	<34	+16
4	16	38	+39
-5	17	40	38
-3	17	<35	-4
-1	17	36	32
+1	17	<34	+19
3	17	27	+24
-4	18	29	30
-2	18	<35	13
0	18	42	+39
2	18	<36	-12
4	18	27	+25
-1	19	34	33
+1	19	<28	-4
3	19	27	+31

l = 2

-12	0	<25	-3
-10	0	40	-43
-8	0	21	20
-6	0	80	-83
-4	0	65	62
-2	0	<19	19
0	0	80	73
2	0	25	18
4	0	33	-33
6	0	<17	-9
8	0	19	-17
10	0	<20	8
-13	1	<38	0
-11	1	<26	-16
-9	1	<24	0
-7	1	27	-31
-5	1	25	-35
-3	1	187	171
-1	1	---	-157
+1	1	64	66

TABLE VII - continued

l = 2

3	1	97	-94	-8	6	26	-25	-3	13	32	30	7	1	25	-19
5	1	44	49	-6	6	58	59	-1	13	37	-39	9	1	<27	+2
7	1	25	-25	-4	6	40	-44	+1	13	53	61				
9	1	<26	-5	-2	6	86	-73	3	13	38	-41	-14	2	<30	-0
11	1	<33	-2	0	6	44	38					-12	2	<26	-5
				2	6	22	-18	-4	14	42	43	-10	2	<24	-9
-12	2	<26	1	4	6	16	19	-2	14	<25	-2	-8	2	<23	-3
-10	2	28	-23					0	14	26	24	-6	2	<20	13
-8	2	25	23	-7	7	<26	14					-4	2	<17	-5
-6	2	24	-24	-5	7	21	-23	-3	15	33	36	-2	2	110	-110
-4	2	26	38	-3	7	17	-17	-1	15	<23	0	0	2	65	+65
-2	2	57	-49	-1	7	45	50	+1	15	50	55	2	2	25	-26
0	2	61	-57	+1	7	<18	5					4	2	<21	-2
2	2	<16	-14	3	7	51	53	-4	16	26	28	6	2	<22	+3
4	2	33	-34	5	7	<21	-25	-2	16	---	13	8	2	<25	-8
6	2	23	22									10	2	<27	+1
8	2	<31	-13	-8	8	36	-42	-3	17	---	13				
10	2	<27	2	-6	8	21	22	-1	17	<24	11	-13	3	<24	5
				-4	8	25	-24	[illegible]				-11	3	33	-34
-13	3	<24	0	-2	8	36	36	[illegible]				-9	3	23	26
-11	3	20	-17	0	8	29	25	-2	18	---	16	-7	3	40	-39
-9	3	<20	-8	2	8	<23	8					-5	3	73	65
-7	3	20	-19	4	8	25	29	-1	19	<25	17	-3	3	96	-79
-5	3	<17	2					[illegible]				-1	3	48	-46
-3	3	<16	-17	-5	9	22	20	-2	20	---	14	+1	3	91	+78
-1	3	70	74	-3	9	48	-49					3	3	92	-91
+1	3	56	-45	-1	9	38	40	-1	21	<26	11	5	3	31	+33
3	3	23	19	+1	9	51	-52					7	3	23	-19
5	3	<17	-10	3	9	58	63	-2	22	---	11	9	3	<23	+3
7	3	<20	-9	5	9	31	-32					11	3	<24	-6
9	3	<22	-7					-1	23	27	24				
11	3	<24	-5	-6	10	21	16					-10	4	<28	-20
				-4	10	25	-24	-2	24	---	9	-8	4	<24	13
-8	4	<27	-23	-2	10	49	49					-6	4	55	-53
-6	4	<22	3	0	10	54	-50					-4	4	36	36
-4	4	33	-37	2	10	23	25		l = 3			-2	4	129	-115
-2	4	49	37	[illegible]								0	4	31	13
0	4	69	65	-5	11	<27	16					2	4	34	34
2	4	32	38	-3	11	<23	5	-13	1	<33	9	4	4	43	-44
4	4	27	-22	-1	11	36	42	-11	1	<26	-10				
				+1	11	<23	15	-9	1	23	21	-11	5	26	-22
-7	5	<25	-2	3	11	21	21	-7	1	40	-39	-9	5	<26	12
-5	5	21	21					-5	1	21	21	-7	5	17	-22
-3	5	48	-56	-4	12	34	33	-3	1	74	-84	-5	5	52	-53
-1	5	33	35	-2	12	<23	18	-1	1	<17	-8	-3	5	52	-48
+1	5	52	-49	0	12	22	17	+1	1	14	+14	-1	5	86	-74
3	5	18	21	2	12	<27	12	3	1	14	-14	+1	5	58	-50
5	5	<27	-10					5	1	31	+36	3	5	44	43

TABLE VII-continued

1 = 3

5	5	18	+18
-10	6	<28	-19
-8	6	<24	3
-6	6	43	-53
-4	6	38	41
-2	6	106	-95
-0	6	<13	-10
2	6	17	-17
4	6	<22	-3
-9	7	<27	-8
-7	7	21	-25
-5	7	25	-28
-3	7	<17	-4
-1	7	10	-15
+1	7	68	-64
3	7	<19	-10
5	7	<24	-5
-8	8	31	-34
-6	8	23	-25
-4	8	46	-48
-2	8	17	-18
0	8	68	-61
2	8	<18	-5
4	8	<23	-5
-9	9	29	-27
-7	9	19	-19
-5	9	45	-51
-3	9	68	-61
-1	9	19	18
+1	9	36	-39
3	9	<20	-8
5	9	32	-34
-8	10	52	-49
-6	10	<22	-2
-4	10	44	-45
-2	10	27	23
0	10	81	-73
2	10	<21	-4
4	10	29	-28
-9	11	53	-52
-7	11	<22	8
-5	11	58	-61
-3	11	<19	-8
-1	11	<18	35
+1	11	61	-60
3	11	<22	-4
5	11	31	-35
-8	12	37	-37
-6	12	<23	-15
-4	12	64	-65
-2	12	<20	-14
0	12	31	-33
2	12	<21	-1
4	12	36	-37
-9	13	31	-31
-7	13	<27	-19
-5	13	33	-41
-3	13	24	-26
-1	13	19	-20
+1	13	28	-28
-8	14	25	-26
-6	14	21	-15
-4	14	31	-34
-2	14	<21	-7
0	14	33	-35
2	14	21	-21
-7	15	33	-31
-5	15	16	-12
-3	15	35	-38
-1	15	20	-23
+1	15	<23	-4
-6	16	34	-33
-4	16	24	-24
-2	16	32	-34
0	16	20	-17
-7	17	31	-27
-5	17	17	-19
-3	17	21	-14
-1	17	35	-36
-6	18	27	-29
-4	18	<26	-3
-2	18	36	-37
-5	19	23	-13
-3	19	<27	-18
-1	19	31	-31
-6	20	27	-22
-4	20	<28	-7
-2	20	29	-32

1 = 4

-14	0	25	19
-12	0	64	67
-10	0	67	66
-8	0	138	135
-6	0	245	245
-4	0	335	303
-2	0	171	206
0	0	206	200
2	0	313	311
4	0	79	80
6	0	106	105
8	0	40	41
10	0	25	24
-13	1	35	32
-11	1	82	81
-9	1	87	83
-7	1	240	239
-5	1	167	173
-3	1	315	335
-1	1	239	251
+1	1	214	216
3	1	165	164
5	1	108	108
7	1	74	81
9	1	25	15
11	1	---	22
-14	2	30	19
-12	2	59	59
-10	2	74	73
-8	2	173	162
-6	2	230	227
-4	2	232	228
-2	2	270	288
0	2	231	218
2	2	226	219
4	2	111	111
6	2	93	97
8	2	40	39
10	2	32	23
-15	3	27	20
-13	3	29	32
-11	3	70	73
-9	3	93	97
-7	3	175	175
-5	3	225	228
-3	3	283	282
-1	3	238	237
+1	3	190	208
3	3	184	181
5	3	97	97
7	3	52	58
9	3	33	33
11	3	24	16
-14	4	31	38
-12	4	39	46
-10	4	75	81
-8	4	128	129
-6	4	189	181
-4	4	230	240
-2	4	277	276
0	4	238	233
2	4	187	182
4	4	148	136
6	4	65	66
8	4	48	47
-13	5	---	35
-11	5	44	49
-9	5	138	136
-7	5	125	121
-5	5	186	197
-3	5	258	252
-1	5	290	291

TABLE VII -continued

$k = 4$

+1	5	168	170
3	5	132	131
5	5	108	112
7	5	43	43
9	5	41	35
-14	6	34	31
-12	6	33	33
-10	6	88	94
-8	6	92	107
-6	6	177	165
-4	6	221	233
-2	6	203	201
0	6	259	239
2	6	154	143
4	6	131	132
6	6	36	44
8	6	45	47
-13	7	33	37
-11	7	38	41
-9	7	115	123
-7	7	69	71
-5	7	230	227
-3	7	184	187
-1	7	208	212
+1	7	213	202
3	7	118	116
5	7	84	87
7	7	43	41
9	7	37	36
-14	8	32	29
-12	8	30	28
-10	8	73	82
-8	8	90	90
-6	8	138	132
-4	8	186	175
-2	8	191	205
0	8	260	252
2	8	75	73
4	8	127	121
6	8	45	54
8	8	40	40
-13	9	30	29
-11	9	42	47
-9	9	80	85
-7	9	88	91
-5	9	206	197
-3	9	129	121
-1	9	205	206
+1	9	155	151
3	9	93	100
5	9	69	71
7	9	38	35
-12	10	32	34
-10	10	58	62
-8	10	79	80
-6	10	131	124
-4	10	175	160
-2	10	128	130
0	10	190	175
2	10	106	103
4	10	88	85
6	10	40	47
8	10	30	35
-11	11	39	41
-9	11	48	59
-7	11	96	100
-5	11	114	117
-3	11	135	126
-1	11	169	164
+1	11	117	111
3	11	87	87
5	11	61	62
7	11	34	39
-12	12	30	30
-10	12	37	39
-8	12	72	77
-6	12	91	91
-4	12	117	120
-2	12	150	145
0	12	105	98
2	12	102	102
4	12	59	59
6	10	50	52
-11	13	31	34
-9	13	37	41
-7	13	99	98
-5	13	81	85
-3	13	133	132
-1	13	168	168
+1	13	111	104
3	13	83	85
5	13	32	33
7	13	40	34
-10	14	31	33
-8	14	66	69
-6	14	67	69
-4	14	77	82
-2	14	129	121
0	14	53	52
2	14	93	91
4	14	44	44
6	14	45	46
-9	15	27	26
-7	15	86	82
-5	15	45	48
-3	15	107	107
-1	15	68	66
+1	15	75	69
3	15	67	64
5	15	33	35
7	15	31	27
-8	16	38	42
-6	16	59	64
-4	16	62	66
-2	16	81	82
0	16	42	44
2	16	75	71
4	16	37	35
6	16	30	26
-9	17	27	24
-7	17	51	53
-5	17	48	49
-3	17	61	64
-1	17	50	53
+1	17	58	56
3	17	43	40
5	17	29	27
-8	18	30	33
-6	18	42	43
-4	18	44	43
-2	18	53	55
0	18	44	48
2	18	38	39
4	18	29	29
-7	19	<25	24
-5	19	51	50
-3	19	35	37
-1	19	37	42
+1	19	47	47
3	19	31	26
-6	20	28	29
-4	20	38	40
-2	20	31	30
0	20	46	46
-5	21	34	32
-3	21	<33	23
-1	21	47	38
+1	21	28	26
-4	22	32	26
-2	22	24	19
0	22	34	33
-2	24	29	18

$l = 5$

-13	1	<27	2
-11	1	<25	3
-9	1	21	13
-7	1	<18	-9
-5	1	26	-24
-3	1	60	70
-1	1	28	-35
+1	1	19	+17
3	1	<18	-10
5	1	<20	+9
7	1	<26	-4
9	1	<33	+3

TABLE VII -continued

l = 5

-14	2	<27	-3	-10	6	<28	-7	4	10	46	+51	-2	18	17	17
-12	2	<26	13	-8	6	24	26					0	18	15	+19
-10	2	25	-17	-6	6	10	8	-9	11	17	20	2	18	27	+30
-8	2	49	49	-4	6	14	14	-7	11	<25	2				
-6	2	61	-56	-2	6	23	21	-5	11	55	56	-3	19	27	26
-4	2	41	37	0	6	40	+37	-3	11	12	11	-1	19	---	8
-2	2	<22	-2	2	6	34	+38	-1	11	48	52	+1	19	19	+22
0	2	18	+19	4	6	<19	-1	+1	11	<19	-16			l = 6	
2	2	33	+30	6	6	22	+22	3	11	46	+50	-14	0	<22	-10
4	2	<18	-11									-12	0	<22	-12
6	2	<22	11	-9	7	<21	10	-6	12	42	47	-10	0	19	11
8	2	<27	-5	-7	7	<16	13	-4	12	<17	9	-8	0	31	-35
				-5	7	25	26	-2	12	38	42	-6	0	53	51
-13	3	<23	9	-3	7	23	27	0	12	24	+19	-4	0	81	-71
-11	3	<21	-2	-1	7	14	15	2	12	<19	+10	-2	0	17	20
-9	3	<21	4	+1	7	46	+50	4	12	30	+31	0	0	30	-34
-7	3	45	44	3	7	<19	+6					2	0	<16	7
-5	3	84	-70	5	7	17	+18	-5	13	29	34	4	0	23	23
-3	3	49	49					-3	13	17	16	6	0	25	-27
-1	3	<21	-0	-10	8	<23	19	-1	13	46	48	8	0	<22	6
+1	3	68	+65	-8	8	<18	-5	+1	13	<20	-4				
3	3	<18	-10	-6	8	41	42	3	13	35	+39				
5	3	20	+13	-4	8	37	38								
7	3	<23	-1	-2	8	10	12	-6	14	18	13				
9	3	<24	+2	0	8	37	+36	-4	14	31	34				
				2	8	<17	+6	-2	14	18	20	-13	1	28	-26
-10	4	<27	-7	4	8	27	+27	0	14	25	+23	-11	1	<25	4
-8	4	39	47					2	14	21	+25	-9	1	<23	-7
-6	4	72	-70	-9	9	16	14	4	14	24	+24	-7	1	<19	11
-4	4	92	77	-7	9	<17	14					-5	1	57	-57
-2	4	54	41	-5	9	54	57	-5	15	22	21	-3	1	20	15
0	4	34	-34	-3	9	15	-19	-3	15	19	19	-1	1	30	29
2	4	57	+55	-1	9	55	57	-1	15	21	20	+1	1	24	-25
4	4	<19	---	+1	9	25	+29	+1	15	29	+32	+3	1	24	24
6	4	18	+21	3	9	<20	+7	3	15	18	+11	5	1	27	-24
				5	9	18	+18					7	1	<30	4
-9	5	<25	-0					-4	16	20	20				
-7	5	53	52	-10	10	27	28	-2	16	<20	17	-14	2	<29	-9
-5	5	50	-44	-8	10	16	-16	0	16	29	+28	-12	2	<28	-17
-3	5	47	41	-6	10	45	50	2	16	20	+22	-10	2	<25	8
-1	5	22	20	-4	10	17	18					-8	2	29	-32
+1	5	51	+54	-2	10	44	44	-3	17	32	33	-6	2	28	27
3	5	<18	-5	0	10	25	+17	-1	17	<21	8	-4	2	47	-51
5	5	<20	+1	2	10	<18	+7	+1	17	28	+33	-2	2	47	46

TABLE VII -continued

l = 6

-0	2	<12	-6	-11	7	22	-21	-5	15	<20	11	2	2	28	+26
2	2	18	18	-9	7	<18	-1	-3	15	<18	-5	4	2	25	-21
4	2	<18	-7	-7	7	<17	1	-1	15	14	16	6	2	<26	+7
6	2	23	-18	-5	7	<12	6					8	2	<27	-1
8	2	<27	-1	-3	7	32	35	-6	16	25	28				
				-1	7	43	-42	-4	16	17	-11	-15	3	<24	1
-13	3	<25	-12	+1	7	26	27	-2	16	21	25	-13	3	<23	-9
-11	3	<21	1	3	7	25	-28					-11	3	<22	15
-9	3	<16	-14	5	7	19	20	-3	17	<21	-1	-9	3	44	-48
-7	3	<14	-7					-1	17	27	26	-7	3	13	14
-5	3	26	22	-10	8	20	-19					-5	3	51	-45
-3	3	47	-47	-8	8	30	33	-4	18	<22	5	-3	3	13	13
-1	3	32	34	-6	8	50	-49	-2	18	18	18	-1	3	22	-25
+1	3	15	-18	-4	8	72	66					+1	3	<14	+9
3	3	<18	4	-2	8	18	-20	-3	19	21	17	3	3	<17	+6
5	3	<22	-4	0	8	17	13					5	3	21	-15
7	3	<24	-3	2	8	<17	-13	-4	20	22	21	7	3	<24	+9
-10	4	<25	-11	-9	9	<26	9	-3	21	24	18	-12	4	<25	11
-8	4	14	-11	-7	9	<22	-16					-10	4	15	-17
-6	4	13	17	-5	9	13	16					-8	4	36	-36
-4	4	< 9	4	-3	9	35	37		l = 7			-6	4	18	18
-2	4	27	-26	-1	9	<14	-6					-4	4	43	-40
-0	4	<11	-2	+1	9	12	13					-2	4	43	40
2	4	<16	8					-15	1	<32	-2	0	4	37	-31
4	4	<21	-14	-6	10	<18	-1	-13	1	<27	-5	2	4	<16	-13
				-4	10	12	14	-11	1	<24	5	4	4	<21	-14
-11	5	---	-17	-2	10	15	17	-9	1	23	-19				
-9	5	<17	-4					-7	1	<17	12	-11	5	<19	8
-7	5	<15	-11	-5	11	16	10	-5	1	<24	1	-9	5	50	-51
-5	5	<10	10	-3	11	<16	3	-3	1	24	19	-7	5	19	-20
-3	5	13	12	-1	11	<15	7	-1	1	11	-10	-5	5	37	-33
-1	5	<10	6					+1	1	<14	+2	-3	5	13	14
+1	5	16	20	-6	12	18	15	3	1	24	-24	-1	5	<11	-10
3	5	24	-26	-4	12	<15	-7	5	1	<26	+0	+1	5	30	-33
5	5	<22	4	-2	12	25	26	7	1	<30	+5	3	5	<18	+8
												5	5	26	-26
-10	6	29	-31	-5	13	<17	9	-14	2	<27	-10				
-8	6	21	19	-3	13	<16	6	-12	2	<25	9	-12	6	<25	-2
-6	6	40	-43	-1	13	17	16	-10	2	<22	-4	-10	6	20	-19
-4	6	92	82					-8	2	38	-44	-8	6	15	-16
-2	6	40	-39	-6	14	26	29	-6	2	35	33	-6	6	35	-36
0	6	36	30	-4	14	20	-21	-4	2	45	-40	-4	6	25	-23
2	6	<16	-6	-2	14	19	20	-2	2	41	35	-2	6	<17	12
4	6	<21	-8					0	2	46	-43	0	6	30	-36

TABLE VII -continued

l = 7

2	6	<17	+1
4	6	<21	+2
-11	7	<21	-12
-9	7	16	-15
-7	7	18	-17
-5	7	44	-44
-3	7	20	-18
-1	7	13	-10
+1	7	<16	-8
3	7	<18	-6
-12	8	21	-19
-10	8	<18	-9
-8	8	11	-12
-6	8	31	-32
-4	8	<12	-6
-2	8	<12	-10
0	8	28	-30
2	8	<17	-11
-11	9	29	-29
-9	9	<17	4
-7	9	39	-39
-5	9	<14	-0
-3	9	34	-35
-1	9	25	-27
+1	9	<17	+2
3	9	17	-18
-12	10	17	-19
-10	10	<21	-9
-8	10	<17	-11
-6	10	49	-47
-4	10	<14	-13
-2	10	50	-48
0	10	15	+11
2	10	14	-17
-11	11	22	-21
-9	11	<18	-3
-7	11	34	-38
-5	11	<17	4
-3	11	65	-64
-1	11	<16	-4
+1	11	<18	-1
3	11	18	-13
-12	12	21	-17
-10	12	20	-15
-8	12	<18	-11
-6	12	26	-27
-4	12	<16	8
-2	12	62	-59
0	12	13	+12
2	12	24	-25
-11	13	23	-21
-9	13	<21	-8
-7	13	28	-28
-5	13	<18	-12
-3	13	29	-33
-1	13	<17	-11
+1	13	<19	-6
-10	14	<23	-11
-8	14	22	-22
-6	14	20	-21
-4	14	24	-25
-2	14	22	-24
0	14	<19	-2
-9	15	<22	-13
-7	15	18	-19
-5	15	17	-20
-3	15	<18	-9
-1	15	18	-21
+1	15	<22	-5
-10	16	<24	-14
-8	16	22	-17
-6	16	<21	-8
-4	16	23	-25
-2	16	<19	7
0	16	23	-27
-9	17	28	-23
-7	17	<22	-9
-5	17	31	-29
-3	17	<21	-3
-1	17	<22	-5
+1	17	19	-18
-10	18	23	-16
-8	18	<23	-15
-6	18	<22	-12
-4	18	24	-21
-9	19	27	-20
-7	19	<24	-3
-5	19	18	-20

l = 8

-16	0	<32	10
-14	0	51	52
-12	0	45	49
-10	0	131	133
-8	0	92	98
-6	0	172	172
-4	0	169	174
-2	0	148	152
0	0	120	117
2	0	64	67
4	0	74	73
6	0	25	22
8	0	---	22
-15	1	35	31
-13	1	45	48
-11	1	83	83
-9	1	110	117
-7	1	110	119
-5	1	194	205
-3	1	120	125
-1	1	172	174
+1	1	106	106
3	1	54	54
5	1	38	43
7	1	28	21
-16	2	28	15
-14	2	48	46
-12	2	54	54
-10	2	100	104
-8	2	95	102
-6	2	149	161
-4	2	177	184
-2	2	140	145
0	2	157	150
2	2	73	74
4	2	54	54
6	2	28	23
8	2	25	18
-15	3	32	29
-13	3	46	47
-11	3	70	72
-9	3	127	132
-7	3	108	115
-5	3	180	178
-3	3	132	140
-1	3	148	162
+1	3	67	70
3	3	76	77
5	3	37	38
7	3	26	23
-16	4	26	20
-14	4	35	33
-12	4	55	61
-10	4	83	88
-8	4	130	142
-6	4	126	138
-4	4	156	161
-2	4	125	132
0	4	107	99
2	4	80	81
4	4	52	55
6	4	29	30
-15	5	25	24
-13	5	40	45
-11	5	59	64
-9	5	84	95
-7	5	146	159
-5	5	131	117
-3	5	159	166
-1	5	113	114
+1	5	101	103
3	5	60	61
5	5	28	33
-16	6	27	23
-14	6	27	23
-12	6	60	61
-10	6	61	68

TABLE VII - continued

l = 8

-8	6	119	123
-6	6	125	130
-4	6	126	132
-2	6	172	159
0	6	82	77
2	6	86	89
4	6	45	42
6	6	27	27
-13	7	34	40
-11	7	60	66
-9	7	73	79
-7	7	156	169
-5	7	74	71
-3	7	169	180
-1	7	52	53
+1	7	94	99
3	7	49	52
5	7	33	39
-14	8	24	16
-12	8	55	61
-10	8	53	53
-8	8	118	116
-6	8	117	133
-4	8	100	105
-2	8	108	98
0	8	88	81
2	8	81	83
4	8	24	26
6	8	28	32
-13	9	28	32
-11	9	55	57
-9	9	60	65
-7	9	113	108
-5	9	105	110
-3	9	116	121
-1	9	80	82
+1	9	81	82
3	9	42	48
5	9	26	26
-14	10	<30	17
-12	10	43	49
-10	10	38	47
-8	10	91	92
-6	10	84	86
-4	10	108	115
-2	10	84	87
0	10	85	79
2	10	55	59
4	10	25	27
-13	11	24	28
-11	11	41	48
-9	11	60	64
-7	11	80	80
-5	11	109	111
-3	11	58	63
-1	11	79	80
+1	11	52	57
3	11	37	42
5	11	24	21
-14	12	25	23
-12	12	26	27
-10	12	50	55
-8	12	57	62
-6	12	80	79
-4	12	76	82
-2	12	76	73
0	12	64	69
2	12	36	38
4	12	28	30
-13	13	<32	22
-11	13	31	34
-9	13	52	53
-7	13	50	48
-5	13	76	77
-3	13	77	83
-1	13	70	70
+1	13	39	43
3	13	28	32
5	13	25	23
-14	14	29	26
-12	14	<31	14
-10	14	46	50
-8	14	44	42
-6	14	64	63
-4	14	54	58
-2	14	63	67
0	14	53	57
2	14	24	24
4	14	24	27
-11	15	23	27
-9	15	49	50
-7	15	31	35
-5	15	64	69
-3	15	37	42
-1	15	55	56
+1	15	30	29
3	15	26	25
-10	16	38	38
-8	16	30	32
-6	16	43	42
-4	16	52	54
-2	16	42	47
0	16	37	43
-9	17	33	32
-7	17	23	25
-5	17	55	55
-3	17	23	31
-1	17	50	51
+1	17	16	20
-10	18	24	23
-8	18	25	26
-6	18	41	38
-4	18	36	34
-2	18	24	29
0	18	32	31
-9	19	24	19
-7	19	33	32
-5	19	24	26
-3	19	33	32
-1	19	16	18
-8	20	24	21
-6	20	28	28
-4	20	26	22
-2	20	23	27
-7	21	26	28
-5	21	<28	13
-3	21	26	29
-4	22	25	18

l = 9

-15	1	<29	6
-13	1	<27	-5
-11	1	<26	-10
-9	1	<25	16
-7	1	<24	3
-5	1	<24	21
-3	1	<24	-8
-1	1	30	24
+1	1	<36	-23
3	1	<26	+7
5	1	<27	-2
7	1	<22	+2
-16	2	<26	1
-14	2	<27	7
-12	2	<28	-10
-10	2	<27	12
-8	2	<24	-5
-6	2	26	24
-4	2	<26	-13
-2	2	26	27
0	2	24	-20
2	2	<28	+12
4	2	<26	+7
6	2	<26	+0
-15	3	<24	15
-13	3	<23	-11
-11	3	<20	11
-9	3	<23	4
-7	3	<23	-4
-5	3	29	36
-3	3	25	-31
-1	3	23	30
+1	3	<22	-14
3	3	25	+26
5	3	<24	-1
0	4	---	1
0	6	21	-17

l = 10

-16	0	---	-11

TABLE VII -continued

l = 10

-14	0	<24	2	-5	5	<25	6	-1	3	43	49
-12	0	24	-17					+1	3	36	38
-10	0	<24	-1					3	3	24	18
-8	0	<21	7		l = 11						
-6	0	21	-13					-6	4	72	75
-4	0	27	25								
-2	0	<24	-12	-17	1	---	-1	-6	6	76	78
0	0	<24	-7	-15	1	<26	-3				
2	0	<24	-9	-13	1	<27	-1	-6	8	72	75
4	0	<23	4	-11	1	<26	-5				
				-9	1	<26	+7	-6	10	59	61
-15	1	<32	-13	-7	1	<32	-10				
-13	1	<27	13	-5	1	<26	14	-6	12	42	41
-11	1	39	-41	-3	1	<26	-13				
-9	1	<31	18	-1	1	<29	2	-6	14	34	29
-7	1	<25	-7	+1	1	<27	+1				
-5	1	<25	5	3	1	<26	-1	-6	16	27	21
-3	1	<25	8								
-1	1	<31	-7	-16	2	<25	-6	-6	18	27	20
+1	1	<29	5	-14	2	<27	1				
3	1	<30	-9	-12	2	<26	-9				
5	1	<28	5	-10	2	<26	+8		l = 13		
				-8	2	<28	-6				
-16	2	23	-8	-6	2	<28	-12	-15	1	<27	-2
-14	2	<27	0	-4	2	<28	+9	-13	1	<29	7
-12	2	<26	-11	-2	2	26	-24	-11	1	<30	-6
-10	2	<28	-18	0	2	<29	15	-9	1	<30	4
-8	2	<25	6	2	2	<29	-8	-7	1	<30	2
-6	2	<31	-16	4	2	<28	+3	-5	1	<30	-2
-4	2	31	33					-3	1	<30	-4
-2	2	<27	-13	-17	3	<23	-2	-1	1	<29	-0
0	2	<28	12	-15	3	<24	-7	+1	1	<27	+3
2	2	<26	-9	-13	3	<24	3				
4	2	<27	3	-11	3	<23	-11	-16	2	<26	-2
				-9	3	<23	12	-14	2	<26	3
-15	3	<24	-7	-7	3	27	-28	-12	2	<27	8
-13	3	<24	-6	-5	3	<23	12	-10	2	<38	-9
-11	3	<23	-6	-3	3	27	-28	-8	2	<27	18
-9	3	<22	0	-1	3	<23	4	-6	2	<27	-15
-7	3	<22	-6	+1	3	<24	+2	-4	2	<27	9
-5	3	<25	10	3	3	<24	+0	-2	2	<27	6
-3	3	<22	1	5	3	<23	+1	0	2	<26	2
-1	3	<25	-4					2	2	<25	-1
+1	3	<23	3								
3	3	<24	-5								
5	3	<24	0								

l = 12

-16	0	24	27
-14	0	24	18
-12	0	81	74
-10	0	56	51
-8	0	109	105
-6	0	75	78
-4	0	74	74
-2	0	61	59
0	2	42	42
2	2	31	33
-15	1	31	20
-13	1	49	45
-11	1	62	62
-9	1	75	76
-7	1	92	92
-5	1	73	77
-3	1	71	74
-1	1	40	38
+1	1	52	48
3	1	29	19
-16	2	29	24
-14	2	37	27
-12	2	67	61
-10	2	62	57
-8	2	97	93
-6	2	68	74
-4	2	83	82
-2	2	57	59
0	2	41	39
2	2	35	34
4	2	23	14
-17	3	24	17
-15	3	30	26
-13	3	47	43
-11	3	56	56
-9	3	76	74
-7	3	90	93
-5	3	61	66
-3	3	67	73

TABLE VII - continued

l = 13

-15	3	<24	-4	-13	1	<27	-2	-6	2	54	36
-13	3	<24	16	-11	1	<28	2	-4	2	27	24
-11	3	<24	-11	-9	1	<29	-6				
-9	3	<24	17	-7	1	<29	1	-15	3	25	22
-7	3	<24	-6	-5	1	<29	-0	-13	3	27	25
-5	3	<24	-3	-3	1	<27	-0	-11	3	37	33
-3	3	<24	16	-1	1	<23	-1	-9	3	30	31
-1	3	<24	-2					-7	3	35	36
+1	3	<24	+5	-14	2	<25	-8	-5	3	30	28
				-12	2	<26	5				
				-10	2	<26	-8	-8	4	43	39
				-8	2	<27	-0				
				-6	2	<27	-1	-8	6	45	40
				-4	2	<26	2				
				-2	2	<27	-1	-8	8	36	33
				0	2	<23	-3				

l = 14

-14	0	---	-6	-15	3	<23	-4
-12	0	<23	-1	-13	3	<24	-5
-10	0	<21	0	-11	3	<24	4
-8	0	<22	1	-9	3	<24	-15
-6	0	<22	1	-7	3	<24	6
-4	0	<23	-11	-5	3	<24	-3
-2	0	22	16	-3	3	<24	4
				-1	3	<23	-5
-13	1	<28	-8				
-11	1	<29	11				
-9	1	<30	-14				
-7	1	<26	14				
-5	1	<30	-12				
-3	1	<29	6				
-1	1	<28	3				

l = 16

-14	2	<28	-7	-16	0	---	19
-12	2	<29	2	-14	0	---	25
-10	2	<27	-1	-12	0	29	26
-8	2	<27	-1	-10	0	51	44
-6	2	<27	2	-8	0	25	20
-4	2	<27	-4	-6	0	52	44
-2	2	<26	7				
0	2	<25	-3	-13	1	31	24
				-11	1	40	36
-15	3	<23	-4	-9	1	37	34
-13	3	<24	-5	-7	1	32	29
-11	3	<24	2	-5	1	40	37
-9	3	<24	-3				
-7	3	<24	3	-16	2	23	17
-5	3	<24	0	-14	2	36	25
-3	3	<24	2	-12	2	36	27
-1	3	<24	2	-10	2	40	39
+1	3	<23	0	-8	2	38	29

DISCUSSION OF THE STRUCTURES OF THE COPPER AND SILVER COMPLEXES

COMPARISON OF THE TWO STRUCTURES

There are similarities between the structures of the copper and the silver complexes. Formally, the silver compound is built up of $\left[(Me_3P)_2Ag\right]^+$ and linear $\left[(PhC{\equiv}C-)_2Ag\right]^-$ units alternating along infinite chains. Ag2 is bonded to two phosphorus atoms, with the angle P-Ag2-P" equal to 118°, and interaction with two ethynyl groups of different $\left[(PhC{\equiv}C-)_2Ag\right]^-$ units completes a tetrahedral arrangement around Ag2.

One can regard the copper compound as built up from $\left[(Me_3P)_2Cu\right]^+$ and $\left[(PhC{\equiv}C-)_2Cu\right]^-$ units in an analogous way, except that these latter units are not linear, as in the silver compound. In this case, it is ethynyl groups of the same $\left[(PhC{\equiv}C-)_2Cu\right]^-$ unit that complete a tetrahedral arrangement around Cu2. The units are joined in pairs to form tetramers by $\sigma\pi$-bonds between Cu1 and C9'-C10' and Cu1' and C9-C10, with these ethynyl groups adopting a trans configuration, as in the first excited state of acetylene. (Ingold and King 1953).

To regard the copper complex in this way brings out the similarity with the silver compound, but it is also

possible to consider the structure as built up from two kinds of PhC≡CCu units. In the first kind, the ethynyl group C1-C2 is linear, while in the second kind, the ethynyl group C9-C10 adopts a cis configuration, as in the complex of copper(I) chloride with dimethyl acetylene. (Carter and Hughes, 1957). However, the possibility that the uncomplexed acetylides, PhC≡CM, are built up from M^+ and $\left[(PhC{\equiv}C-)_2M\right]^-$ units is an interesting one.

THE INTERACTION OF Cu1 and Ag1 WITH ETHYNYL GROUPS

One of the chief difference between the structures of the copper and silver complexes is the formation of a symmetrical $\sigma\pi$-bond between Cu1 and C9'-C10' in the copper compound. The copper-carbon distances, 2.06 and 2.09Å., are similar to the metal-carbon distances in π-bonded systems of iron and cobalt, which are usually around 2.1Å., (e.g. in ferrocene, 2.05Å., Dunitz, Orgel and Rich, 1956; in tricarbonyliron butadiene, 2.1Å., Mills and Robinson, 1960; and references in the introduction), and in the cyclooctadiene complex of rhodium(I) chloride, (2.12Å.), and in tetramethylcyclobutadiene nickel(II) chloride, (2.02Å.) (Ibers and Snyder, 1962; Dunitz et al., 1962). The ethynyl group is in the plane of the sp^2 hybridised orbitals of Cu1, which is different to the arrangement in the olefin complexes of palladium and platinum, where the double bond

is perpendicular to the plane of the dsp^2 hybridisation. If the bonding is of the $\sigma\pi$-type discussed in the introduction, the π-bonding must use a d-orbital in the plane of the sp^2 hybridised orbitals, rather than a dp^2 hybrid orbital using the unoccupied p-orbital on Cu1, since this orbital is perpendicular to the plane of the bonding. The bond distance for the carbon-carbon triple bond is very near the usual value, which is unusual, in view of the extension of the double or the triple bond often found in olefin or acetylene complexes, and in view of the distortion of the angle C9-C10-C11. Evidently the conjugation in the phenylethynyl, system is not greatly reduced by the distortion, as the length of the bond C10-C11 is not significantly greater than that of C2-C3.

In the copper compound, the ethynyl group C9-C10 lies more or less symmetrically with respect to the copper atoms Cu1 and Cu2, with angles Cu1-C9-C10 and Cu2-C9-C10 of 152° and 136° respectively, and C9 almost equidistant from the copper atoms, Cu1-C9 and Cu2-C9 being 2.07 and 2.11Å., equal within experimental error. C9 would seem to be bonded equally to Cu1 and Cu2. The system is very similar to the electron deficient compounds of beryllium, boron and aluminium, where amine nitrogen or methyl carbon atoms act

as bridging groups. The angle Cu1-C9-Cu2 is 72°, similar to the B-N-B angle of 76° in aminodiborane, and the angles of 66° and 70° for Be-C-Be and Al-C-Al in dimethylberyllium and trimethylaluminium. (Hedburg and Stosick, 1952; Snow and Rundle, 1951; Lewis and Rundle, 1953). The Be...Be and Al...Al distances in the last two compounds are 2.10 and 2.56Å. respectively, considerably shorter than the distances in beryllium and aluminium metal, which are 2.23 and 2.29Å, and 2.86Å. The distance Cu1-Cu2 in the present compound is 0.1Å. shorter than in the metal, consistent with some metal-metal bonding due to a three-centred bond. Bond lengths to bridging atoms appear to be usually 0.1-0.2Å. greater than the normal bond lengths. Here the Cu-C distances are 0.11 and 0.15Å. greater than Cu1-C1, although some of the difference may be due to π-bonding between Cu1, and C1. They are, however, very little greater than the sum of the tetrahedral covalent radius for copper(I) and the covalent radius for carbon in the sp hybridised state. (2.05Å.). In the electron deficient compounds mentioned above, there are two electrons available to form the three-centred bond, and similarly in this case, if we consider the bonding separately from the $\sigma\pi$-bonding of Cu1' to C9-C10, there are just two electrons available. It is convenient, therefore, to consider the system Cu1, C9, Cu2 as a bridge structure. In practise, there may well be considerable delocalisation of electrons over C9-C10 and the three copper atoms Cu2, Cu1,

and Cu1'.

The possibility of 'end-on' π-bonding in the complexes studied is of interest. Experiments by Cass, Coates and Hayter, (1954), and by Arhland and Chatt, (1955), seem to indicate that the tendency for π-bond formation is strong enough to make a trigonal coordination around Cu(I) and Ag(I) preferred in bonding to tertiary phosphines, rather than the usual tetrahedral coordination. The trigonal coordination found in the complex cyanides of copper(I) could be due to a similar reason. However, π-bonding is said not to occur to any great extent in the cyanide complexes, (Griffith, 1962, p. 190, and refs. given there) and Nyholm, (1961, p. 282) takes the view that π-bonding in complexes with the d^{10} configuration is relatively uncommon. Any π-bonding in cyanides, or in ethynyl compounds, would reduce the metal-carbon bond length, but it is difficult to be sure what the single bond lengths should be if no π-bonding occurred. In the present compounds, there would appear to be at least some evidence of bond shortening, particularly in the gold compound.

THE INTERACTION OF Cu2 and Ag2 WITH ETHYNYL GROUPS

There appears to be evidence for an oblique form of side-on bonding of ethynyl groups in the copper and silver

compounds. Such bonding is clearest in the silver compound, where the angle of 118° for P-Ag2-P" seems difficult to explain, if there is no bonding between Ag2 and the ethynyl groups C1-C2 and C1"-C2". Oblique bonding between Cu2 and the ethynyl group C1-C2 in the copper compound is invoked by analogy, because in this case too, the bonding completes a tetrahedral arrangement around Cu2. The bond angles Cu2-C1-C2 and Ag2-C1-C2 are 117° and 102°, and the copper- and silver-carbon bond lengths are 2.22 and 2.97Å. and 2.55 and 3.04Å. respectively, with the distances to the midpoints of the ethynyl groups 2.60 and 2.80Å. The corresponding angles for Cu1 and Ag1 are close to 180°, and the metal-carbon distances Cu1-C1 equal to 1.96Å, and Ag1-C1 equal to 2.04Å., so that it seems natural to consider the bonding of the ethynyl groups to Cu1 and Ag1 separately from the bonding to Cu2 and Ag2.

The infra red stretching frequencies for the ethynyl groups are 2019 and 2045 $cm.^{-1}$ in the copper compound, and 2075 $cm.^{-1}$ in the silver compound. (Coates and Parkin, 1961). These values are less than the value of 2122 $cm.^{-1}$ in the gold compound (Coates and Parkin, 1962), where no 'side-on' bonding occurs, indicating some electronic effect over and above that due to end-on bonding to metal atoms for the ethynyl group in the silver compound, and for both the ethynyl groups in the copper compound.

Strong π-bonds can be formed with only two ligands by an atom in tetrahedral coordination. (Kimball, 1940; Arhland and Chatt, 1955). π-bonding to the phosphorus atoms is indicated for both Cu2 and Ag2 by the shortening of the metal-phosphorus bond, and by the valence angles at the phosphorus atoms, so that π-bonding to the ethynyl groups would be weak. π-donation to the ethynyl group would also be hindered by the residual negative charge on the ethynyl groups resulting from the end-on bonding to copper or silver. From the view of 'side-on' σπ-bonding given in the introduction, the symmetrical arrangement would be due mainly to the principle of maximum overlap in the formation of the π-type bond, and if there were very little π-bonding, the symmetry might be less essential. The easily deformed bond could then become oblique due to steric factors, depending on the requirements of other bonds. The larger values of the metal-carbon distances are in agreement with the weaker bonding.

Unsymmetrical 'side-on' bonding is reported in the styrene complex of palladium(II) chloride. (Dempsey and Baenziger, 1955; 1961). The angle between the direction of the double bond, and the line joining the palladium atom to the centre of the double bond is 70°. The analogous angles in the present case are 51° for the copper compound, and 66° in the silver compound.

THE STRUCTURE OF PHENYLETHYNYL(ISOPROPYLAMINE)GOLD(I)

INTRODUCTION

The amine complexes of phenylethynylgold(I) are associated in solution, with n=3-4, in contrast to the phosphine complexes, which are monomeric. The possibility of metal-ethynyl group interaction of the 'side-on' type, giving the gold atom a coordination number of more than two, made the study of an amine complex of especial interest. Coordination to more than two ligands is unusual for gold(I).

The isopropylamine complex presented the simplest problem for detailed analysis, but was too insoluble in benzene to obtain molecular weights, or to estimate dielectric constants. Confirmation that this compound had basically the same structure as the more soluble higher amine complexes was obtained by comparison of the unit cell dimensions of three of the complexes, and from similarities in their X-ray diffraction patterns. The space groups and unit cell dimensions of the complexes were:

$^{i}PrNH_2AuC{\equiv}CPh$ Pccn a=17.9 b=17.2 c=7.2 Z=8

$^{n}C_5H_{11}NH_2AuC{\equiv}CPh$ $P2_1/c$ a=22.0 b=17.0 c=7.2 β=98° Z=8

$^{n}C_9H_{19}NH_2AuC{\equiv}CPh$ Pccn a=29.2 b=17.0 c=7.2 Z=8

The 'b' and 'c' axes have almost the same length, and

presumably the differences in the lengths of 'a' axes are because the hydrocarbon chains extend along this direction.

EXPERIMENTAL

CRYSTALS

The compound can be crystallised from acetone as white needles, relatively stable to air, but sensitive to light, and deteriorating rapidly on exposure to X-radiation. After 20-30 hours exposure, the reflections obtained from a crystal were generally distorted, and in some cases the crystal itself had become deformed. A crystal selected from freshly recrystallised material was used for each X-ray photograph, and no crystal was used after exposure for more than 30 hours, except in one case.

CRYSTAL DATA

Phenylethynyl(isopropylamine)gold(I)

$^{i}PrNH_2AuC{\equiv}CPh$ M=357.2

Orthorhombic; needles elongated in the direction of 'c'.

a = 17.924 b = 17.149 c = 7.222Å.

U = 2220Å.^{3} Z = 8 formula units

D_m = 2.08 D_x = 2.14 gm/cm.^{3} F(000) = 1328 electrons

Absorption coefficient for CuKα radiation, μ = 245 cm^{-1}

Reflections observed:	hkl	No conditions
	hk0	h + k = 2n
	0kl	l = 2n
	h0l	l = 2n

The space group is therefore uniquely determined as Pccn, (D_{2h}^{10}), no. 56 in the International Tables for Crystallography.

The unit cell dimensions 'a' and 'b' were obtained from a Weissenberg photograph of the (hk0) layer, calibrated with sodium chloride powder lines. The positions of 23 high angle reflections were measured, making use of resolved $K\alpha_1$ and $K\alpha_2$ reflections, and a least squares method was used to obtain 'a' and 'b'. Most of the high order reflections observed had much greater values of h than of k, so that 'b' was determined less accurately than 'a'. The value of 'c' was determined from a rotation photograph, calibrated by means of some of the high order reflections. The calculated standard deviations in the values of 'a', 'b', and 'c' were 0.002, 0.018, and 0.009Å. respectively. The true uncertainties are probably around 0.1% for 'a' and 'c', and 0.3% for 'b'.

The density was determined by flotation in a concentrated solution of zinc bromide. The 3% difference between calculated and observed densities may be due to insufficient wetting of the crystals.

COLLECTION OF INTENSITIES

Three-dimensional data were obtained on layers with l = 0-5 by equi-inclination Weissenberg techniques, using unfiltered copper radiation. It was found difficult to obtain good photographs by the precession method. The (0kl) and (h0l) reflections obtained by this method were used in calculating the projections of the Patterson function along the 'a' and 'b' axes, but with the exception of the (002) and (004) reflections, were not included in the subsequent refinement.

The intensities of the $K\alpha$ reflections were estimated visually, by comparison with a calibrated scale made using reflections from a very small crystal of hydroquinone. On average, the intensity of each reflection was estimated on three films within each series.

The multiple film technique was used, the films being packed without interleaving black paper. Mean film ratios were measured for each layer, and the values adjusted so that the variation with equi-inclination angle, ν_n, roughly fitted the curve

$$\ln\left(R_n/R_0\right) = \mu t(\sec \nu_n - 1)$$

where R_0 is the ratio for the zero layer, R_n is the ratio

for layer n, and μt is a constant, taken as 1.0 (Grenville-Wells, 1955). The values observed, and those used, are given in table I.

TABLE I. Film Ratios for Copper Radiation, without interleaving black paper.

	v_n	Observed	Used
hk0	0	3.10	3.05
hk1	6.1	3.17	3.11
hk2	12.3	3.08	3.14
hk3	18.6	3.34	3.30
hk4	25.2	3.14	3.27
hk5	32.1	3.46	3.55

The (hk4) reflections were much extended, and this may account for the low value observed for the film ratio. In this case, a lower value was adopted.

Intensity estimations were made on the extended reflections, except for the (hk2) reflections, and those used for correlation. Empirical corrections for spot extension were applied. The extensions were irregular, and varied with w as well as with θ. The range of the spot extension varied from 35% for the (hk0) reflections, to 500% for the (hk4) reflections.

The usual Lorentz and polarisation corrections were applied, but no correction was made for absorption. In all, 1032 independent reflections were observed. The sizes of the crystals used are given in table II. With these crystals, μt varied between 0.4-0.8, and the extreme error in the intensities due to neglect of absorption errors was about 15%.

TABLE II. The Crystals Used to Record the Data.

Layer	Cross-section, mm.	Total Exposure, hours
hk0	0.018x0.030	20
hk1	0.015x0.025	25
hk2	0.018x0.030	20
hk3	0.015x0.025	23
hk4 (1)	0.022x0.036	30
hk4 (2)	0.018x0.030	48 (Same crystal as for hk2)
hk5	0.025x0.035	28
Correlation: hk0,1,0	0.024x0.045	7
hk0,2,3,0	0.014x0.030	9
hk0,4,5,0	0.014x0.028	18

The intensities were placed on the same relative scale by taking moving film photographs of two or more levels on different parts of the same film. The first and last exposures on each film were always of the zero layer, in order

to check on any decomposition of the crystals during exposure. In two of the cases, the intensities decreased by about 10% during the exposure. The random error in the scale factors for the intensities was estimated to be about 4%, but appreciable systematic errors may occur.

STRUCTURE DETERMINATION

POSITION OF THE GOLD ATOM

The position of the gold atom was found by inspection of the Patterson function in projection along the crystal axes. In these projections, the Patterson function is equally satisfied by gold atoms in positions (x, y, z) and (x, y, $\frac{1}{4}$-z). However, it was possible to obtain the coordinates unambiguously when the three-dimensional data became available. Indeed, good estimates of each of the gold atom coordinates can be obtained simply by inspection of the intensities.

First, there were marked fringe patterns in the reciprocal lattice. Reflections with l = 0,2,4, were very weak when k = 3,8, and 14, while reflections with l = 1,3,5, were very weak when k = 5-6, and 11. For space group Pccn, the geometrical part in the expression for the structure factor always contains the term $\cos 2\pi ky$ when k + l is

even, and the term sin2 ky when k + l is odd. Since the gold atom will make an overwhelming contribution to the magnitudes of the observed structure factors, its y-coordinate must be such that cos2π8y, cos2π14y, cos2π5y, cos2π11y, sin2π3y, and sin2π6y are each very small. These conditions give an average value of 0.160 for the y-coordinate for the gold atom.

Secondly, reflections with h + k even were almost absent when l = 5, and were weak when l = 4. When l = 1 reflections with h + k odd were weak. The expression for the structure factor contains the term cos2π lz when h + k is even, and sin2πlz when h + k is odd, and the z-coordinate for the gold atom must be such that cos2π5z is approximately zero, and cos2π4z and sin2πz are both small. This gives the z-coordinate as 0.05.

Thirdly, reflections with l odd are generally much weaker than those with l even, indicating that the 'c' axis is halved for the gold atom. With these y- and z-coordinates the x-coordinate of the gold atom must be near 0.25. The related positions (x,y,z) and $(\frac{1}{2}-x,y,\frac{1}{2}+z)$ then become $(\frac{1}{4},y,z)$ and $(\frac{1}{4},y,\frac{1}{2}+z)$, and so on.

The coordinates obtained by the Patterson method are compared with those arrived at by inspection, and with the final coordinates, in table III. The gold atoms are

arranged in pairs of infinite zig-zag chains along the 'c' axis, with gold-gold distances of 3.3Å. between chains, and 3.7Å. along chains.

TABLE III. Coordinates of the Gold Atom.

	x/a	y/b	z/c
By inspection:	0.25	0.160	0.05
By Patterson methods:	0.222	0.158	0.051
Final Coordinates:	0.225	0.158	0.048

POSITIONS OF THE LIGHT ATOMS

The coordinates of the gold atom were refined through one cycle of least squares, refinement, using arbitrary initial values for scale and temperature factors. Structure factors were calculated on the basis of the refined parameters, (R = 0.23), and were used to calculate an (F_o-F_c) synthesis. The function was evaluated at intervals of 0.30Å. in the 'x' direction, (a/60), 0.28Å. in the 'y' direction, (b/60), and 0.36Å. in the 'z' direction, (c/20).

The positions of all the light atoms were clearly indicated, and the mean height of the peaks representing ten of the carbon atoms was 4.2 e/Å.^{3} The peak heights for the two atoms attached to the gold atom were exceptionally large, being

9.3 e/Å^3 for the carbon atom, and 7.3 e/Å^3 for the nitrogen atom. There were two spurious peaks in the electron density distribution related to the position of the gold atom by translations of $^c/_5$, and the electron density around the gold atom gave evidence of anisotropic thermal motion. Apart from these regions the background electron density was within the limits -2.0 to +2.5 e/Å^3.

REFINEMENT

The introduction of the light atom contributions to the structure factors improved the agreement to R = 0.125. The structure was refined through one cycle of least squares using isotropic temperature factors, and then through two further cycles in which the gold atoms were given anisotropic temperature factors. These were followed by four cycles in which all the atoms were given anisotropic temperature factors. The factor R was 0.073 at this stage. The anisotropic refinement of the light atoms occasioned several shifts of 0.02-0.03Å. in the atomic coordinates.

A check was now made on the relative scaling of the layers by calculating mean values of $|F_c|/|F_o|$ for each layer. The values obtained were 1.04, 0.98, 1.02, 0.91, 0.97, and 1.07 for l = 0,1,2,3,4,5 respectively. The scaling for two of the layers appeared to be in error by more than 5%. The above factors were used to rescale the layers, and the structure was refined through two further cycles,

rescaling the layers after each cycle. There were coordinate shifts of up to 0.02Å. (for C7) during these two cycles, but the main effect was to improve the agreement to R = 0.064, and to improve the estimated standard deviations. The mean shift in coordinates during the final cycle was 0.0025Å., with a maximum shift of 0.0072Å., and only two parameter shifts were more than a half of the corresponding estimated standard deviations. The change in the overall scale factor during the final cycle was 0.3%, and changes in scaling for the various layers were all less than 1½%.

Finally, an (F_o-F_c) synthesis was calculated, in which the F_c were the structure factors calculated during the final cycle. Near the gold and the nitrogen atoms, there were regions of electron density 1-2 e/Å.^{3} in the form of ridges extending in the direction of 'c'. Over the rest of the unit cell, the electron density was always between -0.6 and +0.7 e/Å.^{3} Of 12-13 sites where the electron density was greater than 0.4e/Å.^{3}, 10 were in positions expected for hydrogen atoms.

The refinement is summarised in table IV, which also gives details of the least squares weighting. The weighting analysis after the final cycle is given in table V. The values of $w|\Delta|^2$ fall off noticeably with $\sin\theta/\lambda$ and with $|F_o|$.

The scattering factors for carbon and nitrogen were those given by Berghuis et al., (1955). The scattering factors for the gold atom were those given by Thomas and Umeda, (1957). The dispersion corrections for gold are $\Delta f' = -5$ electrons, and $\Delta f'' = +8$ electrons, for CuKα radiation, where $f = f_o + \Delta f' + i\,\Delta f''$. (Dauben and Templeton, 1955). Corrections for dispersion were made by using the expression $f = \left[(f_o + \Delta f')^2 + \Delta f''^2\right]^{\frac{1}{2}}$ for the gold scattering factors. This corrects for $\Delta f'$, and makes an allowance for $\Delta f''$ which is of the right sign, and about the right magnitude, and is very much simpler to use than the true expression involving complex coefficients.

The shifts in the atomic coordinates during the final cycle are listed in table VI and the shifts in the anisotropic temperature parameters in table VII. The structure factors calculated during the final cycle are given in table VIII. They include structure factors for 552 unobserved planes, and very few of these are greater than the maximum expected value, F_{min}. The final values of the atomic coordinates and their estimated standard deviations are given in table IX, and the final values of the temperature parameters, together with the corresponding standard deviations, in table X.

TABLE IV. $^{i}PrNH_2AuC{\equiv}CPh$: Analysis of the Structure.

	Coordinate Shift Mean	Max.	R	R'	Weights
1. Refinement of the gold atom.	0.0094	0.015	0.42	0.1465	const.
2. "	0.0086	0.018	0.225	0.0595	"
3. Introduction of light atoms.	0.0455	0.283	0.125	0.0173	"
4. Gold atom anisotropic.	0.0231	0.084	0.094	0.0163	W(1)
5. "	0.0065	0.020	0.080	0.0113	"
6. All atoms anisotropic.	0.0090	0.028	0.074	0.0088	W(2)
7. "	0.0037	0.016	0.073	0.0083	"
8. "	0.0031	0.009	0.072	0.0081	"
9. "	0.0030	0.009	0.073	0.0083	"
10. Rescaling layers.	0.0044	0.015	0.063	0.0058	"
11. "	0.0025	0.007	0.064	0.0057	"

W(1): $w = {}^{4}/A + K|F_o| + B(K|F_o|)^2$,

A = 33.6
B = 0.002
K = 1.1

W(2): $w = {}^{4}/A + K|F_o| + B(K|F_o|)^2$ if $K|F_o| \geq 32$,

$w = C + D(K|F_o|)$ if $K|F_o| < 32$

A = 33.6
B = 0.003
C = 0.0164
D = 0.00134
K = 1.00,
(0.99 in cycles 10 and 11).

TABLE V. Weighting Analysis after the Final Cycle.

$K\|F_o\|$	Mean $w\|\Delta\|^2$	No. of planes
8-16	0.31	22
16-32	0.59	305
32-64	1.22	372
64-128	1.02	209
128-	2.96	124

$\sin\theta/\lambda$	Mean $w\|\Delta\|^2$	No. of planes
0-0.1	8.48	8
0.1-0.2	2.28	62
0.2-0.3	1.35	165
0.3-0.4	1.20	250
0.4-0.5	0.95	275
0.5-0.6	0.88	212
0.6-0.7	0.70	60

TABLE VI. Shifts in the Atomic Coordinates during the Final Cycle.(Å.)

	x	y	z
Au	0.0003	0.0000	0.0006
N	0.0060	-0.0006	0.0020
C1	0.0047	-0.0039	0.0000
C2	0.0029	-0.0005	-0.0036
C3	-0.0059	0.0000	-0.0050
C4	0.0006	0.0000	0.0051
C5	-0.0041	0.0012	0.0072
C6	0.0018	0.0016	-0.0017
C7	-0.0050	0.0032	0.0030
C8	-0.0014	0.0037	0.0030
C9	0.0008	0.0004	0.0023
C10	0.0026	0.0018	0.0030
C11	0.0009	-0.0038	0.0032

TABLE VII. Shifts in the Anisotropic Thermal Parameter during the final cycle.(Å^2)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Au	-0.0002	-0.0002	0.0010	0.0002	0.0000	-0.0002
N	0.0033	0.0002	0.0007	0.0021	-0.0007	0.0021
C1	-0.0008	0.0003	-0.0001	0.0015	-0.0033	-0.0008
C2	0.0009	-0.0045	0.0027	-0.0008	-0.0014	-0.0010
C3	-0.0009	0.0004	0.0017	0.0028	0.0022	0.0007
C4	-0.0002	0.0009	0.0005	0.0015	0.0002	-0.0001
C5	-0.0011	0.0035	-0.0016	-0.0025	0.0014	-0.0001
C6	-0.0011	0.0030	0.0002	-0.0019	-0.0016	-0.0058
C7	-0.0002	-0.0011	0.0009	0.0013	-0.0008	0.0016
C8	-0.0027	0.0005	0.0004	-0.0045	0.0009	-0.0014
C9	-0.0014	0.0026	-0.0017	0.0023	0.0019	0.0004
C10	-0.0036	-0.0006	0.0042	-0.0030	0.0011	0.0024
C11	0.0006	-0.0015	0.0058	-0.0013	0.0018	0.0041

TABLE IX. $^{i}PrNH_2AuC{\equiv}CPh$. Final Values of the Atomic Co-ordinates (in Å.) and the Standard Deviations. (10^3 x Å.)

	x		y		z		$\sigma(r)$
Au	4.031	(1)	2.714	(1)	0.344	(1)	0.0009
N	6.052	(13)	2.582	(14)	0.261	(16)	0.014
C1	2.102	(19)	2.757	(20)	0.496	(20)	0.020
C2	0.908	(21)	2.697	(20)	0.679	(20)	0.020
C3	-0.558	(19)	2.640	(21)	0.870	(22)	0.021
C4	-1.298	(22)	1.657	(21)	0.234	(23)	0.022
C5	-2.698	(21)	1.638	(24)	0.418	(26)	0.024
C6	-3.332	(21)	2.538	(25)	1.243	(29)	0.025
C7	-2.581	(20)	3.481	(22)	1.864	(28)	0.024
C8	-1.205	(21)	3.572	(23)	1.718	(25)	0.023
C9	6.695	(22)	1.236	(20)	0.677	(24)	0.022
C10	8.212	(22)	1.423	(26)	0.798	(24)	0.024
C11	6.314	(19)	0.199	(21)	-0.320	(24)	0.021

TABLE X. $^{i}PrNH_2AuC{\equiv}CPh$: Final Values of the Anisotropic Temperature Parameters, (in Å^2), and their Standard Deviations. (in 10^{-3} Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Au	0.0622(.4)	0.0767(.5)	0.0863(.8)	0.0097(.9)	-0.0031(1.1)	-0.0015(1.1)
N	0.060(7)	0.062(8)	0.052(10)	-0.005(13)	-0.002(17)	0.019(15)
C1	0.074(10)	0.082(12)	0.054(15)	0.022(21)	-0.013(25)	0.011(22)
C2	0.089(12)	0.069(12)	0.053(17)	0.007(23)	0.000(22)	0.015(20)
C3	0.072(11)	0.076(12)	0.064(15)	0.018(21)	0.025(22)	0.017(19)
C4	0.088(13)	0.082(13)	0.062(16)	-0.011(22)	0.010(24)	-0.013(25)
C5	0.076(13)	0.102(17)	0.101(20)	-0.030(23)	0.019(32)	0.025(29)
C6	0.074(12)	0.120(20)	0.111(23)	0.050(27)	0.046(34)	0.045(29)
C7	0.081(13)	0.076(15)	0.108(18)	-0.010(22)	-0.007(29)	0.030(27)
C8	0.083(13)	0.095(15)	0.069(16)	0.036(23)	-0.005(29)	0.026(25)
C9	0.082(13)	0.067(12)	0.103(22)	0.033(22)	0.001(24)	-0.011(26)
C10	0.078(13)	0.115(19)	0.088(21)	0.041(25)	-0.008(29)	-0.033(24)
C11	0.072(12)	0.075(13)	0.106(18)	-0.017(20)	-0.003(28)	0.015(26)

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure is illustrated in perspective in fig. 1. The bond lengths and angles are illustrated in fig. 2, and tabulated in table XI. Standard deviations were calculated using the formula on page 31. Contacts and angles between atoms of different molecules are given in table XII. The distances between atoms of different molecules are all 3.27Å. or greater, and hence the complex appears to exist in the crystal essentially as monomer units, unlike the copper and silver complexes.

The gold atoms are arranged in infinite zig-zag chains, extended along the 'c' axis, with the plane of the zig-zag parallel to (010). The gold-gold distances along the chains are 3.72Å., with angles of 153°. The chains are grouped in pairs around the two-fold axes through $(\frac{1}{4},\frac{1}{4},0)$ and $(\frac{3}{4},\frac{3}{4},0)$, with gold-gold distances of 3.27Å. between the chains. Each gold atom is linearly coordinated to a nitrogen atom and to an ethynyl group in the 'end-on' position, with the bonding almost parallel to the 'a' axis, i.e., in the plane of the chain of gold atoms. Thus each gold atom has an ethynyl carbon and an amine nitrogen as near neighbours, and three gold atoms as more distant neighbours.

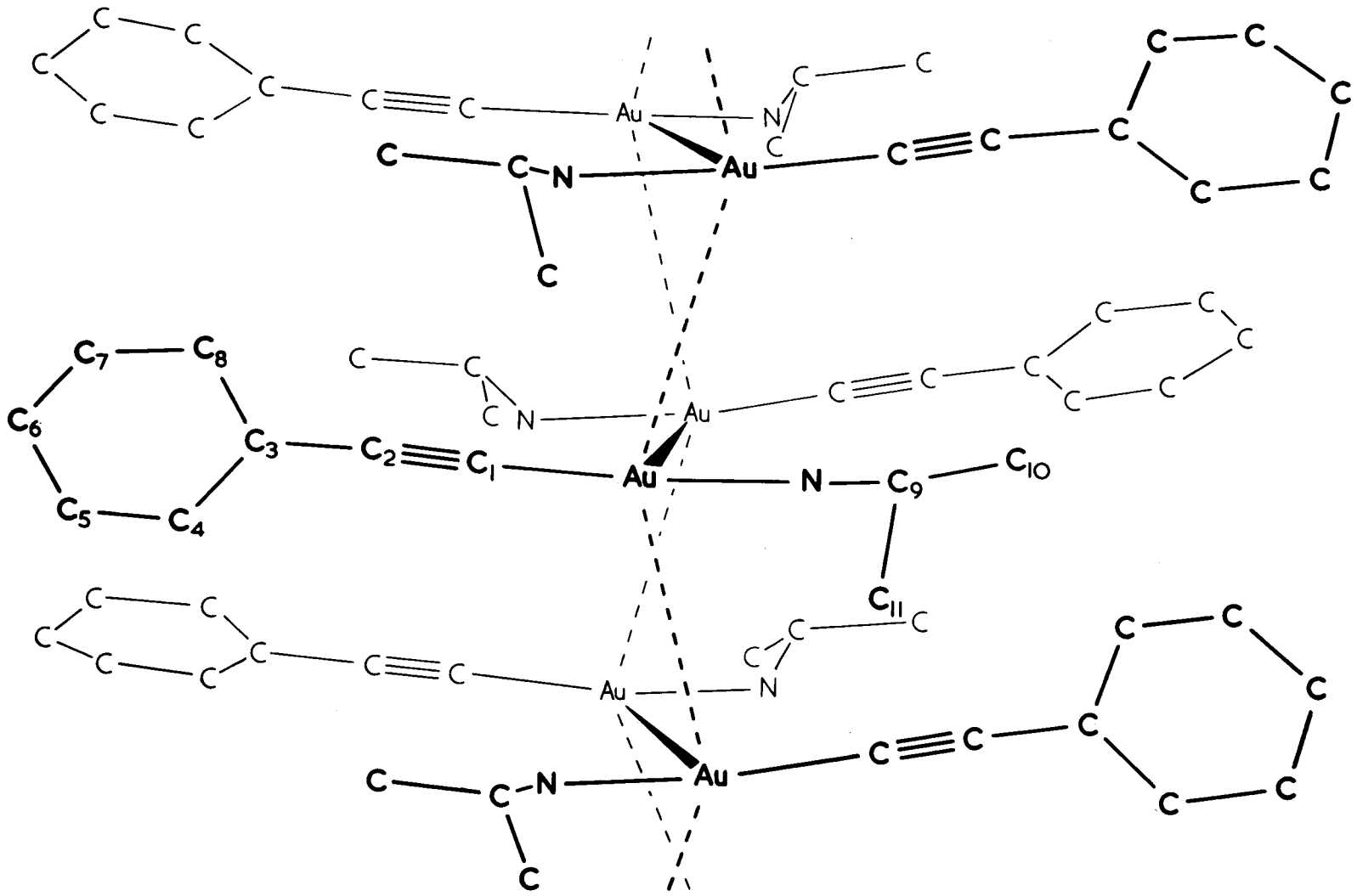
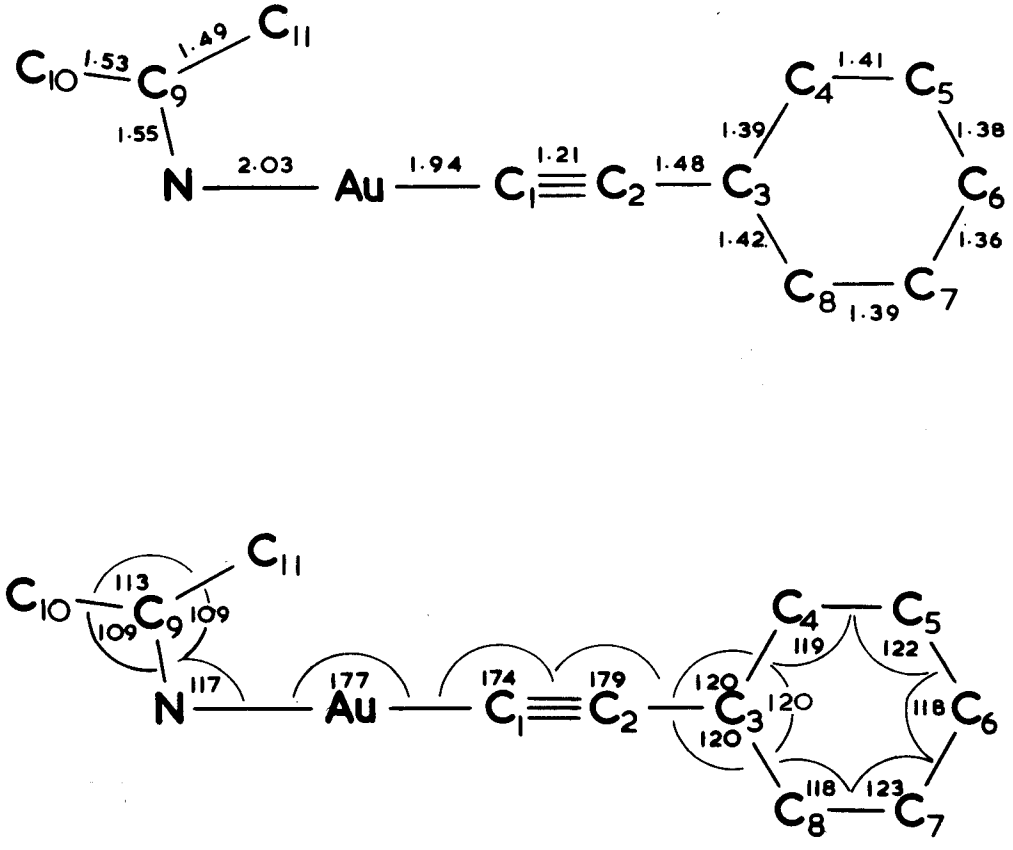


fig 1 130a



'PrNH$_2$AuC≡CPh. Bond lengths and angles

TABLE XI. $^{i}PrNH_2AuC{\equiv}CPh$: Bond Lengths and Bond Angles.

	Length (Å.)	e.s.d.		Angle (Degrees)	e.s.d.
Au-C1	1.935	0.019	C1-Au-N	176.8	0.7
Au-N	2.028	0.013	Au-C1-C2	174.2	1.8
C1-C2	1.210	0.028	C1-C2-C3	178.6	2.1
C2-C3	1.479	0.028	C2-C3-C4	119.8	1.9
C3-C4	1.385	0.030	C2-C3-C8	120.3	1.9
C4-C5	1.413	0.030	C3-C4-C5	118.7	2.0
C5-C6	1.375	0.035	C4-C5-C6	121.7	2.2
C6-C7	1.356	0.034	C5-C6-C7	118.3	2.3
C7-C8	1.387	0.029	C6-C7-C8	123.1	2.2
C8-C3	1.416	0.031	C7-C8-C3	118.3	2.0
N-C9	1.549	0.025	C8-C3-C4	119.8	1.9
C9-C10	1.533	0.031	Au-N-C9	117.2	1.1
C9-C11	1.488	0.033	N-C9-C10	109.0	1.7
			N-C9-C11	108.6	1.7
			C10-C9-C11	112.9	1.8

TABLE XII. $^{i}PrNH_2AuC{\equiv}CPh$: Intermolecular Contacts and Angles

	Length (Å.)		Angle (°)
Au(I)-Au(II)	3.274	Au(II)-Au(I)-Au(III)	86.2
Au(I)-Au(III)	3.722	Au(IV)-Au(I)-Au(III)	152.7
Au(I)-N(II)	3.47	Au(II)-Au(I)-N(I)	77.8
Au(I)-N(III)	3.70	Au(III)-Au(I)-N(I)	78.4
Au(I)-N(IV)	3.86	Au(IV)-Au(I)-N(I)	73.7
N(I)-C1(II)	3.34	Au(II)-Au(I)-C1(I)	104.6
N(I)-C1(III)	3.93	Au(III)-Au(I)-C1(I)	99.5
N(I)-C1(IV)	3.48	Au(IV)-Au(I)-C1(I)	108.5
N(I)-C2(IV)	3.77	Au(I)-N(I)-C1(II)	100.1
C1(I)-C11(IV)	3.83	Au(I)-N(I)-C1(IV)	105.6
N(I)-C2(II)	3.88	C9(I)-N(I)-C1(II)	136.2
C8(I)-C8(VI)	3.88	C9(I)-N(I)-C1(IV)	102.0
C6(I)-C11(V)	3.90	C1(II)-N(I)-C1(IV)	88.9
C2(I)-C10(IV)	3.94		
C7(I)-C7(VI)	3.95		
C3(I)-C10(IV)	3.96		
C8(I)-C10(IV)	3.96		

Position (I) refers to x y z
(II) to $\frac{1}{2}$-x $\frac{1}{2}$-y z
(III) to $\frac{1}{2}$-x y $\frac{1}{2}$+z
(IV) to $\frac{1}{2}$-x y $-\frac{1}{2}$+z
(V) to $-\frac{1}{2}$+x -y $\frac{1}{2}$-z
(VI) to x $\frac{1}{2}$-y $\frac{1}{2}$+z

Other contacts are greater than 4.0Å.

The arrangement is approximately octahedral, but with one site unoccupied, the angles being distorted by the zig-zag of the chains of gold atoms. The gold atoms are nearer to nitrogen atoms of adjacent molecules than to ethynyl carbons, and gold-nitrogen distances between the molecules are similar to the gold-gold distances.

Distances from gold atoms to ethynyl carbon atoms of adjacent molecules are all greater than 4.2Å., which would appear to rule out gold-ethynyl interaction of the 'side-on' type. The gold-gold distances of 3.27 and 3.72Å. are considerably greater than in the metal, (2.884Å.), whereas in the previous compounds, the copper-copper and silver-silver distances were comparable to the distances in copper and silver metal. Rundle, (1954), postulated gold-gold bonding at distances of 3.26Å. in dimethylglyoxime gold chloride, $Au(III)(DMG)_2Au(I)Cl_2$, where the coordination of the gold(I) atoms is square planar if gold-gold bonding is included. In the present compound, the coordination including gold atoms is less simple to describe, and it seems reasonable to consider each atom as forming just two collinear bonds. The angle N-Au-Cl is $176.8 \pm 0.7^{\circ}$, close to 180°, although the difference is significant on the basis of the calculated standard deviations.

The distance Au-Cl is 1.94 ± 0.02Å., shorter than the corresponding distance in the silver compound, (2.04Å.), and shorter than the Au-C distance in $KAu(CN)_2$.(2.12 ± 0.14Å., Rosenzweig and Cromer, 1959) 'End-on' π-bonding to the ethynyl group is again thought to occur, possibly to a greater extent than in the copper or silver complexes. The distance Au-N is 2.03Å. A covalent radius of 1.33Å. for linearly coordinated gold(I) may be deduced from the Au(I)-Cl bond lengths in $Cs_2Au(I)Au(III)Cl_6$ and in $AuCl.PCl_3$. (2.31 and 2.33Å. respectively, Elliott and Pauling, 1938; Arai, 1962). Since the covalent radius of nitrogen is 0.70Å., the gold-nitrogen distance is as expected for a single covalent bond.

The distance C1-C2 is 1.210 ± 0.028Å., in good agreement with usual values for carbon-carbon triple bonds. The angle Au-C1-C2 is 174.2 ± 1.8°. In the copper compound, the corresponding angle Cu1-C1-C2 is 172°, and in the silver compound the angle Ag1-C1-C2 is 173°, and the simil arity of the three angles is interesting. The angle Au-C1-C2 is significantly different from 180°, and the distortion is almost perpendicular to the plane of the phenyl group, as the plane through Au, C1, and C2 makes an angle of 84° with this plane. The angle C1-C2-C3 is 178.6 ± 2.1°, not significantly different from 180°.

The bond C2-C3 is contracted to 1.48Å., a value similar to the corresponding lengths in the copper and silver compounds. The carbon-carbon bond lengths in the phenyl group range from 1.36-1.42Å., with a mean value of 1.389Å., and the

angles from 118-123°, with a mean value of 120.0°. If the phenyl ring is assumed to be a regular hexagon, the standard deviations in the bond lengths and bond angles are 0.023Å. and 2.0°. The mean values calculated from the least squares estimates of the coordinate standard deviations are 0.032Å. and 2.1°.

The lengths of the bonds C9-C10 and C9-C11 are 1.53 ± 0.03Å. and 1.49 ± 0.03Å., not significantly different from the length of a single covalent bond. The distance N-C9 is 1.55 ± 0.03Å., and this is slightly longer than the expected value of 1.48Å. The valence angles at C9 are very close to the tetrahedral values, but the angle Au-N-C9 is significantly greater, being 117.2 ± 1.1°.

The equation of the best plane through the phenyl carbons (C3-C8) is

$$-0.1237\ x + 0.6143\ y - 0.7793\ z = 1.0058$$

with coordinates in Å., referred to the crystal axes. The distances of the atoms C3 to C8 from the plane are respectively 0.007, -0.011, 0.009, and -0.003, -0.001, -0.002Å., with a mean value of 0.005Å. The atoms C1 and C2 are at distances 0.040 and 0.010Å., so that C2 is in the plane of the phenyl group, but probably not C1. The atoms Au and N are at distances -0.106 and -0.371Å. from the plane.

The temperature factors for the gold atom are greatest in the 'y' and 'z' directions, i.e. in directions perpendicular to the direction of the bonding. The temperature parameters for the carbon atoms increase as their distance from the gold atoms increases. For instance, the temperature factors for carbon atoms C1 to C8 correspond approximately to B values of 5.6, 5.7, 5.6, 6.2, 7.5, 8.2, 7.1 and 6.5Å.^{2} respectively.

Apart from the gold-gold and gold-nitrogen contacts, the shortest distances between atoms of different molecules are nitrogen-carbon distances. All other contacts between molecules are greater than 3.8Å. The distance N(I)-C1(II) is 3.34Å., (between chains) and N(I)-C1(IV) is 3.48Å., (along chains), using the same notation as in table XII. The angles Au(I)-N(I)-C1(II) and Au(I)-N(I)-C1(IV) are 100° and 106° respectively, while C9(I)-N(I)-C1(II), C9(I)-N(I)-C1(IV) and C1(II)-N(I)-C1(IV) are 136°, 102° and 88° respectively. Corresponding angles to the midpoints of the ethynyl groups C1-C2, rather than to C1, are 109°, 115°, 127°, 97°, and 84°, respectively. Most of these angles are not far from tetrahedral, and the N-hydrogen atoms must point approximately towards neighbouring ethynyl carbon atoms. One cannot assign positions for the hydrogen atoms with certainty, as with the angle Au-N-C9 being 117°, it is difficult to know

what value to give to the Au-N-H and C9-N-H angles. With values of 108° for these angles, and N-H distances of 1.0Å., the N-H...C1 angles are 130° and 165° for molecules (II) and (IV) respectively.

The possibility of some weak interaction between the nitrogen and carbon atoms cannot be excluded, although the spectroscopic evidence is negative, (Coates and Parkin, 1962). The N-H...C distances are long, but are not much greater than the N-H...N distances of 3.38Å. in solid ammonia. (Olovsson and Templeton, 1959). Such interaction may be linked with the angle Au-N-C9 being greater than tetrahedral, and with the distortion of the angle Au-C1-C2 to 174°.

TABLE VIII. Observed and Calculated Structure Factors.

Successive columns give values of h, k, $|F_o|$, F_c

l = 0

0	0	---	1328	3	19	<16	-3	8	0	87	87	13	7	43	45
0	2	282	-263	3	21	20	23	8	2	21	-25	13	9	35	38
0	4	534	-490					8	4	37	-35	13	11	53	-55
0	6	517	456	4	0	260	266	8	6	80	80	13	13	<21	8
0	8	51	-51	4	2	190	-180	8	8	31	-27	13	15	22	20
0	10	256	-230	4	4	264	-239	8	10	38	-39				
0	12	207	189	4	6	302	284	8	12	38	42	14	0	105	113
0	14	54	57	4	8	16	-15					14	2	32	-35
0	16	120	-112	4	10	184	-181	9	1	59	-59	14	4	49	-50
0	18	31	34	4	12	108	107	9	3	32	-33	14	6	64	68
0	20	29	27	4	14	<22	11	9	5	33	34	14	8	<22	-3
				4	16	71	-67	9	7	29	-28	14	10	29	-33
1	1	---	-455	4	18	27	29	9	9	<20	-7	14	12	26	25
1	3	134	-115					9	11	27	27	14	14	<18	11
1	5	507	448	5	1	268	-265	9	13	<22	-16	14	16	16	-19
1	7	301	-269	5	3	43	-44								
1	9	168	-164	5	5	258	252	10	0	80	-74	15	1	78	-78
1	11	269	251	5	7	128	-127	10	2	<17	-3	15	3	<22	-11
1	13	65	-61	5	9	55	-52	10	4	<18	-2	15	5	87	93
1	15	86	-87	5	11	135	130	10	6	<19	-4	15	7	45	-49
1	17	74	66	5	13	43	-40	10	8	20	12	15	9	49	-49
1	19	<17	-7	5	15	37	-39	10	10	<22	-15	15	11	52	48
1	21	32	-28	5	17	47	46	10	12	<22	-11	15	13	<19	-7
												15	15	21	-22
2	0	422	-461	6	0	176	-194	11	1	44	-49				
2	2	216	193	6	2	118	113	11	3	19	-18	16	0	108	-111
2	4	301	278	6	4	138	131	11	5	19	16	16	2	35	38
2	6	436	-387	6	6	154	-148	11	7	<19	3	16	4	65	70
2	8	17	14	6	8	38	38	11	9	<18	12	16	6	81	-86
2	10	227	211	6	10	91	91	11	11	<17	9	16	8	<22	-3
2	12	145	-133	6	12	73	-72	11	13	<17	-1	16	10	55	53
2	14	22	-26	6	14	<22	-1					16	12	39	-35
2	16	79	77	6	16	43	42	12	0	88	-88				
2	18	33	-32	6	18	22	-21	12	2	22	23	17	1	96	99
2	20	15	-17					12	4	47	54	17	3	19	21
				7	1	181	177	12	6	47	-50	17	5	90	-94
3	1	402	410	7	3	19	21	12	8	<22	7	17	7	48	47
3	3	14	20	7	5	154	-159	12	10	46	44	17	9	26	33
3	5	369	-351	7	7	87	90	12	12	22	-27	17	11	54	-50
3	7	200	175	7	9	40	41	12	14	<21	-15				
3	9	90	91	7	11	84	-84	12	16	18	14	18	0	98	91
3	11	165	-154	7	13	22	23					18	2	33	-39
3	13	45	46	7	15	22	26	13	1	74	77	18	4	59	-60
3	15	61	63	7	17	29	-27	13	3	25	28	18	6	68	72
3	17	67	-63					13	5	79	-83	18	8	<19	-5

TABLE VIII. (continued)

18	10	56	-50
18	12	34	32
19	1	74	-71
19	3	<20	-13
19	5	73	73
19	7	43	-38
19	9	24	-25
19	11	45	42
20	0	69	-66
20	2	25	29
20	4	45	44
20	6	58	-52
20	8	<15	7
20	10	36	34
21	1	49	44
21	3	<16	9
21	5	40	-40
21	7	26	23
22	0	41	41
22	2	15	-16
22	4	25	-24
22	6	26	32

1 = 1

1	1	41	62
1	2	93	-100
1	3	197	-174
1	4	131	118
1	5	<16	3
1	6	<15	-6
1	7	60	68
1	8	28	-30
1	9	45	-46
1	10	<18	-4
1	11	<20	-2
1	12	<21	6
1	13	22	23
1	14	<23	-9
1	15	<23	-25
1	16	<23	-1
1	17	<23	-8
1	18	<21	10
2	1	39	39
2	2	18	-29
2	3	22	-20
2	4	185	180
2	5	<16	-5
2	6	25	25
2	7	72	-72
2	8	116	-117
2	9	33	31
2	10	31	32
2	11	<20	2
2	12	31	35
2	13	<22	-13
2	14	<23	-26
2	15	<23	15
2	16	<23	14
2	17	<23	-4
2	18	<21	14
3	1	74	-79
3	2	85	84
3	3	222	198
3	4	46	-50
3	5	<17	-1
3	6	<17	-9
3	7	72	-76
3	8	27	26
3	9	85	88
3	10	<20	-9
3	11	<22	-1
3	12	<23	-3
3	13	42	-45
3	14	<23	13
3	15	33	36
3	16	<23	1
3	17	<22	10
3	18	<21	-7
3	19	19	-17
4	1	49	47
4	2	217	214
4	3	49	-49
4	4	128	-129
4	5	23	19
4	6	54	-55
4	7	<19	14
4	8	115	119
4	9	24	-24
4	10	65	-66
4	11	<22	2
4	12	49	-48
4	13	<22	21
4	14	62	60
4	15	<23	-10
4	16	<23	-9
4	17	<22	-5
4	18	25	-25
5	1	168	159
5	2	94	-94
5	3	281	-262
5	4	52	50
5	5	63	65
5	6	39	41
5	7	166	162
5	8	72	-73
5	9	153	-147
5	10	23	23
5	11	<23	-17
5	12	34	30
5	13	84	89
5	14	29	-25
5	15	42	-36
5	16	<22	1
5	17	<22	-16
5	18	<20	8
5	19	18	26
6	1	35	-39
6	2	294	-275
6	3	75	78
6	4	208	190
6	5	<19	-21
6	6	65	68
6	7	30	-38
6	8	205	-199
6	9	44	48
6	10	75	73
6	11	<23	1
6	12	69	72
6	13	25	-24
6	14	77	-81
6	15	<25	11
6	16	<25	6
6	17	<24	5
6	18	28	28
6	19	<18	-8
6	20	21	-22
7	1	238	-224
7	2	106	99
7	3	327	307
7	4	62	-68
7	5	74	-76
7	6	28	-31
7	7	198	-200
7	8	62	66
7	9	164	161
7	10	28	-23
7	11	<23	12
7	12	35	-32
7	13	105	-107
7	14	31	26
7	15	44	46
7	16	<23	-2
7	17	<22	22
7	18	<19	-11
7	19	34	-33
8	1	78	74
8	2	369	339
8	3	115	-119
8	4	219	-212
8	5	<19	18
8	6	91	-90
8	7	50	51
8	8	226	220
8	9	52	-54
8	10	73	-79
8	11	<23	-5
8	12	78	-79
8	13	33	34
8	14	94	95
8	15	<24	-15
8	16	<25	-5
8	17	<23	-10
8	18	33	-35
8	19	<16	12
8	20	21	23
9	1	160	168
9	2	67	-69
9	3	300	-287
9	4	45	48
9	5	80	83
9	6	31	33
9	7	190	188
9	8	61	-65

TABLE VIII. (continued)

9 9	161	-162	
9 10	31	26	
9 11	<21	-15	
9 12	27	22	
9 13	96	97	
9 14	23	-24	
9 15	49	-47	
9 16	<21	5	
9 17	<19	-19	
9 18	<17	8	
9 19	31	32	
[illegible]			
10 1	42	-45	
10 2	260	-261	
10 3	86	90	
10 4	198	201	
10 5	30	-28	
10 6	74	78	
10 7	49	-54	
10 8	189	-185	
10 9	37	40	
10 10	64	66	
10 11	<23	6	
10 12	63	61	
10 13	33	-25	
10 14	74	-78	
10 15	<22	15	
10 16	<20	13	
10 17	<18	6	
10 18	32	33	
11 1	116	-120	
11 2	58	65	
11 3	248	245	
11 4	61	-66	
11 5	55	-56	
11 6	<23	-12	
11 7	156	-145	
11 8	47	49	
11 9	131	134	
11 10	<27	-14	
11 11	<28	9	
11 12	<27	-15	
11 13	71	-76	
11 14	22	21	
11 15	44	46	
11 16	<19	-3	
11 17	<17	16	
11 18	<15	-10	
12 1	34	35	
12 2	186	173	
12 3	53	-56	
12 4	147	-152	
12 5	<27	7	
12 6	50	-50	
12 7	53	57	
12 8	136	140	
12 9	40	-41	
12 10	53	-56	
12 11	<28	-3	
12 12	51	-51	
12 13	31	25	
12 14	57	55	
12 15	<22	-14	
12 16	<20	-11	
12 17	<18	-2	
12 18	17	-22	
13 1	87	87	
13 2	44	-44	
13 3	138	-142	
13 4	<22	26	
13 5	<26	16	
13 6	<25	-1	
13 7	63	63	
13 8	<27	-15	
13 9	78	-79	
13 10	<27	14	
13 11	<28	9	
13 12	<26	4	
13 13	45	47	
13 14	<24	-12	
13 15	32	-31	
14 1	<22	-24	
14 2	106	-102	
14 3	25	30	
14 4	74	76	
14 5	<29	-7	
14 6	<25	22	
14 7	<27	-15	
14 8	70	-75	
14 9	<27	18	
14 10	43	40	
14 11	<27	1	
14 12	32	28	
14 13	<24	-13	
14 14	38	-33	
14 15	<20	4	
15 1	53	-49	
15 2	<25	23	
15 3	91	87	
15 4	<23	-16	
15 5	33	-30	
15 6	<16	-10	
15 7	59	-53	
15 8	33	26	
15 9	64	57	
15 10	<27	-12	
15 11	<27	-1	
15 12	<27	-9	
15 13	27	-31	
15 14	<23	10	
16 1	<25	13	
16 2	71	67	
16 3	27	-27	
16 4	47	-49	
16 5	<25	10	
16 6	<25	-13	
16 7	<25	9	
16 8	47	47	
16 9	<25	-12	
16 10	25	-23	
16 11	<24	1	
16 12	<24	-11	
16 13	<24	5	
16 14	28	24	
17 1	29	26	
17 2	<25	-11	
17 3	44	-42	
17 4	<25	12	
17 5	<25	21	
17 6	<25	4	
17 7	32	28	
17 8	<25	-11	
17 9	32	-27	
17 10	<25	5	
18 1	<25	-3	
18 2	31	-26	

1 = 2

0 0	452	478	
0 1	404	-374	
0 2	64	-69	
0 3	159	-141	
0 4	329	-296	
0 5	316	272	
0 6	305	278	
0 7	121	-114	
0 8	<15	0	
0 9	64	-66	
0 10	170	-171	
0 11	145	148	
0 12	136	142	
0 13	29	-29	
0 14	21	20	
0 15	53	-56	
0 16	69	-72	
0 17	37	40	
0 18	27	27	
0 19	<17	2	
0 20	15	15	
0 21	14	-16	
1 0	262	-263	
1 1	416	-390	
1 2	121	111	
1 3	27	-33	
1 4	171	160	
1 5	373	331	
1 6	193	-181	
1 7	208	-203	
1 8	35	35	
1 9	104	-107	
1 10	114	120	
1 11	150	161	
1 12	69	-77	
1 13	35	-32	
1 14	<21	-20	
1 15	53	-66	
1 16	37	43	
1 17	38	48	
1 18	17	-16	
1 19	<17	-2	
1 20	<15	-9	
1 21	20	-22	
2 0	348	-355	
2 1	165	160	
2 2	154	148	
2 3	12	12	
2 4	186	185	
2 5	188	-180	

TABLE VIII. (continued)

2	6	285	-262
2	7	92	94
2	8	26	22
2	9	61	64
2	10	134	144
2	11	83	-88
2	12	92	-97
2	13	21	19
2	14	21	-21
2	15	26	30
2	16	49	59
2	17	25	-28
2	18	19	-24
3	0	168	172
3	1	228	227
3	2	86	-85
3	3	94	84
3	4	109	-104
3	5	259	-249
3	6	163	152
3	7	112	108
3	8	<15	3
3	9	76	79
3	10	73	-76
3	11	120	-132
3	12	46	52
3	13	44	44
3	14	<21	7
3	15	37	43
3	16	30	-37
3	17	40	-44
3	18	<19	14
4	0	227	229
4	1	147	-144
4	2	145	-148
4	3	11	-7
4	4	137	-141
4	5	168	156
4	6	200	193
4	7	84	-87
4	8	33	-34
4	9	59	-59
4	10	101	-107
4	11	65	70
4	12	60	65
4	13	21	-21
4	14	<21	11
4	15	34	-29
4	16	42	-45
4	17	24	26
4	18	18	18
5	0	165	-164
5	1	157	-161
5	2	36	38
5	3	21	-18
5	4	84	85
5	5	153	162
5	6	101	-104
5	7	85	-86
5	8	<16	4
5	9	41	-43
5	10	49	52
5	11	88	93
5	12	48	-50
5	13	26	-27
5	14	<21	-4
5	15	26	-27
5	16	27	28
5	17	37	34
6	0	157	-155
6	1	92	86
6	2	76	77
6	3	<13	7
6	4	108	110
6	5	80	-77
6	6	112	-116
6	7	50	56
6	8	27	24
6	9	22	23
6	10	63	70
6	11	46	-44
6	12	49	-54
6	13	21	18
6	14	<21	-1
6	15	<21	17
6	16	29	30
6	17	19	-16
7	0	103	106
7	1	86	87
7	2	40	-42
7	3	20	16
7	4	64	-58
7	5	85	-86
7	6	80	79
7	7	56	55
7	8	<18	-6
7	9	19	16
7	10	40	-44
7	11	48	-52
7	12	26	29
7	13	21	21
7	14	<21	6
7	15	<21	12
7	16	<20	-16
7	17	19	-17
8	0	86	91
8	1	32	-30
8	2	36	-36
8	3	<15	-5
8	4	37	-33
8	5	26	27
8	6	62	67
8	7	25	-26
8	8	<19	-14
8	9	<20	-2
8	10	32	-33
8	11	25	26
8	12	26	28
8	13	<21	-9
8	14	<21	4
8	15	<21	-4
9	0	41	-40
9	1	38	-40
9	2	<20	12
9	3	<16	-8
9	4	20	23
9	5	24	23
9	6	<18	-7
9	7	19	-24
9	8	<19	14
9	9	<19	-1
9	10	<20	10
9	11	<20	13
9	12	<20	-9
9	13	<20	-12
9	14	<20	-1
10	0	17	-18
10	1	17	14
10	2	21	-20
10	3	<17	13
10	4	<19	10
10	5	<19	-1
10	6	<20	-7
10	7	<20	-1
10	8	<20	-5
10	9	<20	-10
10	10	<20	2
10	11	<20	-8
10	12	<20	-13
11	0	31	-29
11	1	18	-16
11	2	<18	-4
11	3	26	-28
11	4	<19	10
11	5	19	22
11	6	<20	0
11	7	<20	5
11	8	<20	0
11	9	<21	-6
11	10	<21	-1
11	11	<21	17
11	12	<21	-7
11	13	<21	-6
11	14	<21	-2
12	0	50	-49
12	1	40	42
12	2	23	21
12	3	19	21
12	4	31	29
12	5	32	-32
12	6	41	-39
12	7	<21	17
12	8	<21	5
12	9	<21	12
12	10	26	27
12	11	26	-27
12	12	<21	-15
12	13	<21	2
12	14	<21	-8
13	0	57	59
13	1	58	57
13	2	20	-20
13	3	<20	4
13	4	35	-36
13	5	51	-48
13	6	39	38
13	7	26	3
13	8	<21	
13	9	21	

TABLE VIII. (continued)

13	10	26	-30
13	11	25	-25
13	12	27	28
13	13	<21	1
13	14	<21	8
14	0	73	74
14	1	36	-34
14	2	<21	-13
14	3	<21	-7
14	4	52	-50
14	5	37	34
14	6	52	52
14	7	<21	-16
14	8	<21	6
14	9	<21	-12
14	10	36	-36
14	11	20	19
14	12	27	28
14	13	<18	-3
14	14	<16	6
14	15	<15	-7
14	16	19	-16
15	0	40	-38
15	1	60	-61
15	2	26	25
15	3	<21	-6
15	4	34	31
15	5	63	62
15	6	40	-42
15	7	40	-38
15	8	<21	-2
15	9	25	-26
15	10	28	29
15	11	33	32
15	12	<18	-10
15	13	<16	-5
15	14	<15	-5
15	15	17	-16
16	0	83	-86
16	1	41	44
16	2	34	30
16	3	<21	9
16	4	50	50
16	5	50	-47
16	6	61	-62
16	7	21	20
16	8	<20	-1
16	9	20	17
16	10	40	38
16	11	25	-24
16	12	26	-24
17	0	51	57
17	1	56	62
17	2	21	-21
17	3	<21	16
17	4	39	-37
17	5	67	-64
17	6	40	39
17	7	31	32
17	8	<22	0
17	9	22	25
17	10	27	-26
17	11	43	-38
17	12	17	17
18	0	70	70
18	1	38	-37
18	2	32	-30
18	3	<20	-6
18	4	48	-45
18	5	41	38
18	6	56	55
18	7	25	-22
18	8	<17	-4
18	9	<16	-14
18	10	41	-35
18	11	25	22
18	12	24	22
19	0	42	-43
19	1	49	-50
19	2	<19	15
19	3	<22	-9
19	4	29	26
19	5	53	50
19	6	40	-33
19	7	32	-27
19	8	<15	1
19	9	17	-17
19	10	25	20
19	11	33	31
20	0	46	-47
20	1	27	28
20	2	21	20
20	3	<16	5
20	4	34	30
20	5	31	-27
20	6	40	-35
20	7	14	17
20	8	<12	5
20	9	13	10
21	0	32	26
21	1	35	32
21	2	<15	-8
21	3	<14	7
21	4	16	-14
21	5	39	-32
21	6	14	17
21	7	20	18
22	0	32	27
22	1	17	-16
22	2	11	-12
22	3	<10	-4
22	4	15	-15

1 = 3

1	1	22	20
1	2	59	-58
1	3	<16	-13
1	4	41	42
1	5	23	-24
1	6	48	49
1	7	<22	-13
1	8	66	-64
1	9	<24	-7
1	10	<25	11
1	11	<27	11
1	12	<27	10
1	13	<28	4
1	14	28	-25
1	15	<28	-7
1	16	<28	8
1	17	<27	-1
2	1	34	-31
2	2	51	-47
2	3	105	100
2	4	50	55
2	5	85	-91
2	6	<21	10
2	7	70	-62
2	8	46	-46
2	9	46	40
2	10	<25	20
2	11	<27	7
2	12	27	22
2	13	28	-20
2	14	<28	-12
2	15	<28	11
2	16	<27	4
3	1	28	-31
3	2	89	88
3	3	87	85
3	4	44	-47
3	5	19	-17
3	6	29	-30
3	7	35	-33
3	8	64	59
3	9	51	49
3	10	26	-21
3	11	<26	-1
3	12	<26	-13
3	13	28	-23
3	14	41	34
3	15	<28	17
3	16	<28	-7
4	1	89	87
4	2	98	102
4	3	109	-109
4	4	70	-73
4	5	<20	15
4	6	45	-36
4	7	85	76
4	8	73	69
4	9	68	-67
4	10	32	-28
4	11	<27	2
4	12	27	-23
4	13	50	44
4	14	28	29
4	15	28	-21
4	16	<28	-7
5	1	48	51
5	2	142	-147
5	3	97	-99
5	4	107	110
5	5	36	35

TABLE VIII. (continued)

5	6	31	31
5	7	61	63
5	8	104	-101
5	9	62	-61
5	10	41	38
5	11	<27	-3
5	12	45	43
5	13	41	35
5	14	45	-39
5	15	28	-19
5	16	<27	0
5	17	<25	-5
5	18	22	16
6	1	93	-93
6	2	138	-148
6	3	157	166
6	4	99	102
6	5	26	-27
6	6	43	39
6	7	94	-94
6	8	98	-100
6	9	92	94
6	10	33	34
6	11	<26	12
6	12	38	37
6	13	62	-59
6	14	41	-41
6	15	27	27
6	16	<26	2
6	17	<24	12
6	18	21	16
7	1	88	-96
7	2	169	180
7	3	124	136
7	4	120	-127
7	5	28	-30
7	6	55	-55
7	7	86	-93
7	8	126	126
7	9	71	75
7	10	48	-50
7	11	<28	0
7	12	50	-53
7	13	50	-50
7	14	53	49
7	15	27	26
7	16	<25	-4
7	17	<25	10
7	18	25	-22
8	1	106	114
8	2	123	137
8	3	175	-190
8	4	92	-104
8	5	24	18
8	6	35	-36
8	7	109	109
8	8	96	102
8	9	96	-104
8	10	35	-34
8	11	<28	-9
8	12	41	-35
8	13	65	65
8	14	40	42
8	15	32	-32
8	16	<25	-3
8	17	<25	-15
8	18	19	-16
9	1	72	81
9	2	148	-163
9	3	131	-147
9	4	125	134
9	5	44	45
9	6	37	39
9	7	91	96
9	8	115	-117
9	9	74	-82
9	10	40	42
9	11	<28	-10
9	12	45	47
9	13	49	50
9	14	51	-47
9	15	25	-24
9	16	<25	5
9	17	<25	-10
9	18	24	22
10	1	76	-83
10	2	125	-131
10	3	140	153
10	4	70	84
10	5	32	-36
10	6	33	39
10	7	101	-103
10	8	81	-86
10	9	79	83
10	10	33	39
10	11	<28	5
10	12	31	30
10	13	51	-49
10	14	42	-42
10	15	30	31
11	1	61	-66
11	2	123	130
11	3	102	115
11	4	96	-105
11	5	24	-22
11	6	44	-45
11	7	59	-60
11	8	105	109
11	9	61	65
11	10	36	-36
11	11	<28	3
11	12	36	-34
11	13	37	-38
11	14	53	46
11	15	23	19
12	1	60	67
12	2	66	69
12	3	106	-116
12	4	52	-62
12	5	45	45
12	6	<28	-15
12	7	69	67
12	8	59	58
12	9	64	-60
12	10	28	-27
12	11	<27	-3
12	12	26	-21
12	13	44	39
12	14	23	24
13	1	44	44
13	2	76	-82
13	3	72	-79
13	4	40	41
13	5	<28	
13	6	<28	23
13	7	45	44
13	8	53	-52
13	9	45	-43
13	10	34	29
13	11	<27	0
13	12	<24	16
13	13	24	25
13	14	34	-31
14	1	35	-39
14	2	41	-47
14	3	54	57
14	4	45	46
14	5	<28	-16
14	6	<28	9
14	7	35	-34
14	8	45	-40
14	9	38	40
14	10	<24	20
14	11	<24	-2
14	12	<24	11
14	13	27	-23
14	14	<19	-17
15	1	<28	-22
15	2	50	52
15	3	36	39
15	4	43	-45
15	5	<28	-14
15	6	<28	-6
15	7	30	-24
15	8	35	38
15	9	26	23
15	10	<25	-17
15	11	<25	-2
15	12	<24	-14
15	13	<24	-13
15	14	20	15
16	1	28	23
16	2	35	31
16	3	49	-43
16	4	<27	-20
16	5	<27	7
16	6	<26	-5
16	7	22	26
16	8	25	20
16	9	30	-27
17	1	<28	14

TABLE VIII. (continued)

17	2	27	-23
17	3	<27	-20
17	4	26	24
17	5	<26	9
17	6	<26	4
17	7	<26	13
17	8	26	-20

l = 4

0	0	110	99
0	1	302	-248
0	2	57	-54
0	3	79	-74
0	4	33	-32
0	5	260	221
0	6	74	70
0	7	108	-104
0	8	<29	-7
0	9	69	-59
0	10	19	-19
0	11	135	126
0	12	20	19
0	13	38	-32
0	14	<24	3
0	15	48	-47
0	16	<19	-18
0	17	38	41
0	18	<15	7
1	0	232	-262
1	1	72	-69
1	2	127	117
1	3	24	-13
1	4	190	167
1	5	104	93
1	6	213	-198
1	7	51	-46
1	8	25	21
1	9	42	-42
1	10	133	129
1	11	45	46
1	12	73	-78
1	13	<28	-14
1	14	26	-21
1	15	<24	-15
1	16	50	48
1	17	17	15
1	18	17	-18
2	0	111	-115
2	1	175	179
2	2	37	37
2	3	29	23
2	4	72	71
2	5	204	-178
2	6	81	-83
2	7	102	101
2	8	<26	9
2	9	61	58
2	10	47	52
2	11	95	-98
2	12	36	-39
2	13	28	23
2	14	<24	-7
2	15	34	36
2	16	21	20
2	17	30	-33
3	0	184	196
3	1	95	99
3	2	70	-69
3	3	25	22
3	4	128	-120
3	5	62	-60
3	6	143	141
3	7	33	36
3	8	<20	-4
3	9	<18	5
3	10	79	-80
3	11	35	-36
3	12	60	60
3	13	<28	11
3	14	<24	9
3	15	23	16
3	16	36	-38
3	17	<17	-13
4	0	40	41
4	1	123	-129
4	2	22	-19
4	3	<18	-12
4	4	36	-35
4	5	133	136
4	6	37	39
4	7	75	-82
4	8	<18	-9
4	9	51	-52
4	10	33	-32
4	11	69	71
4	12	28	23
4	13	19	-21
4	14	<24	0
4	15	23	-28
4	16	<18	-10
4	17	20	25
5	0	139	-150
5	1	38	-38
5	2	52	50
5	3	<23	3
5	4	72	72
5	5	43	46
5	6	103	-108
5	7	31	-33
5	8	<19	9
5	9	<19	-13
5	10	53	53
5	11	27	27
5	12	42	-47
5	13	<24	-5
5	14	<24	-6
5	15	<19	-5
5	16	25	28
5	17	<14	-8
6	0	43	-45
6	1	87	95
6	2	26	20
6	3	24	18
6	4	30	27
6	5	86	-94
6	6	28	-26
6	7	52	57
6	8	<18	7
6	9	31	31
6	10	<27	14
6	11	49	-52
6	12	<24	-14
6	13	<24	20
6	14	<23	1
6	15	<19	18
6	16	<16	9
6	17	16	-18
7	0	69	77
7	1	22	22
7	2	26	-28
7	3	<23	2
7	4	39	-40
7	5	<20	-13
7	6	54	57
7	7	<18	11
7	8	<19	-12
7	9	<19	-3
7	10	34	-31
7	11	<24	-10
7	12	24	28
7	13	<24	8
7	14	<19	1
7	15	<18	2
7	16	15	-14
8	0	<27	16
8	1	47	-53
8	2	<23	-8
8	3	<23	-5
8	4	<23	-12
8	5	39	43
8	6	25	25
8	7	31	-31
8	8	<23	-1
8	9	<27	-8
8	10	<27	-12
8	11	31	28
9	0	<27	-22
9	1	<27	-9
9	2	<27	11
9	3	<27	1
9	4	<28	19
9	5	<29	14
9	6	<30	-13
9	7	<31	-8
9	8	<31	11
9	9	<30	-6
9	10	<30	12
10	0	<28	-6
10	1	<28	12
10	2	<29	6
10	3	<29	6
10	4	<30	-7
10	5	<31	-7

TABLE VIII. (continued)

10	6	<31	-4
10	7	<31	0
10	8	<30	0
11	0	31	-33
11	1	<29	-17
11	2	<29	-2
11	3	<29	1
11	4	<29	19
11	5	<29	8
11	6	<29	-9
11	7	<29	-3
11	8	<29	-3
11	9	<29	1
12	0	<30	11
12	1	37	36
12	2	<30	5
12	3	<30	7
12	4	<30	-5
12	5	30	-31
12	6	<30	-8
12	7	<30	20
12	8	<30	-2
12	9	<30	12
12	10	<30	3
13	0	44	42
13	1	<31	0
13	2	<31	-18
13	3	<31	1
13	4	31	-29
13	5	<31	-11
13	6	32	33
13	7	<30	3
13	8	<30	-1
13	9	<30	7
13	10	28	-25
14	0	37	35
14	1	43	-44
14	2	<31	-10
14	3	<31	-13
14	4	<31	-15
14	5	43	44
14	6	<30	16
14	7	<30	-18
14	8	<29	-2
14	9	<28	-15
14	10	<27	-6
14	11	26	25
15	0	42	-43
15	1	<30	-20
15	2	29	24
15	3	<30	-7
15	4	32	31
15	5	<30	19
15	6	41	-40
15	7	<28	-11
15	8	<27	2
15	9	<26	-8
15	10	31	28
16	0	<30	-22
16	1	47	49
16	2	<29	7
16	3	<29	11
16	4	<29	14
16	5	53	-50
16	6	<27	-18
16	7	<27	21
16	8	<25	1
16	9	24	20
16	10	<22	12
16	11	33	-27
17	0	58	55
17	1	<27	19
17	2	<27	-21
17	3	<27	2
17	4	35	-35
17	5	<32	-18
17	6	43	41
17	7	<24	11
17	8	<23	-2
17	9	<21	6
17	10	31	-27
18	0	<26	21
18	1	46	-42
18	2	<25	-9
18	3	<25	-8
18	4	<24	-15
18	5	52	44
18	6	<22	16
18	7	<27	-24
18	8	<18	0
18	9	19	-17
19	0	52	-46
19	1	<22	-13
19	2	<22	16
19	3	<22	-2
19	4	29	26
19	5	<19	13
19	6	35	-34
20	0	<18	-14
20	1	31	28
20	2	<18	6
20	3	<17	6
20	4	<15	9
20	5	24	-28

1 = 5

1	1	<11	1
1	2	34	-37
1	3	15	18
1	4	19	17
1	5	<19	-12
1	6	<18	-2
1	7	23	-24
1	8	<17	-4
1	9	<19	9
1	10	<20	6
1	11	<21	6
2	1	19	-25
2	2	<15	7
2	3	43	38
2	4	<17	-15
2	5	19	-18
2	6	<18	-6
2	7	46	-47
2	8	<17	9
2	9	31	36
2	10	<20	3
2	11	<21	3
2	12	<23	-1
2	13	25	-21
2	14	<20	3
2	15	<19	10
3	1	<13	-3
3	2	66	68
3	3	16	9
3	4	51	-50
3	5	<17	-4
3	6	19	-12
3	7	<16	-7
3	8	44	47
3	9	<20	10
3	10	21	-20
3	11	<21	2
3	12	19	-11
3	13	<20	-4
3	14	25	23
3	15	<19	1
4	1	51	52
4	2	<16	4
4	3	91	-81
4	4	<22	-8
4	5	23	22
4	6	<18	2
4	7	50	48
4	8	<19	1
4	9	41	-39
4	10	<21	-2
4	11	<21	-2
4	12	<21	+2
4	13	34	27
4	14	<19	2
4	15	14	-14
5	1	<17	1
5	2	79	-79
5	3	<19	-8
5	4	65	63
5	5	<19	5
5	6	24	25
5	7	<19	7
5	8	65	-68
5	9	<20	-6
5	10	25	26
5	11	<21	1
5	12	29	26
5	13	<20	1
5	14	29	-28
5	15	<19	-3
6	1	71	-68

TABLE VIII. (continued)

6	2	<19	-6
6	3	126	119
6	4	<20	7
6	5	23	-18
6	6	<19	4
6	7	67	-70
6	8	<20	-8
6	9	61	67
6	10	<21	2
6	11	<21	7
6	12	<21	1
6	13	51	-41
6	14	<19	-3
6	15	19	19
7	1	<23	-9
7	2	117	117
7	3	<24	13
7	4	86	-84
7	5	<21	-4
7	6	32	-35
7	7	<20	-3
7	8	79	81
7	9	<21	1
7	10	30	-33
7	11	<21	-3
7	12	40	-35
7	13	<19	-2
7	14	37	36
7	15	<17	3
8	1	66	67
8	2	<20	3
8	3	124	-125
8	4	<21	-11
8	5	25	24
8	6	<20	-2
8	7	65	71
8	8	<21	12
8	9	65	-67
8	10	<21	-3
8	11	<21	-8
8	12	<20	-2
8	13	47	42
8	14	<16	3
8	15	21	-21
9	1	<21	5
9	2	105	-107
9	3	<22	-12
9	4	84	87
9	5	<22	5
9	6	37	37
9	7	<21	10
9	8	87	-92
9	9	<21	-9
9	10	29	33
9	11	<20	-1
9	12	39	35
9	13	<18	5
9	14	37	-36
9	15	<13	-2
10	1	62	-68
10	2	26	-22
10	3	103	114
10	4	<26	6
10	5	28	-25
10	6	<21	2
10	7	62	-67
10	8	<21	-3
10	9	56	60
10	10	<20	6
10	11	<19	2
10	12	<19	4
10	13	41	-39
10	14	<14	-5
10	15	21	22
11	1	<21	-2
11	2	83	92
11	3	<23	-2
11	4	60	-67
11	5	<21	3
11	6	25	-22
11	7	<21	4
11	8	66	65
11	9	<20	3
11	10	22	-26
11	11	<19	-2
11	12	22	-24
11	13	<14	-2
11	14	31	30
12	1	34	38
12	2	<21	3
12	3	56	-62
12	4	<21	-4
12	5	21	19
12	6	<21	0
12	7	46	48
12	8	<20	5
12	9	45	-44
12	10	<19	-3
12	11	<18	0
12	12	<14	-1
12	13	29	26
13	1	<21	3
13	2	61	-63
13	3	<21	-11
13	4	43	43
13	5	<25	6
13	6	<20	13
13	7	<20	6
13	8	42	-39
13	9	<19	-5
13	10	22	18
14	1	26	-24
14	2	<20	-5
14	3	46	44
14	4	<20	8
14	5	22	-16
14	6	<19	3
14	7	35	-27
14	8	<18	-7
14	9	36	28
15	1	<20	0
15	2	30	31
15	3	<20	1
15	4	26	-25
15	5	<19	-2
15	6	<18	-10
15	7	<18	0
15	8	30	28
15	9	<15	1
16	1	20	17
16	2	<17	0
16	3	32	-30
16	4	<16	2
16	5	<17	7
16	6	<17	2
16	7	17	12
16	8	<15	-2
16	9	20	-17
17	1	<18	2
17	2	20	-18
17	3	<14	-1
17	4	23	17
17	5	<15	0
17	6	<16	4
17	7	<16	0
17	8	13	-15
18	1	<17	-5
18	2	<15	2
18	3	12	13

APPENDIX A: THE CORRELATION OF STRUCTURE FACTORS FROM DIFFERENT FILMS

In the structure determinations of the copper and silver compounds, the structure factors were placed on the same relative scale using scale factors for the various reciprocal lattice layers derived by least squares methods from the common reflections. A derivation of the normal equations is as follows:

We write K_i for the scale factor by which the structure factors on layer i must be multiplied to place them on a common scale.

F_{hi} for the magnitude of the structure factor F(hkl) as observed on layer i.

w_h for the weight allotted to F_h in the least squares equations, assumed constant for all the layers on which F_h is measured.

For simplicity, we assume that no reflection occurs on more than two layers, even though there are more than two zone axes concerned. Then the quantity to be minimised can be written as:

$$Q = \sum(w_h K_i F_{hi} - w_h K_j F_{hj})^2$$

the summation being taken over all values of i and j. For Q to be a minimum with respect to each K_i, each $\partial Q/\partial K_i$ must be zero.

now $$\partial Q/\partial K_i = 2\sum w_h F_{hi}(w_h K_i F_{hi} - w_h K_j F_{hj}) = 0$$

There are n such equations for the n unknown K_i, and they may be written in matrix notation as

$$Ai_j.K = 0$$

where $a_{ii} = -\sum w_h F_{hi}^2$, the summation being taken over all those reflections F_h which are common to some other layers.

$a_{ij} = \sum w_h F_{hi} F_{hj}$ the summation being taken over all the reflections F_h which are common to both layers i and j.

The scale factors cannot be obtained from these equations as they stand, because the only exact solution is the trivial one with all the K_i equal to zero. Various means of obtaining exact solutions have been used, such as taking one of the scale factors as unity or introducing another variable. According to Rollett and Sparks, (1960), the proper procedure is to introduce a normalising condition, $\sum_n K_i^2 = 1$, which reduces the problem to one of finding the latent vector associated with the smallest latent root of the matrix A_{ij}. The latent vector can be obtained by the method of inverse iteration.

In the case of the copper compound, the quantity minimised was

$$Q' = \sum_{i,j} (K_i F_{hi} - K_j F_{hj} - e)^2$$

where e is a constant, intended to be very small, compared to the average value of $(K_i F_{hi} - K_j F_{hj})$. Differentiating Q with respect to the various K_i leads to the normal equations:

$$A_{ij} \cdot K_i = e \cdot R_i$$

where $R_i = \Sigma F_{hi}$, summed over all F_h occurring on two or more layers.

Convenient values of the K_i were obtained with a value for e of about 1/30. The mean value of $K_i F_{hi}$ was then around 100, so the quantity minimised, Q', is close to the quantity Q, for which e is zero.

Comparison of observed and calculated structure factors towards the end of the refinement of the copper compound gave rise to misgivings above the relative scaling of the layers. A check on the scaling was made, by calculating scale factors using the methods of Dickerson, (1959) and Kraut, (1958). Both these methods employ the principle of least squares. The scale factors obtained by these methods are compared with those obtained previously in table I, which also gives the values for each layer, of $\Sigma|F_c| / \Sigma|F_o|$ after the final cycle. In spite of the very different effective weighting given to planes by the Dickerson and the Kraut methods, the results given by these two methods

agree quite closely with one another, the mean discrepancy being about 1%. The results also agree reasonably well with the scale factors originally used. The maximum individual discrepancy between scale factors derived by the three methods is less than 4%. The scaling for the (3kl) reflections had been in doubt, but the scale factors for these reflections given by all three methods are in good agreement.

TABLE I. Film to Film Scaling Constants in $(Me_3PCuC{\equiv}CPh)_4$.

	Used	Dickerson	Kraut	$\Sigma\|F_c\| / \Sigma\|F_o\|$
h0l	0.108	0.110	0.108	0.96
h1l	0.125	0.129	0.130	1.01
h2l	0.116	0.115	0.118	1.00
h3l	0.119	0.120	0.119	0.99
h4l	0.120	0.121	0.122	0.99
0kl	1.031	1.024	1.014	0.95
1kl	0.114	0.115	0.117	1.00
2kl	0.409	0.407	0.410	1.01
3kl	0.683	0.684	0.679	1.07
4kl	0.662	0.659	0.651	0.98
5kl	0.749	0.745	0.744	0.98
6kl	0.818	0.809	0.827	1.00
7kl	0.838	0.850	0.866	0.97
hk0	1.000	1.000	0.991	0.98

In the case of the silver compound, the expression minimised was

$$E = \sum_{i,j}(K_i J_{ij} - K_j J_{ji})^2$$

after Dickerson, where J_{ij} is the sum of all reflections on film i common to j

J_{ji} is the sum of all reflections on film j common to i

and $J_{ij} = J_{ji} = 0$ if the films do not intersect.

This method treats the reflections in any one reciprocal lattice row 'en block', and the normal equations are very much easier to set up. The scaling constants were obtained from the normal equations by the method of inverse iteration, rather than by the method given by Dickerson.

APPENDIX B.

COMPUTER PROGRAMMES

The extensive calculations were carried out using the Ferranti 'Pegasus' computer at King's College, Newcastle. Thanks are expressed to those who have kindly made their programmes available.

Structure Factor/least Squares Refinement:

This was done using the least squares programme due to D.W.J. Cruickshank, D.E. Pilling and M.R. Truter of Leeds. The programme computes the contributions to all the least squares totals for each plane in turn, accumulating the totals on drum storage. The block matrix scheme is used, and all the terms in the 3x3 and the 6x6 matrices giving the shifts in the atomic coordinates and the shifts in the anisotropic temperature parameters, are calculated. It is possible also to refine a structure using isotropic temperature factors for some or all of the atoms. The changes in scale are calculated from the 2x2 matrix obtained by correlation of the scale with the overall temperature factor. The programme can handle all space groups. Individual weighting routines may be written for each problem, although standard routines are available.

These authors were also responsible for a programme to calculate bond lengths and angles.

Patterson and Fourier Syntheses:

Patterson and Fourier summations in two dimensions were calculated using a programme due to P.A. Samet, formerly of King's College, Newcastle. The form of the output is suitable for drawing contour levels directly. Summations in three dimensions were obtained by first carrying out preliminary summations of the three dimensional data in one direction, using a programme by H.P. Stadler, and then using the Samet programme to calculate each section in the Patterson function or in the electron density.

The calculation of Fourier series was aided by a programme written by H.M.M. Shearer, which would produce a tape suitable for input to the programme for preliminary summation from the output tape of the structure factor/ least squares programme.

Other Programmes:

I have written a programme which will calculate the Lorentz and polarisation factors for reflections on zero- and upper-layer photographs, obtained by either Weissenberg or precession methods. Depending on the setting of the hand-switches, the output gives values or $\sin\theta$, or of

reciprocal values of the Lorentz-polarisation factors, or of the square root of the corrected intensities, or else of the corrected intensities, weighted, and in a form suitable for calculation of a two-dimensional projection of the Patterson function, using the Samet programme. Both input and output are in tabular form, not requiring values of h, k, or l to be punched.

Other minor programmes have been written for particular needs. A programme for making a rapid calculation of bond lengths at the end of a cycle of least squares refinement was found useful. (Orthorhombic space groups only).

APPENDIX C.

TRANSFORMATION OF U_{ij}'s FROM MONOCLINIC TO ORTHORHOMBIC AXES.

The equations for transforming the U_{ij} in the silver compound, which were referred to the monoclinic crystal axes, to U'_{ij}, referred to orthorhombic axes parallel to a*, b, and c were:

$$U'_{11} = U_{11}$$

$$U'_{22} = U_{22}$$

$$U'_{33} = U_{33}/\sin^2\beta^* + U_{11}\cos^2\beta^*/\sin^2\beta^* - U_{13}\cos\beta^*/\sin^2\beta^*$$

$$U'_{12} = U_{12}$$

$$U'_{23} = -U_{12}\cos\beta^*/\sin\beta^* + U_{23}/\sin\beta^*$$

$$U'_{13} = -2U_{11}\cos\beta^*/\sin\beta^* + U_{13}/\sin\beta^*$$

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