THE X-RAY CRYSTAL STRUCTURE ANALYSES AND THE CHEMICAL SYNTHESES OF AMINOPHOSPHINE COMPLEXES.

A thesis

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by

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PREFACE.

The work described in this thesis was carried out in the Inorganic and Physical Chemistry Department of the University of Glasgow, which is under the direction of Professor J.Monteath Robertson,F.R.S.

I wish to express my sincere thanks to my supervisors- Dr. D.S.Payne and Dr. J.C.Speakman for their instructive supervision, interest and encouragement throughout the period of my research.

I am grateful to Professor D.W.J.Cruickshank for his advice on the refinements of some of the crystal structures, and to Drs. G.S.Harris and H. Mills for helpful discussions.

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SUMMARY.

The work described in this thesis is divided into five main parts and one appendix. Parts I - III deal with the accounts of the X-Ray studies of three derivatives of bis-(diphenyl-phosphino)-ethylamine, $(C_6H_5)_2P.N.(C_2H_5)P(C_6H_5)_2$. Part IV describes the crystal structure analysis of lead thiocyanate and Part V summarises the chemical syntheses of some aminophosphine complexes. The appendix contains some of the methods and theories used in X-Ray Crystallography.

In all the X-Ray work, the heavy atom technique was used to overcome the phase problem. Intensities were estimated visually and the refinement of each structure was by the three-dimensional least-squares analysis.

PART I : This section contains an account of the X-Ray study of dichloro-bis-(diphenyl-phosphino)-ethylamine palladium (II), $C_{26}H_{25}P_2NPdCl_2$. The results obtained show that the ligand is bidentate and that the complex has a cis-configuration. Other features of the palladium complex are described.

PART II : The crystal structure of the ethyl iodide adduct of bis-(diphenyl-phosphino)-ethylamine, $(C_6H_5)_2P.N.(C_2H_5)P(C_2H_5)(C_6H_5)_2{}^+I^-$ is established. The two phosphorus atoms differ significantly in their configuration and the quaternisation takes place at one P-atom only. Other points discussed include the delocalisation of the lone pair on nitrogen and evidence in favour of $d\pi$-$p\pi$ bonding in P-N-P systems.

PART III : This contains information about the X-Ray structure analysis of bis-(diphenyl-phosphino)-ethylamine molybdenum tetracarbonyl, $C_{26}H_{25}NP_2Mo(CO)_4$. The molybdenum atom is octahedrally coordinated with the ligand occupying two neighbouring sites. An attempt is made to obtain the Mo-C bond order from the observed Mo-C bond lengths. Additional evidence was obtained in support of d_{π}-p_{π} back-bonding in P-N-P system.

PART IV : The crystal structure of the lead thiocyanate, supplied by Miss Ida Woodward of Queen's University, Belfast, is reported in this section. Results show a six-fold coordination of Pb and bonding through S and N of different thiocyanate ions.

PART V : The transition metal complexes of some amino-phosphine compounds have been prepared. The ligands used are of the formula - Ph_2P-NR-P.Ph_2(R = H,Me,Et,nPr and iPr). Complexes with the above ligands have been formed with Nickel (II) iodide, bromide, nitrate and thiocyanate. The corresponding complexes of mercury (II) iodide, bromide and chloride were also prepared. With bis-(diphenyl-phosphino)-ethylamine, the palladium (II) chloride complex and the mono-ethyl iodide adduct were prepared, whilst the disulphide and diselenide of the bis-(diphenyl-phosphino)-methylamine were formed.

Part of the work on the chemical syntheses was published in the Journal of the Chemical Society,

(Payne et al., J.C.S., 1964, 1543).

PART I

X-RAY STRUCTURE ANALYSIS OF DICHLORO-BIS(DIPHENYL-PHOSPHINO) ETHYLAMINE-PALLADIUM (II)

1.1. INTRODUCTION

After the extensive work of C.A.A. Michaelis (1890-1905), the study of aminophosphines has developed slowly. Little or nothing was reported in the chemical journals until 1946 when Grimmer and co-workers described the synthesis of PhNHPNPh from PCl_3 and aniline. However, since then several other inorganic chemists have joined in the task of discovering the chemistry of the aminophosphines.

Although much work has now been done in this field of P-N compounds, the interpretation of many of the reactions involved remains confused. Kosolapoff (1950) in his book on organo phosphorus chemistry writes: "Many of the rather interesting reactions used in the synthesis and interconversions of this family are very imperfectly understood For this reason, a considerable confusion exists in the literature on this subject to the present day. The elimination of such confusion is extremely necessary and its accomplishment is one of the great challenges in the field of organo phosphorus compounds". Van Wazer further comments that, "Kosolapoff might have added that some of the structures assigned to a number of organic compounds involving P-N bonds were patently absurd."

As interest grew in the chemistry of aminophosphines, it became evident that X-Ray work was necessary to solve some structural problems in this field. One such problem is the type of bonding in tervalent P-N systems and the bidentate nature of ethyl - bis-(diphenyl-phosphino)-amine in complex formation with the transition metals.

There is clearly a need for X-Ray crystallographic work; but, at the time of writing, no such work has been published, either on the ligand itself or on its complexes. This thesis therefore describes the first structure analysis of compounds of this class.

The ligand, ethyl bis-(diphenyl-phosphino)-amine was first prepared by G. Ewart (1962). He prepared the mercuric iodide adduct of the ligand but the structure of the complex was not known.

It is reasonable to assume that, since the ligand with a PNP skeleton has two phosphorus atoms and one nitrogen, it is capable of behaving as either a bidentate ligand to a 4-co-ordinated mercury or as a monodentate ligand to a 3-co-ordinated mercury.

In further work on complex formation by Payne et al (1964), the chemical studies were more in favour of the bidentate nature of the ligand than of the monodentate; but, since no X-Ray information was available regarding the structure and the stereochemical nature of these complexes, it was not easy to say with any certainty the nature of the bonding of the ligand in complex formation and to explain the exact type of bonding around the two phosphorus atoms and the nitrogen bridging them.

In order to elucidate these problems, the X-Ray structure analysis of the Dichloro-bis-(diphenyl-phosphino)-ethylamine-palladium (II) was undertaken.

Several samples of this complex were prepared as described in Part V of this thesis.

Subsequent chemical analysis showed the formula to be $C_{26}H_{25}$.PNP.$PdCl_2$. The crystals were pale yellow needles and were of such good quality that many faces were visible. Small single crystals were picked for X-Ray work. The preliminary photographic work was kindly done by Mr. Gyte formerly of this Department.

1.2. CRYSTAL DATA

Crystals of $[(C_6H_5)_2P]_2NC_2H_5Pd\ Cl_2$ (mol. wt. 591.13) are orthorhombic with $a = 20{\cdot}90 \pm 0{\cdot}02$ Å, $b = 17{\cdot}60 \pm 0{\cdot}02$ Å, $c = 13{\cdot}87 \pm 0{\cdot}02$ Å; volume of unit cell, V = 5106 Å^3; measured density, $\rho m = 1{\cdot}56$ gm/cc; calculated density $\rho c = 1{\cdot}54$ gm/cc for 8 molecules per unit cell. The total number of electrons per unit cell, F(000) = 2584, $\sum f^2_{Pd} = 2116$, $\sum f^2_{Rest} = 2038$. The linear absorption coefficient, for CuKα - radiation ($\lambda = 1{\cdot}542$ Å), $\mu = 92$ cm^{-1}, M. Pt. = 277 $\pm$ 1°C.

1.3. SPACE GROUP DETERMINATION

The following systematic halvings were observed from Weissenberg photographs of the principal zones -

On hk0 : h = 2n which indicates the presence of a glide plane along a perpendicular to c.

0k0 : k = 2n this indicates a 2_1 axis along b.

h0l : l = 2n, glide plane along c normal to b.

h00 : h = 2n, a 2_1 axis along a.

0kl : k = 2n, a glide plane along b, normal to a and

00l : l = 2n indicates a 2_1 axis along c.

These conditions unambiguously indicate the space group

$P2_1/b2_1/c2_1/a$ i.e. $Pbca(D_{2h}^{15})$.

1.4. INTENSITY DATA

The Weissenberg photographs of the nets h0l, 0kl and hk0–hk10 were taken employing the multiple-film technique due to Robertson (1943). The intensity data which consist of about 3000 independent reflections were visually estimated by comparison with a calibrated intensity step wedge. Crystals of an average width 0·015 cm were used; the value of about 0·5 for μR was sufficiently small that absorption corrections could be neglected. Corrections were however made for the Lorentz, polarisation and rotation factors (Tunell, 1939). The observed intensities were placed on a relative scale before being converted to the structure-factor amplitudes, $|Fo|$, the values of which were later placed on the same scale by correlation with the corresponding values of the calculated structure amplitudes.

1.5. PALLADIUM ATOM POSITION

Patterson projections down the three axes (21, 18 and 14 Å) were computed. The resolution of peaks was very poor in each of the projections when ordinary Fo^2 values were used. Later the Fo^2 values were sharpened by conversion to $F_{OM}^2(\underline{S})$, the values of $F_{OM}^2(\underline{S})$ (Appendix) were used, and the effect of this was that most of the diffuse peaks obtained in the unsharpened maps became very prominent. For example, Fig. (1) is the unsharpened Patterson projection P(VW) with virtually no peak apart from the origin. When this was sharpened (Fig. 2) many peaks such as A, B, C became outstanding and could be attributed to the Pd–Pd vectors. In this way, the other two

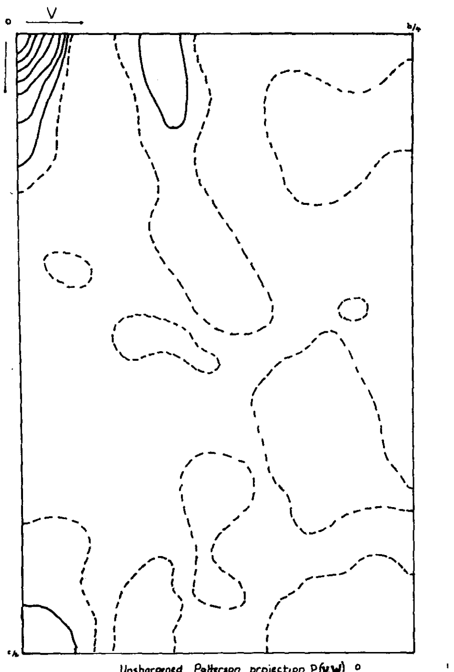


Fig 1 Unsharpened Patterson projection P(V,W)
Contour scale equally arbitrary

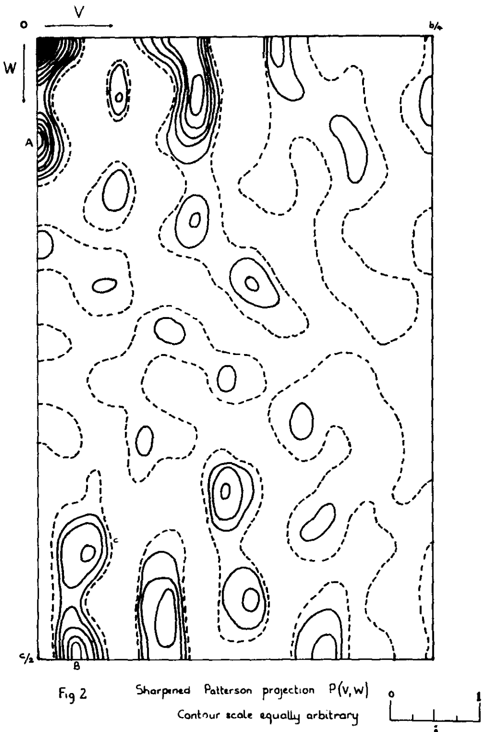


Fig 2 Sharpened Patterson projection P(V, W)
Contour scale equally arbitrary

sharpened Patterson projections P(UV) and P(UW) were obtained and solved. From the eight equivalent positions of the space group (Pbca), positions of the heavy atom - heavy atom vectors were worked out (Table 1).

For the projection P(UV), double weight Pd-Pd vector peaks were expected at $A^1(\frac{1}{2}, \frac{1}{2} - 2y)$ on line $P(\frac{1}{2}, V)$, at $B^1(2x, \frac{1}{2})$ on line $P(U, \frac{1}{2})$ and a single weight peak at $C^1(2x, 2y)$ in a general position. These peaks were found present (Fig. 3) and from these the x and y co-ordinates of palladium atom were determined. In the same way P(U, W), has the corresponding palladium - palladium vector peaks at J, M and O (Fig. 4). these peaks gave the values of x and z. Similar vector peaks found in P(V, W), Fig. (2) confirmed the values of y and z already obtained from other two projections.

The co-ordinates of palladium atom so determined were $x = 0{\cdot}1650$; $y = 0{\cdot}0142$ and $z = 0{\cdot}2097$.

1.6. STRUCTURE DETERMINATION

With the above values of Palladium co-ordinates the first set of structure factors was calculated with an isotropic temperature factor, B = $3{\cdot}7\text{Å}^2$. Structure factors were calculated for 2,735 observable reflections. The starting reliability factor, R, was 46%. Terms with very large ($|F_o| - |F_c|$) and especially with positive signs were considered to have doubtful phases hence discarded. So that only 960 terms were selected for the first 3-dimensional Fourier synthesis. Computation of the Fourier synthesis was along the z-axis. The resulting 3-dimensional map gave part of the structure; four other peaks were revealed around the palladium. These four peaks were

TABLE 1.

Pbca – INTER-ATOMIC VECTORS.

	x, y, z	$\frac{1}{2}+x, \frac{1}{2}-y, -z$	$-x, \frac{1}{2}+y, \frac{1}{2}-z$	$\frac{1}{2}-x, -y, \frac{1}{2}+z$
x, y, z	–	$\frac{1}{2}, \frac{1}{2}+2y, 2z$	$2x, \frac{1}{2}, \frac{1}{2}+2z$	$\frac{1}{2}+2x, 2y, \frac{1}{2}$
$\frac{1}{2}+x, \frac{1}{2}-y, -z$	$\frac{1}{2}, \frac{1}{2}-2y, -2z$	–	$\frac{1}{2}+2x, \frac{1}{2}-2y, \frac{1}{2}$	$2x, \frac{1}{2}, \frac{1}{2}-2z$
$-x, \frac{1}{2}+y, \frac{1}{2}-z$	$-2x, \frac{1}{2}, \frac{1}{2}-2z$	$\frac{1}{2}-2x, 2y, \frac{1}{2}$	–	$\frac{1}{2}, \frac{1}{2}+2y, -2z$
$\frac{1}{2}-x, -y, \frac{1}{2}+z$	$\frac{1}{2}-2x, -2y, \frac{1}{2}$	$-2x, \frac{1}{2}, \frac{1}{2}+2z$	$\frac{1}{2}, \frac{1}{2}-2y, 2z$	–
$-x, -y, -z$	$-2x, -2y, -2z$	$\frac{1}{2}-2x, \frac{1}{2}, 0$	$0, \frac{1}{2}-2y, \frac{1}{2}$	$\frac{1}{2}, 0, \frac{1}{2}-2z$
$\frac{1}{2}-x, \frac{1}{2}+y, z$	$\frac{1}{2}-2x, \frac{1}{2}, 0$	$-2x, 2y, 2z$	$\frac{1}{2}, 0, \frac{1}{2}+2z$	$0, \frac{1}{2}+2y, \frac{1}{2}$
$x, \frac{1}{2}-y, \frac{1}{2}+z$	$0, \frac{1}{2}-2y, \frac{1}{2}$	$\frac{1}{2}, 0, \frac{1}{2}+2z$	$2x, -2y, 2z$	$\frac{1}{2}+2x, \frac{1}{2}, 0$
$\frac{1}{2}+x, y, \frac{1}{2}-z$	$\frac{1}{2}, 0, \frac{1}{2}-2z$	$0, \frac{1}{2}+2y, \frac{1}{2}$	$\frac{1}{2}+2x, \frac{1}{2}, 0$	$2x, 2y, -2z$

	$-x, -y, -z$	$\frac{1}{2}-x, \frac{1}{2}+y, z$	$x, \frac{1}{2}-y, \frac{1}{2}+z$	$\frac{1}{2}+x, y, \frac{1}{2}-z$
x, y, z	$2x, 2y, 2z$	$\frac{1}{2}+2x, \frac{1}{2}, 0$	$0, \frac{1}{2}+2y, \frac{1}{2}$	$\frac{1}{2}, 0, \frac{1}{2}+2z$
$\frac{1}{2}+x, \frac{1}{2}-y, -z$	$\frac{1}{2}+2x, \frac{1}{2}, 0$	$2x, -2y, -2z$	$\frac{1}{2}, 0, \frac{1}{2}-2z$	$0, \frac{1}{2}-2y, \frac{1}{2}$
$-x, \frac{1}{2}+y, \frac{1}{2}-z$	$0, \frac{1}{2}+2y, \frac{1}{2}$	$\frac{1}{2}, 0, \frac{1}{2}-2z$	$-2x, 2y, -2z$	$\frac{1}{2}-2x, \frac{1}{2}, 0$
$\frac{1}{2}-x, -y, \frac{1}{2}+z$	$\frac{1}{2}, 0, \frac{1}{2}+2z$	$0, \frac{1}{2}-2y, \frac{1}{2}$	$\frac{1}{2}-2x, \frac{1}{2}, 0$	$-2x, -2y, 2z$
$-x, -y, -z$	–	$\frac{1}{2}, \frac{1}{2}-2y, -2z$	$-2x, \frac{1}{2}, \frac{1}{2}-2z$	$\frac{1}{2}-2x, -2y, \frac{1}{2}$
$\frac{1}{2}-x, \frac{1}{2}+y, z$	$\frac{1}{2}, \frac{1}{2}+2y, 2z$	–	$\frac{1}{2}-2x, 2y, \frac{1}{2}$	$-2x, \frac{1}{2}, \frac{1}{2}+2z$
$x, \frac{1}{2}-y, \frac{1}{2}+z$	$2x, \frac{1}{2}, \frac{1}{2}+2z$	$\frac{1}{2}+2x, -2y, \frac{1}{2}$	–	$\frac{1}{2}, \frac{1}{2}-2y, 2z$
$\frac{1}{2}+x, y, \frac{1}{2}-z$	$\frac{1}{2}+2x, 2y, \frac{1}{2}$	$2x, \frac{1}{2}, \frac{1}{2}-2z$	$\frac{1}{2}, \frac{1}{2}+2y, -2z$	–

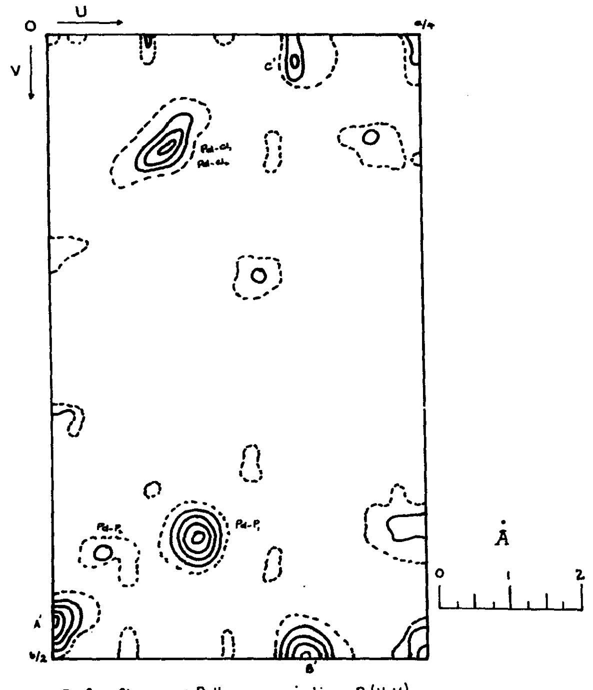


Fig 3. Sharpened Patterson projection P (U,V).
Contour scale equally arbitrary.

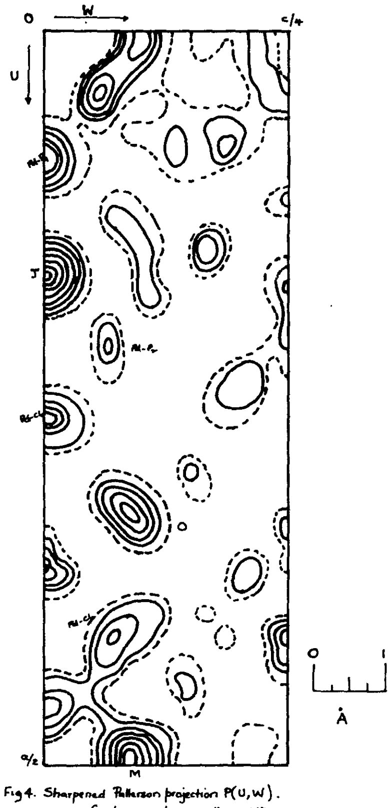


Fig 4. Sharpened Patterson projection P(U,W).
Contour scale equally arbitrary.

considered to be due to the two chlorine and the two phosphorus atoms in the structure. However, it was not possible to say with any certainty which peaks were due to chlorine and which to phosphorus since these atoms have similar atomic numbers (Cl = 17, P = 15). Hence, in the subsequent round of structure-factor calculations, apart from the palladium the other four atoms were put in as phosphorus atoms - that is using the atomic scattering factors of phosphorus for the four.

The value of R fell by 6% from the last value (Table 2) The second round of Fourier synthesis was computed with 1200 terms. Another six peaks which could be attributed to one of the phenyl groups thus became apparent. Apart from these, only the nitrogen atom bridging the two phosphorus atoms could be located with some certainty. No other peak could be assigned to any of the remaining atoms. Instead, there were diffuse peaks especially around palladium, which might be diffraction ripples. Thus only twelve atoms were used in the third set of structure-factor calculations. The R-factor was 37%. 1935 terms were selected for the third Fourier synthesis. The map obtained revealed the structure (Fig. 5) of the complex. The subsequent structure-factor calculations gave an R value of 28·8%. After this, two other Fourier syntheses were computed to ensure best positions for the atoms and to see that there was consistency in the signs of the calculated structure factors.

TABLE 2.

COURSE OF ANALYSIS.

231 Reflections for P(UV) Patterson projection.

127 " " P(UW) " "

80 " " P(VW) " "

Found Palladium atom.

1st Structure-factor calculations, B_{Pd} = 3.7Å^2 (the temp. factor).

R = 46%

960 Reflections for the 1st. 3-D Fourier synthesis.

Found Pd + 4 P/Cl atoms.

2nd. Structure-factor calculations, B_{Pd} = 3.7Å^2, $B_{P/Cl}$ = 4.5Å^2

R = 40%

1200 Reflections for the 2nd. 3-D Fourier synthesis.

Found Pd + 4 P/Cl + 6C + N atoms.

3rd. Structure-factor calculations, B_{Pd} = 3.7, $B_{P/Cl}$ = 4.5, $B_{C/N}$ = 4.5Å^2.

R = 37%

1935 Reflections for the 3rd. 3-D Fourier synthesis.

Found All the 32 atoms except the hydrogen atoms.

4th. Structure-factor calculations, using the above temp. factors.

R = 28.8%

- Cont'd -

TABLE 2. - Cont'd -

Adjustments of Carbon atom positions in the benzene rings obtained from the projections down the a, b, and c axes.

5th. Structure-factor calculations, using the above temp. factors.

R = 26.7%

2500 Reflections for the 4th. 3-D Fourier synthesis.

Found Whole structure.

6th. Structure-factor calculations, temp. factors unchanged.

R = 23.0%

2735 Reflections for the 5th 3-D Fourier synthesis.

Found Whole structure.

7th. Structure-factor calculations, temp. factors unchanged.

R = 21.5%

2735 3-D (Fo - Fc) Fourier synthesis.

All atoms included.

8th. S.F. calculations, $B_{Pd} = 3.3, B_{Cl} = 3.6, B_{P} = 3.8$
$B_{N} = 4.4, B_{C} = 4.7$.

R = 18.4%

TABLE 2. -Cont'd -

1st. Cycle of S.F.L.S. Refinement, B_P, B_{Cl}, B_{Pd} are anisotropic while B_N, B_C, remain isotropic

R = 15.4%

2nd. Cycle of S.F.L.S. Refinement.

R = 15.35%

3rd. Cycle of S.F.L.S. Refinement.

R = 14.52%

4th. Cycle of S.F.L.S. Refinement.

R = 13.20%

5th. Cycle of S.F.L.S. Refinement, Weighting scheme changed.

R = 11.69%

6th. Cycle of S.F.L.S. Refinement.

R = 11.30%

7th. Cycle of S.F.L.S. Refinement, anisotropic temp. factors are calculated for all atoms.

R = 11.26%

Last S.F. calculations.

R = 10.90%

1.7. STRUCTURE REFINEMENT

The first stage involved the elimination of series termination effects by computing one cycle of difference Fourier synthesis. The temperature factors were also adjusted and the R-factor was slightly improved (the value at this stage was 18.4%).

Further refinement was made by the method of Least-squares. The Least-squares block-diagonal programme written by Professor Cruickshank and Mr. J. Smith for the K.D.F. 9 computer at Glasgow University was used.

The weighting scheme first adopted requires $\sqrt{w_{hkl}} = F_{hkl} / 6 \times F_o$ min. If $F_o \leqslant 6 \times F_o$ min (F_o min = 1·50). Later this was found unsuitable for the type of photographic data collected and a change was made after the fourth cycle to one recommended by Professor Cruickshank. This is of the form -

$$\sqrt{w} = 1/[p_1 + |F_o| + p_2 |F_o|^2 + p_3 |F_o|^3]^{\frac{1}{2}}$$

where $p_1 = 2 \times F_o$ min, $p_2 = 2/F_o$ max, $p_3 = 0$.

Throughout the refinement, the ten partial-shift factors (Rollett's) recommended in the Least-squares programme were used with some discretion, depending on the progress achieved in the preceding cycles of refinement. In general, the shift factors 0·8, 0·9 and 0·7 were used and it was only when the structure was converging that the shift 1·26 was applied.

Each atomic position was evaluated from a 3 x 3 matrix while a 2 x 2 matrix was solved for the overall scale-factor. The thermal vibrations were computed from a 6 x 6 matrix for the palladium, chlorine and phosphorus atoms, while the thermal vibrations of the rest of the atoms (mainly carbon) were given isotropic refinement in all but the last cycle, (Table 5).

Seven cycles of least-squares brought the atomic parameters to convergence. The reliability-factor of the last set of scaled structure-factors was 10·90% (Table 2).

The final atomic co-ordinates obtained from the seventh least-squares cycle are shown in Table 3, while the corresponding standard deviations are listed in Table 4. The interatomic bond lengths are listed in Table 6 with estimated standard deviations. The standard deviation, $\sigma(A-B)$, of a bond between atoms (A) and (B) is given by the formula,

$$\sigma(A-B)^2 = \sigma(A)^2 + \sigma(B)^2$$

where $\sigma(A)$ and $\sigma(B)$ are the standard deviations in co-ordinates of the atoms (A) and (B). The inter-bond angles with estimated standard deviations are listed in Table 7
The standard deviation, $\sigma(\beta)$ in radians, for an angle (β) formed at atom (B) by the atoms (A) and (C) is given by the formula,

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

(Robertson and Cruickshank, 1953). The intramolecular non-bonded and intermolecular distances less than 4·0 Å are given in Tables 8 and 9. The shortest of these distances is 3·30 Å, which suggests the absence of any interactions between molecules other than those of the van der Waals type. Table 10 lists the equations of the best mean planes defined by a given number of atoms and the perpendicular distances of these and

TABLE 3.

DICHLORO-BIS(DIPHENYL-PHOSPHINO)-ETHYLAMINE-PALLADIUM II

FRACTIONAL ATOMIC COORDINATES

ATOMS	(x/a)	(y/b)	(z/c)
Pd	0.3351	0.5122	0.2109
Cl(1)	0.4273	0.5902	0.2089
Cl(2)	0.2647	0.6093	0.1586
P(1)	0.2627	0.4201	0.2175
P(2)	0.3831	0.4060	0.2601
N	0.3136	0.3537	0.2675
C(1)	0.3055	0.2717	0.2651
C(2)	0.3437	0.2296	0.3397
C(3)	0.1363	0.4176	0.4439
C(4)	0.0866	0.4645	0.4065
C(5)	0.0909	0.4916	0.3177
C(6)	0.1439	0.4770	0.2618
C(7)	0.1941	0.4295	0.2937
C(8)	0.1904	0.4016	0.3880
C(9)	0.4076	0.3961	0.5540
C(10)	0.3819	0.3981	0.4578
C(11)	0.4199	0.4045	0.3804
C(12)	0.4865	0.4104	0.3863
C(13)	0.5179	0.4098	0.4760
C(14)	0.4769	0.4049	0.5564

- Cont'd -

TABLE 3 - Cont'd -

FRACTIONAL ATOMIC COORDINATES.

ATOMS	(x/a)	(y/b)	(z/c)
C(15)	0.1938	0.3227	0.0952
C(16)	0.1697	0.2994	0.0086
C(17)	0.1857	0.3383	-0.0776
C(18)	0.2210	0.4026	-0.0728
C(19)	0.2443	0.4274	0.0201
C(20)	0.2299	0.3870	0.1061
C(21)	0.4795	0.3039	0.1943
C(22)	0.4350	0.3600	0.1710
C(23)	0.4251	0.3815	0.0777
C(24)	0.4601	0.3481	0.0028
C(25)	0.5056	0.2894	0.0275
C(26)	0.5171	0.2702	0.1221

TABLE 4.

STANDARD DEVIATIONS IN ATOMIC COORDINATES (in Å)

ATOMS	σ(x)	σ(y)	σ(z)
Pd	0.001	0.001	0.002
Cl(1)	0.004	0.005	0.006
Cl(2)	0.005	0.004	0.006
P(1)	0.004	0.004	0.006
P(2)	0.004	0.004	0.006
N	0.013	0.013	0.016
C(1)	0.019	0.020	0.023
C(2)	0.023	0.026	0.028
C(3)	0.018	0.018	0.022
C(4)	0.021	0.022	0.025
C(5)	0.023	0.022	0.025
C(6)	0.021	0.020	0.025
C(7)	0.017	0.017	0.021
C(8)	0.018	0.018	0.023
C(9)	0.024	0.024	0.026
C(10)	0.023	0.023	0.027
C(11)	0.018	0.019	0.023
C(12)	0.020	0.019	0.024
C(13)	0.025	0.026	0.027
C(14)	0.027	0.026	0.031

TABLE 4. - Cont'd -

STANDARD DEVIATIONS IN ATOMIC COORDINATES (in Å)

ATOMS	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C(15)	0.021	0.021	0.024
C(16)	0.019	0.020	0.022
C(17)	0.020	0.021	0.024
C(18)	0.022	0.021	0.024
C(19)	0.022	0.021	0.024
C(20)	0.016	0.016	0.020
C(21)	0.019	0.020	0.023
C(22)	0.017	0.018	0.021
C(23)	0.021	0.022	0.024
C(24)	0.028	0.029	0.028
C(25)	0.021	0.022	0.024
C(26)	0.019	0.020	0.024

TABLE 5.

FINAL ANISOTROPIC THERMAL PARAMETERS (Uij).

ATOMS	(U11)	(U22)	(U33)	(2U23)	(2U31)	(2U12)
Pd	0.026	0.025	0.043	-0.000	-0.002	0.003
Cl(1)	0.034	0.046	0.074	0.000	-0.011	-0.021
Cl(2)	0.046	0.036	0.048	0.004	0.002	0.024
P(1)	0.022	0.027	0.051	0.004	-0.005	0.004
P(2)	0.024	0.026	0.037	0.007	-0.001	0.003
N	0.039	0.023	0.026	0.024	-0.003	-0.004
C(1)	0.056	0.038	0.058	0.029	-0.007	-0.007
C(2)	0.066	0.021	0.142	0.066	-0.045	0.002
C(3)	0.032	0.032	0.073	-0.024	0.011	-0.017
C(4)	0.036	0.063	0.063	-0.023	0.023	-0.034
C(5)	0.053	0.057	0.053	-0.008	0.005	0.010
C(6)	0.034	0.046	0.073	0.023	-0.014	0.034
C(7)	0.042	0.035	0.031	0.004	-0.017	-0.009
C(8)	0.041	0.056	0.017	-0.004	0.010	-0.020
C(9)	0.068	0.072	0.026	-0.010	0.002	0.019
C(10)	0.062	0.044	0.082	0.011	-0.017	0.020
C(11)	0.052	0.044	0.033	-0.009	-0.025	0.006
C(12)	0.044	0.041	0.057	-0.018	-0.023	-0.022
C(13)	0.067	0.062	0.073	-0.007	-0.042	0.007
C(14)	0.098	0.050	0.092	-0.004	-0.057	0.014

- Cont'd -

TABLE 5. - Cont'd -

FINAL ANISOTROPIC THERMAL PARAMETERS (Uij).

ATOMS	(U11)	(U22)	(U33)	(2U23)	(2U31)	(2U12)
C(15)	0.043	0.040	0.093	-0.004	0.006	0.005
C(16)	0.037	0.047	0.052	-0.007	-0.046	0.006
C(17)	0.045	0.063	0.034	-0.036	0.0060.	0.034
C(18)	0.049	0.056	0.055	0.001	-0.009	0.006
C(19)	0.054	0.065	0.037	0.001	0.004	0.008
C(20)	0.031	0.031	0.038	0.022	-0.017	0.011
C(21)	0.025	0.050	0.078	-0.006	-0.001	0.004
C(22)	0.035	0.035	0.042	-0.003	0.006	0.008
C(23)	0.054	0.056	0.040	-0.015	-0.015	0.008
C(24)	0.081	0.075	0.068	-0.014	0.014	-0.033
C(25)	0.051	0.053	0.063	-0.013	0.009	-0.028
C(26)	0.049	0.040	0.059	-0.008	0.001	0.012

TABLE 6.

Inter-atomic Bond Lengths in Å, with estimated Standard Deviations.

Pd	-	P(1)	2.22(0.004)	C(9)	-	C(10)	1.44(0.04)
Pd	-	P(2)	2.23(0.004)	C(9)	-	C(14)	1.46(0.04)
Pd	-	Cl(1)	2.37(0.005)	C(10)	-	C(11)	1.34(0.03)
Pd	-	Cl(2)	2.37(0.005)	C(11)	-	C(12)	1.40(0.03)
P(1)	-	N	1.73(0.01)	C(12)	-	C(13)	1.41(0.04)
P(1)	-	C(20)	1.79(0.02)	C(13)	-	C(14)	1.41(0.04)
P(1)	-	C(7)	1.79(0.02)	C(15)	-	C(16)	1.37(0.03)
P(2)	-	N	1.72(0.01)	C(15)	-	C(20)	1.37(0.03)
P(2)	-	C(22)	1.83(0.02)	C(16)	-	C(17)	1.42(0.03)
P(2)	-	C(11)	1.84(0.02)	C(17)	-	C(18)	1.35(0.03)
C(1)	-	N	1.45(0.02)	C(18)	-	C(19)	1.45(0.03)
C(1)	-	C(2)	1.50(0.03)	C(19)	-	C(20)	1.42(0.03)
C(3)	-	C(4)	1.42(0.03)	C(21)	-	C(22)	1.39(0.03)
C(3)	-	C(8)	1.40(0.03)	C(21)	-	C(26)	1.40(0.03)
C(4)	-	C(5)	1.33(0.03)	C(22)	-	C(23)	1.36(0.03)
C(5)	-	C(6)	1.38(0.03)	C(23)	-	C(24)	1.40(0.04)
C(6)	-	C(7)	1.41(0.03)	C(24)	-	C(25)	1.44(0.04)
C(7)	-	C(8)	1.40(0.03)	C(25)	-	C(26)	1.38(0.03)

TABLE 7.

INTERBOND ANGLES (°).

Cl(1) - Pd - Cl(2)	94.8	C(7) - C(8) - C(3)	119.4
P(1) - Pd - P(2)	71.4	C(8) - C(3) - C(4)	120.3
P(1) - N - P(2)	97.7	C(9) - C(10) - C(11)	121.6
Pd - P(1) - C(7)	117.6	C(10) - C(11) - C(12)	123.3
C(7) - P(1) - C(20)	103.5	C(11) - C(12) - C(13)	121.1
N - P(1) - C(20)	108.6	C(12) - C(13) - C(14)	114.6
Pd - P(1) - N	95.2	C(13) - C(14) - C(9)	126.4
N - P(1) - C(7)	111.2	C(14) - C(9) - C(10)	112.9
Pd - P(1) - C(20)	120.2	C(15) - C(16) - C(17)	120.6
Pd - P(2) - C(11)	118.5	C(16) - C(17) - C(18)	119.5
N - P(2) - C(11)	106.9	C(17) - C(18) - C(19)	118.7
Pd - P(2) - C(22)	115.5	C(18) - C(19) - C(20)	121.8
N - P(2) - C(22)	107.7	C(19) - C(20) - C(15)	115.9
Pd - P(2) - N	95.0	C(20) - C(15) - C(16)	123.3
C(11) - P(2) - C(22)	111.0	C(21) - C(22) - C(23)	121.2
C(3) - C(4) - C(5)	119.8	C(22) - C(23) - C(24)	120.5
C(4) - C(5) - C(6)	120.8	C(23) - C(24) - C(25)	117.9
C(5) - C(6) - C(7)	122.1	C(24) - C(25) - C(26)	121.1
C(6) - C(7) - C(8)	117.4	C(25) - C(26) - C(21)	118.6
		C(26) - C(21) - C(22)	120.5

Some selected interbond angles with their e.s.d.

Cl(1) - Pd - Cl(2)	94.8(0.17)
P(1) - Pd - P(2)	71.4(0.15)
P(1) - N - P(2)	97.7(0.70)

TABLE 8.

INTRA-MOLECULAR NON-BONDED DISTANCES.

Pd	...	N	2.94	P(2)	...	C(2)	3.41
Pd	...	C(22)	3.50	P(2)	...	C(20)	3.99
Pd	...	C(20)	3.50	N	...	C(2)	2.50
Pd	...	C(11)	3.54	N	...	C(11)	2.94
Pd	...	C(23)	3.54	N	...	C(20)	2.95
Pd	...	C(7)	3.60	N	...	C(7)	2.96
Pd	...	C(19)	3.63	N	...	C(22)	2.98
Cl(1)	...	P(2)	3.46	N	...	C(10)	3.13
Cl(1)	...	Cl(2)	3.64	N	...	C(8)	3.28
Cl(2)	...	P(1)	3.43	N	...	C(15)	3.59
Cl(2)	...	C(19)	3.76	N	...	C(23)	3.62
Cl(2)	...	C(6)	3.81	N	...	C(21)	3.87
Cl(2)	...	C(7)	3.99	N	...	C(19)	3.97
P(1)	...	P(2)	2.71	C(1)	...	C(20)	3.42
P(1)	...	C(19)	2.77	C(1)	...	C(22)	3.49
P(1)	...	C(15)	2.84	C(1)	...	C(15)	3.51
P(1)	...	C(1)	2.85	C(1)	...	C(7)	3.72
P(1)	...	C(6)	2.86	C(1)	...	C(11)	3.78
P(1)	...	C(8)	2.87	C(1)	...	C(8)	3.81
P(1)	...	C(22)	3.97	C(1)	...	C(10)	3.86
P(2)	...	C(23)	2.72	C(1)	...	C(21)	3.98
P(2)	...	C(10)	2.74	C(2)	...	C(10)	3.49
P(2)	...	C(12)	2.86	C(2)	...	C(11)	3.55
P(2)	...	C(1)	2.91	C(2)	...	C(21)	3.82

- Cont'd -

TABLE 8. - Cont'd -

INTRA-MOLECULAR NON-BONDED DISTANCES.

P(2)	...	C(21)	2.92	C(11)	...	C(13)	2.53
C(2)	...	C(22)	3.84	C(11)	...	C(14)	2.74
C(3)	...	C(6)	2.74	C(11)	...	C(22)	3.03
C(4)	...	C(8)	2.54	C(11)	...	C(21)	3.39
C(4)	...	C(7)	2.89	C(12)	...	C(21)	3.26
C(5)	...	C(7)	2.53	C(12)	...	C(22)	3.31
C(5)	...	C(8)	2.87	C(15)	...	C(18)	2.78
C(6)	...	C(20)	3.28	C(16)	...	C(19)	2.79
C(6)	...	C(15)	3.73	C(17)	...	C(20)	2.86
C(7)	...	C(20)	2.82	C(18)	...	C(20)	2.50
C(7)	...	C(15)	3.33	C(21)	...	C(24)	2.80
C(7)	...	C(19)	3.95	C(22)	...	C(26)	2.49
C(9)	...	C(13)	2.66	C(22)	...	C(25)	2.81
C(9)	...	C(12)	2.90	C(23)	...	C(25)	2.50
C(10)	...	C(14)	2.49	C(23)	...	C(26)	2.88
C(10)	...	C(12)	2.50	C(24)	...	C(26)	2.49
C(10)	...	C(13)	3.00	C(25)	...	C(16)	3.95
C(26)	...	C(16)	3.99				

TABLE 9.

INTER-MOLECULAR DISTANCES <4Å

Pd	...	C(3)ii	3.95	C(4)	...	C(24)vii	3.67
Pd	...	C(17)i	3.97	C(4)	...	C(25)vii	3.67
Pd	...	C(18)i	3.57	C(4)	...	C(26)vii	3.76
Cl(1)	...	C(3)ii	3.93	C(5)	...	C(12)vii	3.91
Cl(1)	...	C(14)iv	3.87	C(5)	...	C(24)i	3.97
Cl(1)	...	C(24)iii	3.98	C(6)	...	C(9)ii	3.82
Cl(2)	...	C(1)v	3.57	C(7)	...	C(18)i	3.95
Cl(2)	...	C(3)ii	3.71	C(8)	...	C(16)vi	3.94
Cl(2)	...	C(8)ii	3.88	C(8)	...	C(18)i	3.99
Cl(2)	...	C(15)v	3.97	C(8)	...	C(19)i	3.80
Cl(2)	...	C(17)i	3.93	C(9)	...	C(13)iv	3.81
Cl(2)	...	C(18)i	3.75	C(9)	...	C(25)vi	3.92
C(1)	...	C(17)vi	3.92	C(9)	...	C(26)vi	3.90
C(2)	...	C(17)vi	3.84	C(12)	...	C(13)iv	3.70
C(2)	...	C(18)vi	3.76	C(12)	...	C(14)iv	3.46
C(2)	...	C(24)vi	3.67	C(13)	...	C(13)iv	3.34
C(3)	...	C(16)vi	3.99	C(13)	...	C(14)iv	3.30
C(3)	...	C(19)i	3.92	C(13)	...	C(16)viii	3.86
C(3)	...	C(25)vii	3.67	C(13)	...	C(25)vi	3.59

The subscripts refer to the following positions:

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

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

iii $1-x$, $1-y$, $-z$

iv $1-x$, $1-y$, $1-z$

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

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

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

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

TABLE 10.

EQUATIONS OF MEAN PLANES AND DISTANCES(Å) OF ATOMS FROM THESE PLANES.

(a) Plane through Pd, Cl(1), Cl(2), P(1), P(2).

$$0.1808x - 0.2475y - 0.9519z + 3.7348 = 0$$

Pd	-0.014	C(5)	-2.257	C(11)	-1.463
Cl(1)	0.021	C(6)	-1.255	N	-0.152
Cl(2)	-0.013	C(7)	-1.281	C(1)	0.206
P(1)	0.026	C(9)	-3.765	C(20)	1.517
P(2)	-0.019	C(10)	-2.600	C(22)	1.552

(b) Plane through P(1), P(2), N, C(1),

$$0.2082x - 0.1829y - 0.9608z + 3.1580 = 0$$

P(1)	0.050	Pd	0.157
P(2)	0.052	C(2)	-0.614
N	-0.181		
C(1)	0.079		

Dihedral angle between plane (a) and plane (b) is 178°.

other atoms from the planes. Some of the more important dihedral angles between planes are presented in Table 10. Table 11 lists the observed structure amplitudes and calculated structure factors.

1.8. DISCUSSION

This analysis has established the structure and the essential stereochemistry of Dichloro-bis-(diphenyl-phosphine)-ethylamine palladium (II) and proves unambiguously the bidentate nature of the P.N.P ligand. Figs (5), (6), III + IV.

The mean plane through the atoms Pd, Cl(1), Cl(2), P(1) and P(2) was calculated (Table 10). The deviations from this plane are insignificant. The planarity is supported by the angles at palladium which add up to about 360°. Normally the substituents on palladium occupy the corners of a square, but the formation of the four membered ring and the rigid nature of P.N.P skeleton make a square arrangement impossible. The P-$\hat{Pd}$-P is 71.4 ± 0.15°. If this were to be about 90°, this would require an angle of about 50° for the P.N.P which is not feasible in view of the fact that the P.N.P angle in the free ligand is of the order 110° (Part III). On the other hand, if P-$\hat{N}$-P were to be about 100° and P-$\hat{Pd}$-P were to retain normal 90°, this would call for narrower angles at the phosphorus atoms and of course nearness of Pd and the nitrogen atoms, which obviously would involve more strain. The structure obtained therefore is probably optimum for a stable system.

DICHLORO BIS (DIPHENYL PHOSPHINO) ETHYLAMINE PALLADIUM II MOLECULE.

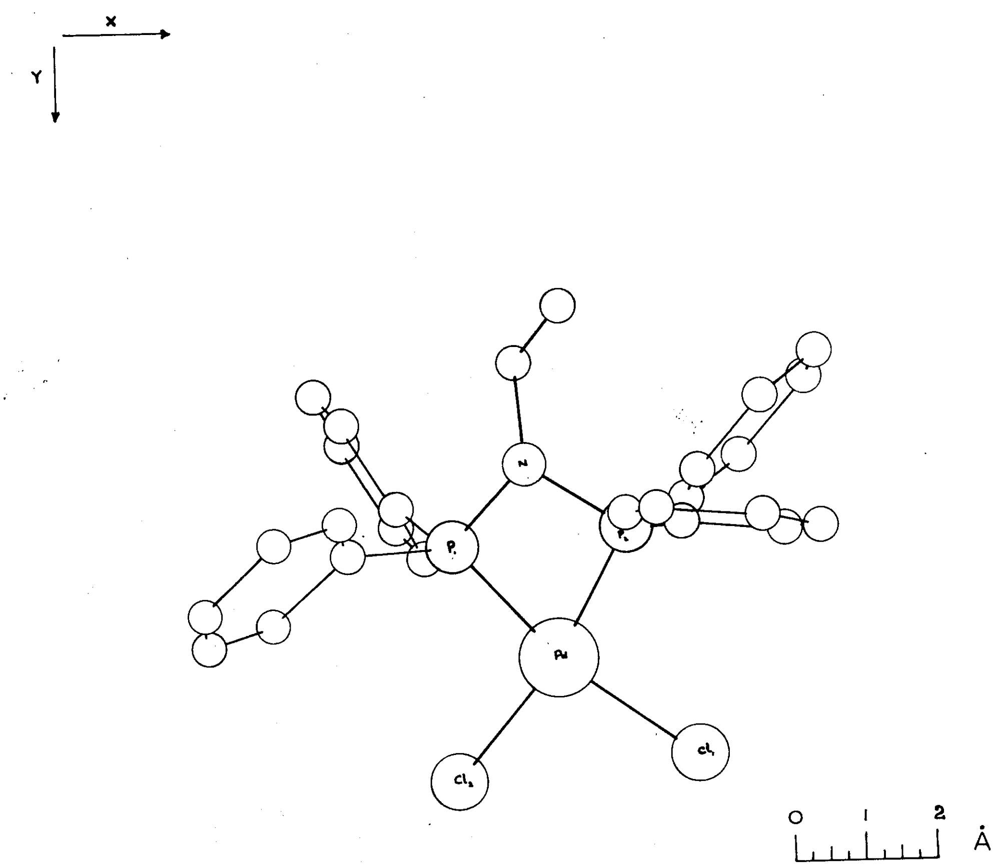


Fig 5. Atomic arrangements as viewed in projection down the c axis.

The mean Pd-P bond length of 2·22Å (individual e.s.d.±0·004Å) is significantly different from the value (2·38Å) expected for Pd-P single bond (sum of covalent radii). This shortening of Pd-P bond distance might have risen from two sources.

The P-$\hat{Pd}$-P angle of 71·4° is very much smaller than 90° and thus makes impossible a clear-cut end-on overlap of the d-orbitals between both atoms, Pd and P involved in the σ-bond; but may lead to a non-linear, interaction which might conceivably result in bond shortening, Figs. III + IV.

The second is probably more important - namely the effect of the π-bonding in the system. This view is strengthened by the observed lengthening of the Pd-Cl bond, (Cl in trans position to P) which can be discussed in terms of the trans effect. The two independent Pd-Cl bond lengths of 2·37Å (individual e.s.d ± 0·005 Å) when compared with the two unsymmetrical bridge Pd-Cl bond lengths in [(styrene) $PdCl_2]_2$, Baenziger et al, 1958, differ significantly from the bridge Pd-Cl distance (2·324 ± 0·01 Å) cis to the olefin - Pd bond; but, agrees with the bridge Pd-Cl distance (2·394 ± 0·015 Å) trans to the olefin - Pd bond. The corresponding unsymmetrical Pd-Cl distances in one of the two crystallographically different dimers of [$(C_2H_4)Pd\,Cl_2]_2$, Carpenter et al, 1961, follow the same trend. The trans effect was also pointed out by Holden et al (1958) who discovered a similar lengthening of the metal-chlorine bond trans to an olefin linkage in Zeise's salt, $K[(C_2H_4)\,Pt.Cl_3].H_2O$, Wunderlich et al, 1954).

DICHLORO-BIS-(DIPHENYL-PHOSPHINO)-ETHYLAMINE PALLADIUM (II).

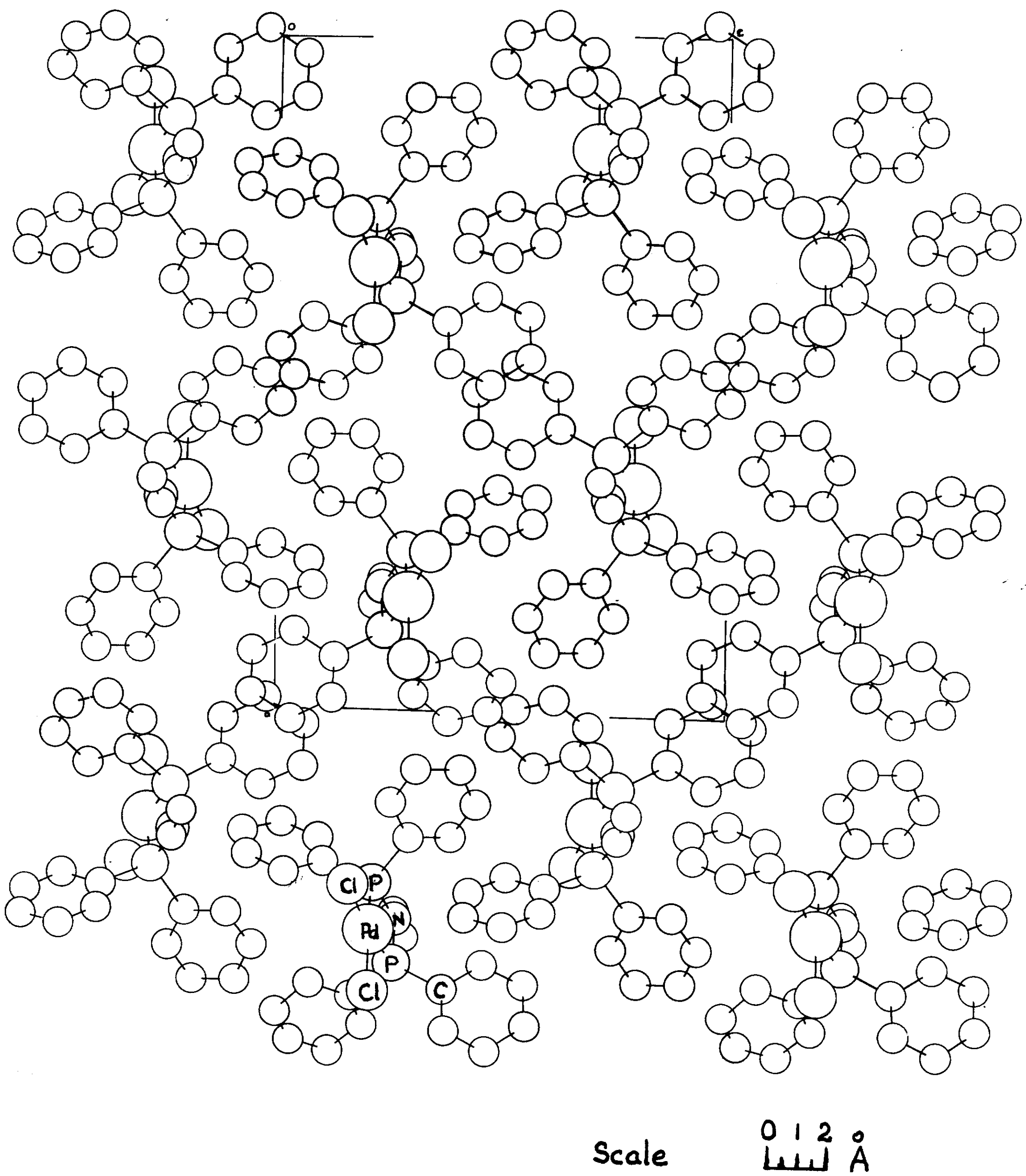
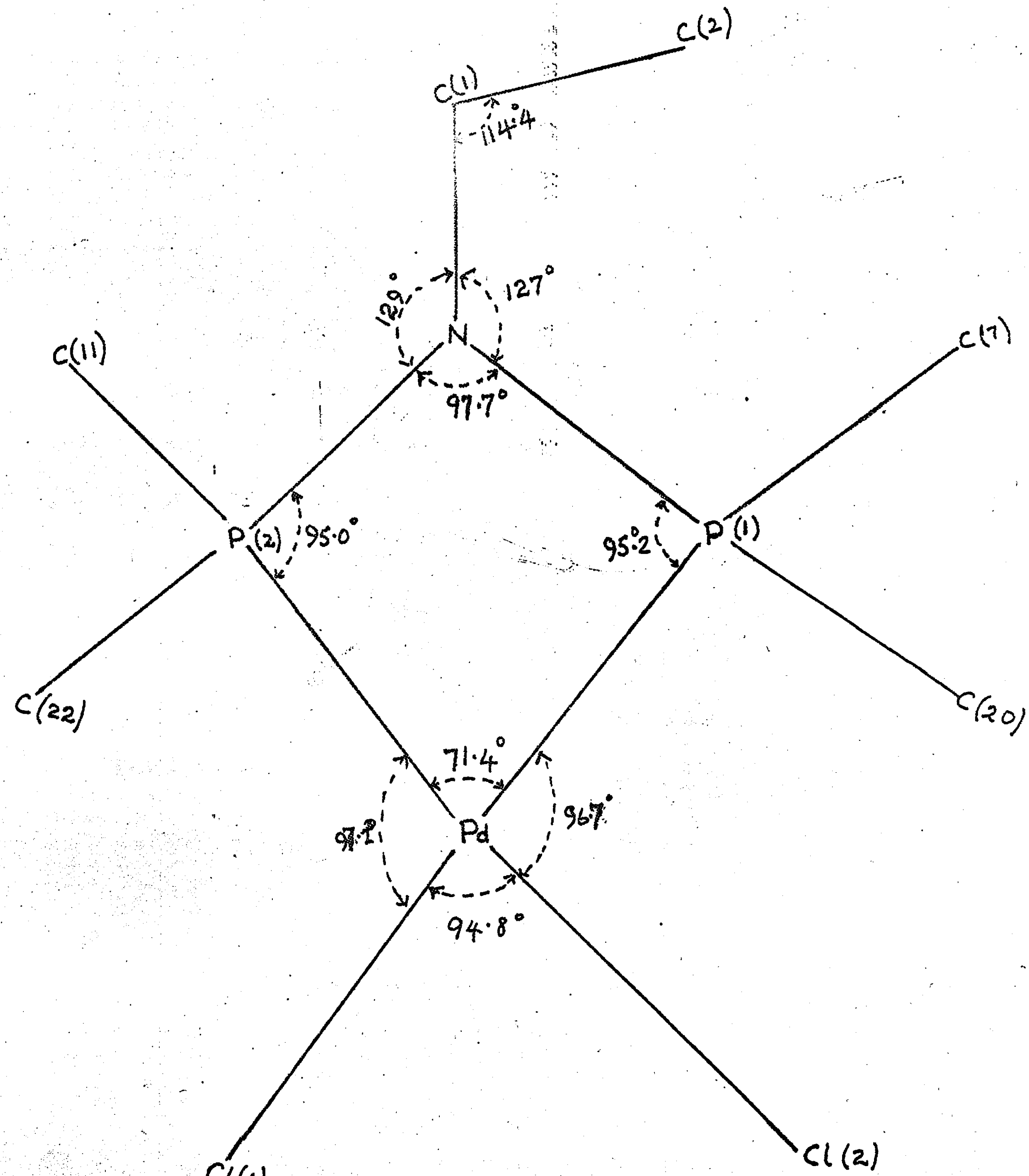


Fig. 6. Packing of the molecules in projection down the b-axis.

In the studies of π-allyl complex of Palladium, Rowe (1962) and Oberhansli et al. (1965) independently recorded the value of 2·40 Å for Pd–Cl; also, Smith (1965) determined the same structure $[(C_3H_5)\ PdCl]_2$ at − 140°C and obtained a value of about 2·40 Å for the Pd–Cl in this allyl compound. Even though the chlorine atoms in PNP palladium complex are non-bridging the mean value of Pd–Cl (2·37 Å) compares quite well with the values recorded for bridge Pd–Cl where Cl is trans to an allylic group. The $C_1'–\hat{Pd}–C_3'$ in the allyl complex studied by Oberhansli (1965) is 69 ± 1°, this value is quite close to the $P–\hat{Pd}–P$ angle of 71·4 ± 0·15° recorded in the present work so that a strong similarity exists between them. It seems possible therefore that the $P–\hat{Pd}–P$ of 71·4° is not the chief factor responsible for the shortening of Pd–P; rather this might be due to dπ–dπ bonding, the effect of which results as well in Pd–Cl lengthening, Figs. III + IV.

The argument of trans effect was advanced by Chatt and Wilkins, (1952) to explain the possibility of dπ–dπ bond formation in cis-trans conversion of $[P(Et)_3]_2PtCl_2$. In their discussion, they postulated that the amount of double bond character in the Pt–P bond would be more in the trans-complex than in the cis-complex. This will in effect give rise to longer Pt–Cl bond in the trans-complex. In complexes with a variety of phosphine ligands of different π-bonding capacity, the formation of the trans-isomer might be impossible where the trans effect is very large. An

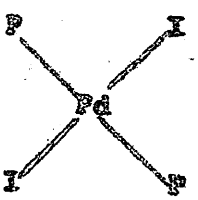


C(2)
C(1)
114·4°
129°
127°
N
C(11)
C(7)
97·7°
P(2)
95·0°
95·2°
P(1)
C(22)
C(20)
71·4°
96·7°
Pd
94·8°
Cl(1)
Cl(2)

Fig III

interesting application of this argument has been found in PF_3 where it is only possible to form the cis-form of $PtCl_2(PF_3)_2$ (Chatt et al., 1951).

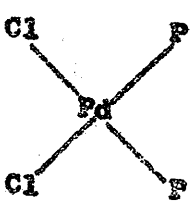
The structure under investigation provides another piece of evidence in favour of the trans effect especially when compared with the other available Pd-P bond lengths in related complexes. Quite recently, Bailey et al.(1965) published the structure of trans-di-iodo-bis-(dimethyl phenyl-phosphine) Pd(II). A comparison of bond lengths with sum of the calculated single-bond covalent radii in Bailey's compound and in the present structure shows some evidences of π-bonding in the Pd-P of the latter. Fig.I shows Bailey's results while Fig.II is the result of the present work.



$Pd\text{-}P_{obs.} = 2.34 \pm 0.015Å$, $Pd\text{-}I_{obs.} = 2.61 \pm 0.013Å$

$^{*}Pd\text{-}P_{cal.} = 2.38Å$, $^{*}Pd\text{-}I_{cal.} = 2.63$

Trans-complex
(Bailey's)
Fig.(I)



$Pd\text{-}P_{obs.} = 2.22 \pm 0.004Å$, $Pd\text{-}Cl_{obs.} = 2.37 \pm 0.003Å$

$^{*}Pd\text{-}P_{cal.} = 2.38Å$, $^{*}Pd\text{-}Cl_{cal.} = 2.27Å$

Cis-complex
(Present work)
Fig.(II)

*(values obtained from the sum of single-bond covalent radii).

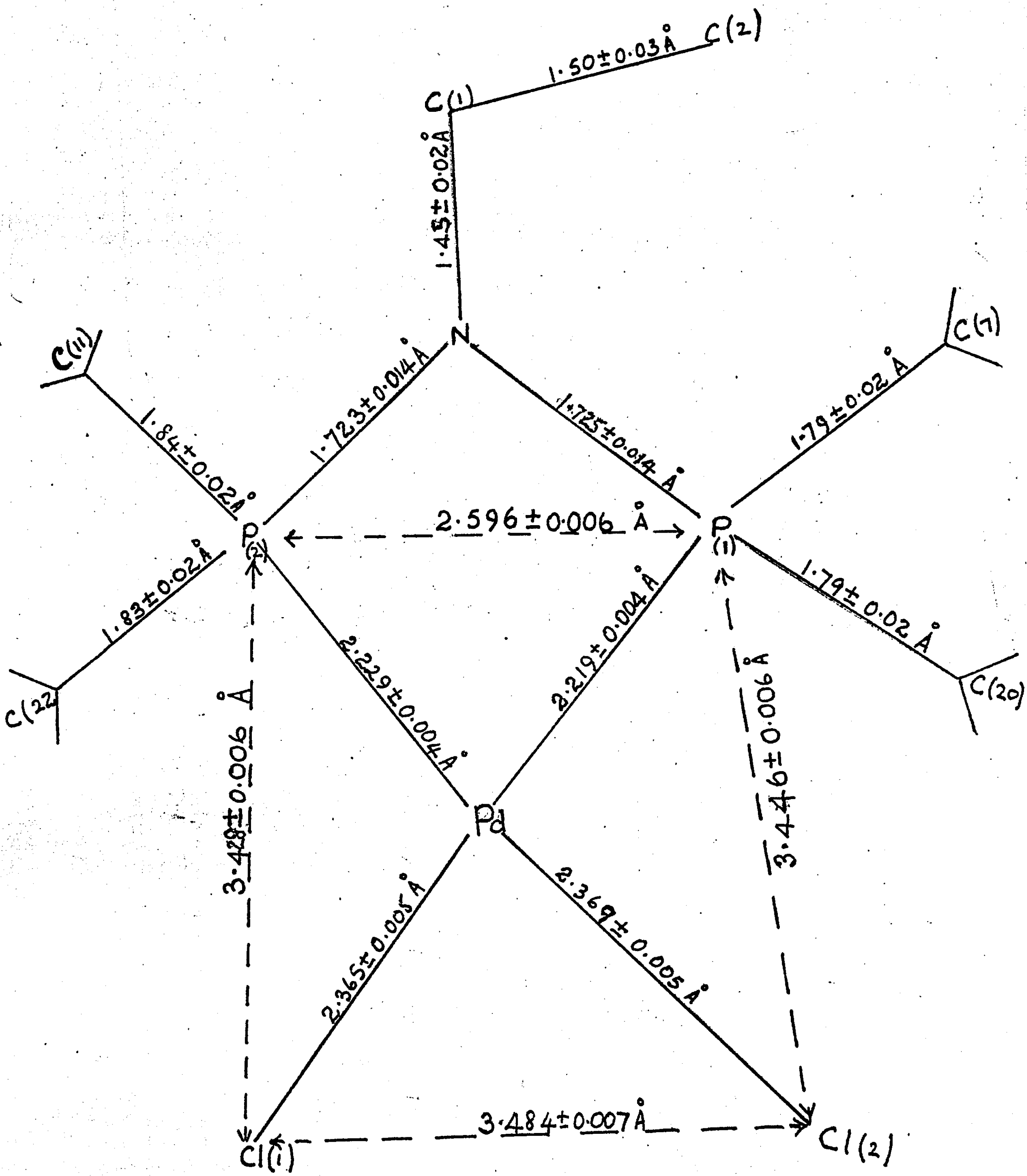

C(2)
1·50±0·03Å
C(1)
1·45±0·02Å
N
C(11)
1·723±0·014Å
1·725±0·014Å
C(7)
1·84±0·02Å
1·79±0·02Å
2·596±0·006 Å
P(2)
P(1)
1·83±0·02Å
1·79±0·02Å
C(22)
C(20)
2·229±0·004Å
2·219±0·004Å
3·428±0·006 Å
3·446±0·006Å
Pd
2·365±0·005Å
2·369±0·005Å
3·484±0·007Å
Cl(1)
Cl(2)

Fig. IV.

Within the accuracy of the data, Bailey's figures compare quite favourably with the calculated values whereas the Pd-P bond in the present work is about 0.16Å short of the expected and the Pd-Cl probably in compensating for the shortening is about 0.10Å longer than the theoretical. This can be attributed to the trans-effect in accordance with Chatt-Wilkins' Theory.

In the crystal study of Di-iodo-(o-phenylene-bis-dimethyl-arsine)-palladium (II), Stephenson (1962) recorded a value of 2.39Å for Pd-As bond instead of the theoretical value of 2.50Å and claimed that this shortening represents the first direct d_π-d_π bonding between Pd and As. If this is true of Pd-As it is probably true of Pd-P under the conditions discussed above.

The deviations (Table 10) of the atoms P(1), P(2), N and C(1) from their mean plane are insignificant, therefore PNP system is almost planar. The two independent P-N bond lengths of 1.725$\pm$0.014Å and 1.723$\pm$0.014Å, (Table 6), are equal. Their mean value (1.724Å) is much shorter than the sum of the single bond covalent radii (1.84Å). In phosphonitrilics and associated compounds (Paddock, 1962), $P\hat{N}P$ tends to be greater than 120°, but the PNP angle in this compound of 97.7$\pm$0.7° shows that its nitrogen is in substantially different environment. The comparison of 1.72 with 1.84Å for P-N bond length shows there is shortening which may be due to π-bonding thus substantiating the theory of delocalisation dealt with in Part II. In phosphonitrilics

TABLE 11.

H	K	L	|Fo|	Fc
0	4	0	199.1	-218.2
0	6	0	256.3	-214.0
0	8	0	256.3	238.4
0	10	0	387.3	448.6
0	12	0	280.2	262.5
0	14	0	46.1	52.0
0	16	0	70.1	-81.5
0	18	0	18.4	-14.5
0	20	0	25.8	20.7
0	22	0	18.4	23.1
2	2	0	195.5	-217.6
2	3	0	79.3	-82.2
2	4	0	18.4	-40.2
2	5	0	182.5	-193.5
2	6	0	64.5	-67.3
2	7	0	241.6	-267.3
2	8	0	105.1	-91.3
2	9	0	97.8	-105.7
2	10	0	59.0	-66.2
2	11	0	127.2	-139.2
2	12	0	75.6	-69.7
2	13	0	112.5	-136.4
2	14	0	35.0	-29.5
2	15	0	99.6	-106.8
2	16	0	71.9	-53.0
2	17	0	119.9	-134.1
2	18	0	29.5	-38.2
2	19	0	119.9	-112.9
2	20	0	25.8	26.7
2	21	0	79.3	-75.3
2	22	0	29.5	37.6
4	0	0	25.8	-8.1
4	1	0	171.4	181.9
4	2	0	236.0	-254.6
4	3	0	217.6	234.7
4	4	0	263.7	-270.3
4	5	0	92.1	-73.6
4	6	0	230.5	-231.6
4	7	0	97.8	93.1
4	8	0	158.5	-144.4
4	9	0	86.6	82.0
4	10	0	53.5	-61.9
4	11	0	169.6	180.4
4	12	0	60.8	-65.0
4	13	0	114.3	133.2
4	14	0	18.4	-15.0
4	15	0	51.6	51.9
4	16	0	25.8	11.0
4	17	0	79.3	90.1
4	18	0	24.0	4.1
4	19	0	106.9	92.6
4	20	0	24.0	-26.0
4	21	0	101.4	99.5
4	22	0	25.8	-27.7
6	0	0	167.8	133.5
6	1	0	103.3	-100.0
6	2	0	46.1	-11.8
6	3	0	147.5	-147.7
6	4	0	368.7	518.8
6	5	0	1.9	-2.0
6	6	0	387.3	416.0
6	7	0	143.8	159.1
6	8	0	125.4	125.1
6	9	0	127.2	109.8
6	10	0	47.9	38.1
6	11	0	49.8	-47.5
6	12	0	64.5	54.8
6	13	0	62.7	-71.4
6	14	0	108.8	111.8
6	15	0	36.9	42.3
6	16	0	60.8	60.4
6	17	0	68.2	67.5
8	0	0	66.4	-54.3
8	1	0	24.0	20.2
8	4	0	121.7	-124.7
8	5	0	138.2	-130.5
8	6	0	261.8	-267.5
8	7	0	112.5	-115.5
8	8	0	97.8	-90.1
8	9	0	84.8	-81.7
8	10	0	75.6	57.7
8	11	0	83.0	-79.9
8	12	0	16.6	-17.9
8	13	0	106.9	-118.2
8	14	0	64.5	-61.9
8	15	0	121.7	-153.9
8	16	0	47.9	-44.5
8	17	0	116.1	-122.7
8	18	0	16.6	-10.3
8	19	0	75.6	-69.2
8	21	0	49.8	-46.5
10	0	0	106.9	-96.3
10	1	0	46.1	42.7
10	2	0	184.4	-182.4
10	3	0	123.6	124.1
10	4	0	114.3	-117.4
10	5	0	143.8	135.3
10	6	0	94.1	-87.1
10	7	0	127.2	116.2
10	8	0	106.9	-91.0
10	9	0	60.8	-57.5
10	10	0	59.0	-59.9
10	11	0	51.6	53.7
10	12	0	62.7	-54.7
10	13	0	165.9	166.1
10	14	0	47.9	-53.5
10	15	0	125.4	154.9
10	16	0	35.0	-35.3
10	17	0	90.4	94.2
10	19	0	24.0	14.5
10	21	0	35.0	34.3
12	0	0	339.2	343.6
12	1	0	51.6	50.0
12	2	0	247.0	237.9

H	K	L	|Fo|	Fc
12	3	0	121.7	123.3
12	4	0	175.2	194.8
12	5	0	14.7	-6.7
12	6	0	121.7	127.4
12	7	0	81.1	-77.9
12	8	0	136.4	137.5
12	9	0	16.6	-11.6
12	10	0	149.3	151.8
12	11	0	86.6	98.2
12	12	0	94.1	85.9
12	13	0	71.9	75.2
12	14	0	53.5	66.8
12	15	0	16.6	6.9
12	16	0	29.5	31.4
14	0	0	94.1	-78.7
14	1	0	57.2	-50.8
14	2	0	55.3	-51.3
14	3	0	59.0	-56.6
14	4	0	47.9	-41.2
14	5	0	24.0	-33.3
14	6	0	66.4	-62.7
14	7	0	16.6	-16.2
14	8	0	25.8	-20.2
14	9	0	156.7	-147.5
14	10	0	36.9	-33.9
14	11	0	180.7	-179.6
14	12	0	51.6	-50.1
14	13	0	106.9	-108.2
14	14	0	24.0	-24.2
14	15	0	60.8	-59.6
14	16	0	14.7	-13.9
14	17	0	20.2	-25.9
14	18	0	11.0	-16.3
14	19	0	60.8	-62.3
16	0	0	16.6	-9.6
16	1	0	16.6	-13.9
16	2	0	86.6	-92.8
16	3	0	47.9	-53.2
16	4	0	175.2	-178.9
16	5	0	42.4	-30.4
16	6	0	173.3	-149.2
16	7	0	62.7	65.6
16	8	0	97.8	-101.8
16	9	0	118.0	117.9
16	10	0	36.9	-37.9
16	11	0	127.2	123.4
16	12	0	18.4	10.3
16	13	0	16.6	21.1
16	14	0	16.6	-12.4
16	15	0	14.7	-15.3
16	16	0	51.6	-47.8
16	17	0	36.9	39.8
16	18	0	31.3	-31.1
18	0	0	95.9	92.0
18	1	0	18.4	-11.1
18	2	0	114.3	116.1
18	3	0	18.4	28.0
18	4	0	112.5	117.9
18	5	0	18.4	22.2
18	6	0	112.5	111.2
18	7	0	31.3	41.9
18	8	0	112.5	114.5
18	9	0	18.4	8.2
18	10	0	95.9	92.8
18	11	0	29.5	-7.6
18	12	0	47.9	37.5
18	13	0	16.6	12.6
18	14	0	42.4	36.2
18	15	0	40.5	47.0
18	16	0	33.2	32.5
20	0	0	110.7	-109.3
20	1	0	18.4	13.6
20	2	0	53.5	-49.6
20	3	0	18.4	16.9
20	4	0	31.3	31.1
20	5	0	64.5	-57.9
20	7	0	84.8	-73.4
20	8	0	44.2	-32.7
20	9	0	59.0	-56.3
20	10	0	73.8	-71.8
20	11	0	20.2	-19.4
20	13	0	35.0	-29.8
20	15	0	79.3	-87.2
22	0	0	99.6	-95.6
22	1	0	16.6	4.1
22	2	0	68.2	-68.5
22	3	0	16.6	15.6
22	4	0	49.8	-54.2
22	5	0	36.9	44.5
22	6	0	31.3	19.5
22	6	0	16.8	-17.6
22	7	0	57.2	43.1
22	8	0	35.0	-36.0
22	9	0	20.2	19.8
22	10	0	71.9	-68.1
22	11	0	24.0	15.2
22	12	0	55.3	-56.8
22	13	0	24.0	28.6
24	0	0	53.5	46.3
24	1	0	14.7	-17.0
24	2	0	90.4	85.6
24	3	0	14.7	-5.8
24	4	0	105.1	99.4
24	5	0	12.9	-12.9
24	6	0	75.6	75.7
24	7	0	12.9	17.1
24	8	0	60.8	57.2
24	9	0	25.8	27.7
24	10	0	44.2	53.6
26	0	0	62.7	43.5
26	1	0	11.0	3.0
26	2	0	9.2	4.1
26	3	0	9.2	17.4
26	4	0	66.4	-64.6

H	K	L	|Fo|	Fc
26	6	0	31.3	-57.1
0	4	1	20.0	-19.3
0	6	1	33.5	-30.5
0	8	1	136.5	-154.2
0	10	1	149.4	-191.4
0	12	1	161.6	-178.8
0	14	1	92.7	-78.9
0	16	1	52.6	-42.9
0	18	1	110.1	-100.3
0	20	1	147.2	-128.9
0	22	1	78.1	-82.0
1	3	1	44.1	37.3
1	4	1	141.1	-160.2
1	5	1	171.5	172.4
1	6	1	63.9	35.8
1	7	1	74.3	57.2
1	8	1	21.4	21.3
1	10	1	73.6	-64.8
1	11	1	69.1	-56.4
1	12	1	81.6	-72.1
1	13	1	30.4	27.9
1	14	1	45.0	-40.6
1	15	1	40.1	28.4
1	18	1	22.4	-2.6
1	22	1	21.7	-25.3
2	2	1	17.9	-15.9
2	3	1	88.2	-85.5
2	4	1	74.8	-83.2
2	5	1	26.3	7.1
2	6	1	29.0	21.6
2	7	1	142.5	-143.0
2	8	1	89.0	89.6
2	9	1	159.0	-201.2
2	10	1	150.8	183.2
2	11	1	172.5	-189.3
2	12	1	129.7	122.3
2	13	1	96.7	-102.1
2	16	1	33.2	-6.0
2	18	1	83.7	34.9
2	20	1	46.0	70.2
2	22	1	65.3	63.2
3	1	1	103.3	-106.7
3	2	1	109.7	-140.4
3	3	1	172.6	-238.8
3	4	1	132.1	-148.4
3	5	1	105.9	104.4
3	6	1	58.3	-51.0
3	8	1	73.8	71.9
3	9	1	67.9	-60.7
3	10	1	54.7	57.4
3	11	1	80.2	-64.2
3	12	1	41.3	-25.9
3	13	1	48.6	-42.1
3	14	1	50.7	-47.9
4	1	1	167.5	162.1
4	2	1	17.2	-20.9
4	3	1	210.7	279.3
4	4	1	54.9	-28.3
4	5	1	271.0	334.7
4	6	1	156.2	168.8
4	7	1	238.7	267.2
4	8	1	48.3	54.8
4	9	1	128.5	129.2
4	11	1	39.4	34.7
4	12	1	20.8	-21.5
4	13	1	88.0	76.5
4	14	1	72.2	67.2
4	15	1	57.3	60.9
4	16	1	102.4	109.4
4	17	1	51.6	50.5
4	18	1	79.5	99.9
4	20	1	31.6	29.3
5	1	1	66.7	-48.5
5	2	1	77.8	67.1
5	3	1	25.9	28.2
5	4	1	96.7	83.1
5	5	1	35.4	27.4
5	6	1	35.2	-21.7
5	8	1	49.8	50.8
5	9	1	71.0	66.4
5	14	1	32.6	26.4
5	16	1	57.3	56.6
5	18	1	30.9	31.1
6	1	1	51.9	-55.3
6	2	1	46.4	39.5
6	3	1	53.3	51.2
6	4	1	96.7	-96.0
6	5	1	31.6	-15.7
6	6	1	134.0	-138.4
6	7	1	16.0	-11.7
6	8	1	167.0	-174.9
6	10	1	106.2	-110.8
6	11	1	54.3	43.5
6	12	1	93.9	-87.4
6	14	1	126.9	-128.3
6	16	1	134.4	-144.4
6	18	1	107.6	-121.9
6	20	1	65.1	-71.3
6	22	1	35.6	-44.3
7	1	1	33.5	-20.5
7	2	1	92.0	79.1
7	4	1	105.0	-85.3
7	5	1	118.4	108.8
7	6	1	38.7	-35.0
7	13	1	32.0	29.9
7	14	1	32.8	-28.1
7	16	1	51.9	-43.1
7	18	1	36.6	-34.1
8	1	1	106.6	-115.8
8	2	1	88.7	82.6
8	3	1	191.1	-265.8
8	4	1	146.8	164.2
8	5	1	235.0	-341.4
8	6	1	93.8	77.1

H	K	L	|Fo|	Fc
8	7	1	203.8	-250.0
8	8	1	71.2	-75.7
8	9	1	64.4	-61.2
8	10	1	54.0	-48.1
8	11	1	60.6	-60.7
8	12	1	94.6	94.6
8	13	1	51.4	-38.8
8	14	1	117.2	127.3
8	15	1	93.9	-92.7
8	16	1	92.2	87.3
8	17	1	31.1	-43.9
9	1	1	114.8	-116.7
9	3	1	65.6	-59.0
9	4	1	73.4	63.1
9	5	1	62.3	56.2
9	7	1	72.9	-59.6
9	9	1	49.0	-50.0
9	10	1	21.0	-16.0
9	11	1	48.8	-45.5
9	13	1	32.8	-33.3
10	1	1	146.5	135.1
10	2	1	113.9	98.4
10	3	1	156.2	160.3
10	4	1	33.7	33.6
10	5	1	171.2	198.8
10	6	1	54.7	51.7
10	7	1	190.6	192.9
10	9	1	90.4	84.1
10	10	1	89.2	93.6
10	11	[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
10	13	1	87.8	78.4
10	14	1	94.1	86.4
10	15	1	51.6	45.0
10	16	1	22.1	22.8
10	17	1	21.0	18.8
10	18	1	38.4	36.0
10	20	1	44.1	43.8
11	1	1	16.7	-3.2
11	2	1	24.1	-20.0
11	3	1	76.2	76.2
11	5	1	55.5	44.7
11	8	1	61.8	55.3
11	9	1	21.2	28.1
11	12	1	57.1	51.9
11	14	1	23.4	27.5
11	16	1	21.7	15.1
12	1	1	113.9	110.3
12	2	1	99.8	-94.8
12	3	1	32.0	29.8
12	4	1	89.0	-87.4
12	5	1	84.9	-84.8
12	6	1	49.0	-46.7
12	7	1	35.8	-28.9
12	8	1	37.0	-25.8
12	9	1	31.1	26.4
12	10	1	98.8	-100.4
12	11	1	56.9	52.1
12	12	1	152.2	-145.4
12	13	1	23.4	20.5
12	14	1	130.9	-132.4
12	16	1	63.4	-62.1
12	18	1	57.5	-51.3
12	20	1	63.7	-61.5
13	1	1	68.9	68.8
13	5	1	40.8	28.0
13	7	1	21.4	21.6
13	9	1	45.2	36.1
13	10	1	51.6	-57.1
13	12	1	33.2	-27.2
14	1	1	196.5	-205.4
14	2	1	60.8	-67.1
14	3	1	145.6	-152.9
14	4	1	46.7	-41.7
14	5	1	85.1	-85.8
14	6	1	37.7	35.9
14	7	1	89.0	-79.4
14	8	1	99.1	108.7
14	9	1	83.3	-82.6
14	10	1	93.6	88.2
14	11	1	110.4	-123.5
14	12	1	33.0	28.1
14	13	1	32.3	-40.6
14	15	1	59.0	-57.5
14	18	1	43.8	43.9
15	3	1	48.1	-46.8
15	5	1	54.3	-50.6
15	7	1	55.9	-57.8
16	1	1	188.5	192.6
16	2	1	79.9	73.0
16	3	1	141.3	129.4
16	4	1	38.9	43.8
16	5	1	55.9	57.9
16	6	1	61.6	65.9
16	7	1	88.0	85.4
16	9	1	52.3	53.7
16	10	1	83.0	86.0
16	11	1	44.8	43.4
16	12	1	64.4	59.6
16	13	1	75.8	70.7
16	14	1	18.4	17.8
16	15	1	52.3	50.0
16	16	1	37.7	38.2
17	8	1	52.6	60.5
17	9	1	23.4	19.1
18	1	1	96.0	-102.2
18	3	1	52.3	56.7
18	5	1	102.6	119.6
18	6	1	91.0	-91.9
18	7	1	57.3	66.6
18	8	1	86.8	-95.8
18	9	1	22.6	-19.5
18	10	1	89.2	-85.5
18	11	1	50.6	-54.6

H	K	L	|Fo|	Fc
18	12	1	61.1	-51.6
18	14	1	62.5	-58.3
18	16	1	66.0	-74.2
19	5	1	52.3	45.9
19	7	1	22.9	26.3
20	1	1	123.6	-126.5
20	3	1	137.5	-123.0
20	5	1	114.4	-102.4
20	7	1	96.7	-88.4
20	9	1	75.2	-72.0
20	11	1	81.6	-73.8
20	13	1	30.9	-26.9
20	14	1	22.6	24.8
20	15	1	18.1	-17.8
21	5	1	49.0	-42.1
21	7	1	51.4	-39.2
22	1	1	75.2	67.5
22	3	1	85.6	74.7
22	4	1	42.2	36.2
22	5	1	77.4	69.1
22	6	1	34.6	45.2
22	7	1	64.4	62.4
22	8	1	52.3	50.2
22	9	1	67.7	58.9
22	10	1	36.1	34.0
22	11	1	50.2	46.2
22	12	1	29.9	27.3
24	1	1	97.4	93.4
24	5	1	50.5	-46.7
24	6	1	42.4	[illegible]
[illegible]	[illegible]	[illegible]	25.9	-24.8
24	8	1	47.7	-44.9
24	9	1	46.7	39.6
24	10	1	39.8	-42.4
26	1	1	83.5	-84.0
26	2	1	22.0	15.2
26	3	1	71.9	-73.7
26	4	1	22.6	22.1
26	5	1	34.4	-41.9
0	4	2	253.5	-260.1
0	6	2	110.4	-105.7
0	8	2	214.8	-199.5
0	10	2	176.6	-174.2
0	12	2	162.3	-185.2
0	14	2	82.3	-96.1
0	22	2	22.8	-20.2
1	2	2	121.8	-134.5
1	3	2	69.8	-71.5
1	4	2	25.2	25.3
1	5	2	42.3	-33.6
1	6	2	80.2	-75.8
1	7	2	31.2	26.5
1	8	2	121.3	-106.7
1	9	2	36.6	31.6
1	10	2	125.2	-117.0
1	12	2	22.3	-21.7
1	13	2	75.0	-72.0
1	15	2	44.2	-39.1
1	16	2	36.3	-41.6
1	18	2	24.4	-23.9
2	2	2	143.6	153.2
2	3	2	131.2	132.1
2	4	2	69.3	68.8
2	5	2	82.8	96.9
2	6	2	20.2	22.3
2	7	2	112.7	96.6
2	8	2	126.2	110.2
2	8	2	144.9	110.2
2	10	2	52.7	56.1
2	11	2	144.7	139.3
2	12	2	67.7	60.9
2	13	2	114.5	116.7
2	14	2	60.7	60.9
2	15	2	72.2	74.9
2	16	2	25.7	3.9
2	17	2	110.6	100.3
2	19	2	106.2	102.8
2	21	2	77.3	75.8
2	22	2	25.7	-12.2
3	0	2	149.6	133.9
3	1	2	115.9	110.7
3	2	2	63.1	75.7
3	3	2	128.8	-126.4
3	4	2	27.5	11.8
3	5	2	35.8	30.7
3	6	2	53.5	48.7
3	7	2	55.8	56.2
3	8	2	17.3	18.6
3	10	2	53.2	46.8
3	11	2	117.9	107.2
3	13	2	48.0	44.4
3	14	2	43.1	-37.5
3	15	2	25.4	31.8
3	16	2	25.7	0.5
3	17	2	35.8	41.3
3	19	2	63.6	62.6
3	21	2	44.9	38.7
4	0	2	238.4	234.9
4	1	2	196.9	187.6
4	2	2	172.2	183.1
4	3	2	26.7	31.0
4	4	2	148.0	146.0
4	5	2	113.3	-109.7
4	6	2	116.9	119.4
4	7	2	163.3	-157.4
4	8	2	117.2	121.2
4	9	2	143.6	-149.0
4	11	2	102.6	95.0
4	12	2	129.1	-126.0
4	13	2	56.6	68.3
4	14	2	68.5	-71.5
4	15	2	57.4	-51.8
4	16	2	25.7	-29.0
4	17	2	90.8	-93.8

H	K	L	|Fo|	Fc
4	19	2	96.9	-88.8
4	21	2	72.2	-70.6
5	0	2	130.9	-147.5
5	1	2	16.3	16.7
5	2	2	102.9	91.5
5	3	2	22.3	-23.5
5	4	2	258.4	291.1
5	5	2	29.5	27.4
5	6	2	181.5	210.0
5	7	2	61.8	-57.4
5	8	2	41.0	37.2
5	9	2	98.2	-103.3
5	11	2	62.8	-64.1
5	12	2	32.9	29.5
5	14	2	56.3	46.2
5	16	2	25.4	27.6
5	17	2	24.9	-28.6
5	19	2	43.6	-41.7
6	0	2	99.8	-90.5
6	1	2	28.8	-26.7
6	2	2	200.0	-209.8
6	3	2	97.7	89.6
6	4	2	298.7	-320.3
6	6	2	292.8	-308.7
6	7	2	77.6	-76.3
6	8	2	187.0	-207.5
6	9	2	63.9	-64.6
6	13	2	24.7	29.6
6	14	2	50.8	-53.7
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]
6	17	2	24.7	-29.5
6	18	2	74.0	-48.3
7	0	2	13.7	5.0
7	1	2	28.0	27.5
7	2	2	112.7	-117.4
7	3	2	29.8	-22.0
7	4	2	182.3	-178.3
7	5	2	40.5	-34.7
7	6	2	177.6	-175.8
7	7	2	66.7	-64.5
7	8	2	34.0	-26.1
7	9	2	75.0	-74.3
7	10	2	30.9	-35.3
7	12	2	34.0	-35.7
7	14	2	36.1	-34.0
7	15	2	51.4	-51.5
7	16	2	25.2	-25.9
7	17	2	48.8	-43.3
8	0	2	127.8	116.5
8	1	2	15.0	-16.0
8	2	2	95.9	78.8
8	3	2	92.1	81.6
8	4	2	101.5	97.9
8	5	2	95.6	90.6
8	6	2	66.2	57.7
8	7	2	122.3	112.0
8	8	2	81.5	73.5
8	9	2	117.6	114.1
8	11	2	57.9	60.2
8	12	2	24.4	26.5
8	13	2	104.4	112.5
8	14	2	62.8	67.2
8	15	2	112.2	118.0
8	16	2	25.2	23.6
8	17	2	102.1	93.1
8	19	2	69.6	65.6
8	21	2	44.9	45.3
9	0	2	92.4	-84.9
9	2	2	91.4	-79.4
9	3	2	41.8	-44.3
9	4	2	30.6	23.6
9	5	2	112.2	116.7
9	7	2	90.1	88.3
9	9	2	31.2	30.2
9	10	2	39.9	-33.7
9	13	2	50.8	49.4
9	15	2	88.5	89.2
9	17	2	70.6	63.9
9	19	2	33.2	30.9
10	0	2	136.9	150.9
10	1	2	63.3	-59.3
10	2	2	150.4	141.9
10	3	2	183.4	-194.4
10	4	2	102.9	104.5
10	5	2	131.9	-149.5
10	6	2	72.6	78.7
10	7	2	36.3	26.3
10	8	2	69.6	72.9
10	9	2	64.7	59.2
10	10	2	85.9	85.2
10	11	2	65.1	-63.2
10	12	2	43.8	45.0
10	13	2	145.5	-142.3
10	15	2	136.4	-129.1
10	17	2	82.5	-78.1
10	19	2	31.4	-31.3
11	0	2	204.1	218.4
11	1	2	26.4	35.0
11	2	2	135.6	137.1
11	5	2	20.2	-30.5
11	7	2	37.9	-40.3
11	8	2	85.4	87.2
11	10	2	88.0	85.4
11	11	2	24.9	33.2
11	12	2	51.1	57.2
11	13	2	35.7	-21.7
11	14	2	25.4	28.6
11	15	2	55.6	-59.1
11	17	2	38.2	-39.8
12	0	2	211.4	-185.7
12	1	2	56.3	-63.4
12	2	2	198.7	-209.8
12	4	2	114.8	-137.1
12	6	2	140.2	-142.3

-cont'd-

TABLE 11 -cont'd-

H	K	L	|Fo|	Fc
12	8	2	118.2	-132.4
12	10	2	78.9	-89.9
12	11	2	56.8	-59.7
12	12	2	92.7	-106.7
12	13	2	36.3	-42.8
12	14	2	61.8	-60.7
12	16	2	22.8	-30.9
13	0	2	59.4	-68.6
13	1	2	36.6	-39.2
13	2	2	82.5	-82.3
13	3	2	74.8	-65.7
13	4	2	38.2	-35.8
13	6	2	32.7	-30.2
13	7	2	47.5	44.2
13	8	2	34.3	-33.5
13	10	2	67.2	-72.1
13	11	2	57.4	-61.7
13	12	2	25.7	-33.1
13	13	2	50.8	-51.3
13	19	2	23.6	-28.9
14	0	2	62.8	63.1
14	1	2	22.1	20.2
14	2	2	54.8	55.7
14	3	2	45.4	46.4
14	4	2	39.9	36.6
14	6	2	23.9	19.5
14	7	2	24.4	24.4
14	8	2	43.1	43.0
14	12	2	25.4	32.2
14	13	2	117.4	116.4
14	15	2	64.1	62.5
14	17	2	18.4	30.5
14	19	2	44.6	47.6
15	1	2	23.3	25.9
15	3	2	23.6	30.9
15	9	2	62.8	74.4
15	11	2	72.4	77.9
15	15	2	21.3	12.2
16	1	2	24.1	28.3
16	2	2	59.7	64.5
16	7	2	67.7	-82.4
16	4	2	124.2	144.9
16	6	2	110.6	135.5
16	7	2	72.4	-82.4
16	8	2	57.4	63.1
16	9	2	120.7	-122.1
16	10	2	25.4	33.8
16	11	2	79.4	-73.7
16	16	2	43.6	45.4
16	17	2	36.3	-34.9
16	18	2	21.3	26.5
17	0	2	56.0	66.0
17	2	2	61.5	66.8
17	3	2	43.6	-41.7
17	4	2	56.8	66.2
17	6	2	57.4	51.3
17	8	2	51.4	56.1
17	10	2	24.9	26.1
17	11	2	48.8	-56.7
18	0	2	108.6	-115.4
18	1	2	36.1	-38.5
18	2	2	114.8	-138.2
18	3	2	25.7	-33.6
18	4	2	68.0	-78.9
18	6	2	72.6	-78.7
18	10	2	80.4	-69.5
18	12	2	73.2	-70.0
18	15	2	49.1	-46.4
18	16	2	22.5	-15.5
19	0	2	63.1	-72.4
19	2	2	57.6	-61.3
19	4	2	25.7	-29.0
19	5	2	36.1	-37.2
19	6	2	43.8	-41.1
19	7	2	50.1	-50.9
19	8	2	49.1	-43.8
19	15	2	41.0	-43.1
20	0	2	50.8	62.7
20	2	2	35.8	39.1
20	3	2	25.2	33.2
20	5	2	49.8	50.5
20	7	2	48.3	57.3
20	9	2	50.6	43.4
20	10	2	48.0	40.7
20	12	2	37.1	29.7
20	13	2	46.7	45.6
20	15	2	126.5	71.3
21	2	2	34.8	-21.0
21	3	2	34.5	38.6
21	5	2	47.7	46.6
21	6	2	23.3	-29.5
21	7	2	22.5	22.2
21	14	2	25.7	-8.2
22	0	2	103.4	108.0
22	2	2	62.0	65.4
22	4	2	22.8	32.9
22	5	2	22.3	-28.5
22	9	2	18.7	-15.6
22	11	2	15.3	-10.3
22	13	2	22.5	-33.9
23	0	2	54.0	50.7
23	2	2	43.6	44.1
23	4	2	46.9	44.5
23	6	2	34.3	32.9
23	11	2	16.1	6.8
24	0	2	48.8	-46.9
24	2	2	85.6	-75.3
24	4	2	75.3	-62.9
24	6	2	57.1	-55.6
24	9	2	54.8	-22.1
24	10	2	12.2	-49.8
24	10	2	69.8	-49.8
25	4	2	38.9	-39.4
25	6	2	30.9	-34.2
25	6	2	30.9	-34.2
26	5	2	27.7	-3.6
0	2	3	8.0	8.2
0	4	3	80.3	63.3
0	6	3	105.2	91.6
0	8	3	80.8	83.3
0	10	3	131.5	134.4
0	12	3	129.8	130.9
0	14	3	51.1	50.4
0	16	3	52.7	53.6
0	18	3	74.1	86.3
0	20	3	87.0	77.4
0	22	3	35.3	40.8
1	2	3	129.5	181.7
1	3	3	114.6	-95.6
1	4	3	136.0	108.9
1	5	3	48.2	-53.8
1	6	3	20.8	24.2
1	7	3	39.6	-33.1
1	8	3	30.5	33.2
1	9	3	114.8	-115.9
1	10	3	94.2	105.6
1	11	3	69.6	-73.4
1	12	3	130.1	137.7
1	13	3	34.8	-37.8
1	14	3	62.6	66.1
1	16	3	37.2	45.5
1	18	3	34.8	40.5
1	20	3	79.2	75.8
1	22	3	54.1	61.6
2	2	3	141.0	157.3
2	3	3	137.6	120.0
2	4	3	86.5	65.6
2	5	3	51.1	48.2
2	6	3	15.0	-26.8
2	7	3	46.6	34.1
2	8	3	107.3	-120.3
2	9	3	152.0	144.6
2	10	3	80.3	-74.2
2	11	3	127.2	145.0
2	12	3	93.9	-90.4
2	13	3	88.8	91.7
2	18	3	34.8	-38.4
2	20	3	49.8	-51.9
2	21	3	29.4	35.0
2	22	3	33.9	-37.0
3	1	3	236.6	254.7
3	2	3	42.8	-39.3
3	3	3	160.1	174.3
3	4	3	46.3	48.0
3	6	3	48.7	59.7
3	7	3	111.6	117.9
3	9	3	125.3	134.5
3	10	3	75.5	-62.2
3	11	3	70.6	78.1
3	13	3	49.5	53.1
3	14	3	57.6	62.2
3	15	3	45.5	39.9
3	16	3	45.5	48.6
3	17	3	25.7	32.2
3	20	3	34.5	-29.5
4	1	3	137.3	-139.9
4	2	3	46.3	-39.1
4	3	3	116.7	-105.4
4	4	3	87.0	-77.5
4	5	3	189.7	-183.5
4	9	3	66.1	-110.7
4	7	3	141.5	-170.1
4	8	3	37.2	-43.2
4	9	3	127.7	-110.7
4	11	3	39.0	-40.6
4	12	3	23.8	-29.0
4	13	3	55.9	-57.9
4	14	3	36.4	-37.0
4	15	3	45.5	-54.5
4	16	3	69.3	-75.0
4	17	3	44.2	-42.4
4	18	3	59.4	-58.6
4	20	3	39.3	-32.2
5	1	3	103.6	-106.4
5	2	3	100.1	80.4
5	3	3	68.7	-58.6
5	4	3	32.1	34.3
5	6	3	131.1	-126.9
5	8	3	145.6	-146.9
5	9	3	50.0	-53.4
5	10	3	57.6	-57.4
5	11	3	60.7	-55.2
5	12	3	48.4	-49.3
5	14	3	44.9	-44.9
5	16	3	94.2	-121.1
5	18	3	67.7	-68.1
5	20	3	33.2	-38.2
6	3	3	48.2	-36.3
6	4	3	72.0	72.4
6	5	3	58.9	64.9
6	6	3	105.7	92.4
6	8	3	19.5	16.0
6	10	3	49.5	49.6
6	11	3	40.4	-41.3
6	12	3	107.0	95.9
6	14	3	97.7	104.8
6	16	3	93.9	99.2
6	18	3	84.9	77.4
6	20	3	32.1	53.5
7	1	3	53.0	32.0
7	2	3	33.4	37.4
7	3	3	99.8	-96.7
7	4	3	43.1	39.8
7	5	3	198.1	-204.9
7	6	3	72.8	77.1
7	7	3	88.3	-91.4
7	8	3	76.2	70.8
7	9	3	30.5	-34.7
7	10	3	22.7	25.0
7	14	3	78.7	80.6
7	16	3	93.2	98.0
7	18	3	65.2	57.9
7	20	3	53.6	29.5
8	1	3	107.9	102.7
8	2	3	103.8	-103.3
8	3	3	130.6	130.3
8	4	3	136.8	-146.2
8	5	3	163.8	175.8
8	7	3	137.9	136.3
8	8	3	51.9	57.2
8	9	3	94.5	106.3
8	11	3	54.6	45.9
8	12	3	121.5	-125.2
8	13	3	44.9	42.4
8	14	3	69.6	-79.1
8	15	3	52.5	48.7
8	16	3	36.1	-44.3
8	17	3	34.2	37.3
8	20	3	50.6	3.8
9	1	3	118.6	120.1
9	2	3	38.8	-28.4
9	3	3	127.4	142.1
9	4	3	31.8	-25.0
9	5	3	194.9	199.6
9	6	3	39.9	-38.8
9	7	3	86.5	90.6
9	8	3	53.8	51.8
9	9	3	72.8	80.5
9	10	3	47.9	44.3
9	11	3	55.7	55.5
9	15	3	51.9	40.7
9	20	3	31.3	24.8
10	1	3	105.2	-99.8
10	2	3	26.2	-27.9
10	3	3	135.7	-150.0
10	5	3	144.5	-161.1
10	7	3	140.2	-144.7
10	8	3	45.5	-37.4
10	9	3	62.6	-64.9
10	10	3	55.1	-50.3
10	11	3	25.4	-28.4
10	12	3	25.9	-31.7
10	13	3	26.2	-24.5
10	14	3	45.5	-50.9
10	15	3	25.7	-23.1
10	16	3	34.8	-43.9
10	18	3	36.1	-25.9
11	1	3	47.7	-39.6
11	2	3	44.2	-52.1
11	3	3	72.5	-78.0
11	4	3	50.6	-50.3
11	5	3	90.2	-94.7
11	6	3	49.3	-47.8
11	7	3	55.7	-54.0
11	8	3	23.5	-30.3
11	8	3	56.2	-30.3
11	11	3	25.7	-32.2
11	12	3	123.1	-129.2
11	13	3	26.2	-30.2
11	16	3	41.5	-48.0
11	18	3	34.2	-32.8
12	2	3	86.5	86.2
12	3	3	52.2	-50.8
12	4	3	87.0	86.1
12	5	3	22.2	20.7
12	6	3	39.6	48.4
12	7	3	23.5	16.0
12	9	3	24.8	34.2
12	10	3	96.4	91.3
12	11	3	25.9	-30.3
12	12	3	105.4	109.5
12	13	3	26.2	-38.2
12	14	3	92.4	97.3
12	15	3	24.6	-35.2
12	16	3	56.4	56.5
12	18	3	36.9	25.0
12	20	3	20.0	37.4
13	1	3	156.8	-169.6
13	2	3	38.3	37.4
13	3	3	38.8	-44.4
13	4	3	32.1	28.3
13	6	3	23.8	25.5
13	7	3	49.0	-46.2
13	7	3	50.3	-46.2
13	9	3	62.9	-81.4
13	10	3	63.9	65.3
13	11	3	58.9	-58.1
13	12	3	58.7	54.8
13	13	3	36.4	-43.3
13	14	3	61.3	48.4
13	16	3	38.3	36.9
13	18	3	38.0	36.1
13	18	3	38.0	36.1
14	1	3	103.3	129.8
14	2	3	92.9	99.1
14	3	3	112.9	134.6
14	4	3	33.7	33.9
14	5	3	97.2	115.9
14	6	3	49.5	-51.0
14	7	3	61.8	66.5
14	8	3	81.3	-90.1
14	9	3	52.2	52.4
14	10	3	58.9	-58.2
14	11	3	37.2	36.6
14	13	3	50.6	43.9
14	15	3	55.7	47.8
14	17	3	18.2	19.9
14	18	3	37.2	-40.6
15	1	3	145.1	147.7
15	3	3	[illegible]	88.4
15	4	3	24.6	33.7
15	5	3	[illegible]	89.1
15	7	3	57.8	50.1
15	9	3	114.8	105.8
15	11	3	63.7	69.3
15	17	3	23.2	24.1
16	1	3	117.8	-128.5
16	2	3	25.1	-28.7
16	3	3	91.6	-97.1
16	4	3	25.4	-24.4
16	5	3	25.7	-27.4
16	6	3	25.9	-27.9
16	7	3	58.7	-54.0
16	8	3	45.5	-47.0
16	9	3	64.2	-55.9
16	10	3	36.7	-41.7
16	11	3	84.6	-64.5
16	12	3	24.6	-23.0
16	13	3	57.6	-46.3
16	14	3	65.8	-50.5
16	15	3	34.5	-30.4
16	16	3	43.1	-38.2
17	1	3	68.2	-69.9
17	2	3	25.7	14.4
17	4	3	25.9	22.0
17	5	3	26.2	29.1
17	6	3	26.2	-45.6
17	6	3	83.0	-45.6
17	9	3	25.9	-25.0
17	10	3	67.1	-61.2
17	11	3	24.6	-31.8
17	12	3	47.1	-46.5
17	16	3	59.7	-54.2
18	1	3	58.7	48.4
18	2	3	26.2	-23.9
18	3	3	26.2	-22.2
18	4	3	26.2	-11.1
18	5	3	69.6	-67.2
18	6	3	64.2	59.5
18	7	3	69.1	-64.4
18	8	3	99.8	87.1
18	10	3	84.9	73.0
18	11	3	40.6	35.0
18	13	3	41.2	35.0
18	14	3	45.5	29.0
18	16	3	49.0	57.7
19	3	3	69.6	-68.0
19	4	3	36.9	31.7
19	5	3	86.5	-96.7
19	7	3	80.3	-75.4
19	12	3	50.0	47.2
19	14	3	43.1	42.4
19	15	3	18.2	-20.1
20	3	3	85.6	76.5
20	5	3	87.8	86.3
20	7	3	77.1	70.1
20	9	3	78.7	65.1
20	11	3	53.2	41.0
20	11	3	22.7	41.0
20	14	3	18.5	-19.6
21	1	3	50.3	50.8
21	3	3	49.5	48.0
21	4	3	24.3	25.7
21	7	3	68.7	54.5
21	9	3	41.7	40.0
21	13	3	25.7	24.3
22	1	3	58.4	-49.0
22	3	3	81.1	-65.6
22	5	3	63.7	-50.5
22	7	3	62.9	-54.7
22	8	3	49.0	-42.9
22	9	3	45.8	-40.7
22	10	3	33.9	-27.5
22	11	3	33.4	-31.4
22	12	3	21.1	-15.4
23	1	3	21.9	25.1
23	2	3	21.6	-23.6
23	3	3	37.2	-31.4
23	4	3	36.4	-29.9
23	5	3	64.7	-51.2
23	6	3	27.8	-30.7
23	7	3	45.8	-38.3
24	1	3	65.6	-61.1
24	5	3	26.2	27.1
24	6	3	35.8	34.5
24	7	3	23.8	21.6
24	8	3	40.1	45.9
24	8	3	40.1	45.9
25	1	3	56.4	-54.9
25	3	3	48.7	-41.7
25	6	3	19.0	26.9
26	1	3	61.3	67.1
26	3	3	45.2	53.7
0	4	4	135.8	132.1
0	6	4	60.5	58.0
0	10	4	94.8	105.9
0	12	4	120.3	135.0
0	14	4	103.5	114.5
0	18	4	61.7	-56.3
0	19	4	22.9	0.0
1	2	4	190.5	270.7
1	3	4	149.2	137.9
1	4	4	51.9	47.7
1	5	4	82.7	78.6
1	6	4	64.7	60.3
1	7	4	38.4	-38.9
1	8	4	128.7	124.1
1	10	4	152.6	156.5
1	11	4	69.5	65.5
1	12	4	98.5	109.2
1	13	4	85.5	90.0
1	14	4	26.6	26.7
1	15	4	60.8	70.7
1	19	4	32.5	28.1
2	1	4	34.2	53.1
2	2	4	[illegible]	-92.1
2	3	4	30.3	33.2
2	4	4	170.3	-176.9
2	5	4	95.1	-88.5
2	6	4	27.5	-35.5
2	7	4	89.1	-99.5
2	9	4	79.1	-71.1
2	10	4	21.8	26.6
2	11	4	61.7	-68.3
2	12	4	55.2	-58.0
2	13	4	36.4	-31.5
2	14	4	88.9	-91.1
2	15	4	47.1	-51.9
2	17	4	79.3	-83.2
2	19	4	60.8	-60.0
2	21	4	23.5	-34.1
3	0	4	63.1	-47.4
3	1	4	84.7	-75.6
3	2	4	29.2	-33.2
3	3	4	40.6	-48.7
3	4	4	57.7	51.3
3	5	4	33.4	-41.4
3	6	4	40.1	34.5
3	7	4	85.5	-77.0
3	8	4	47.1	-53.7
3	9	4	124.5	-125.8
3	10	4	49.6	-52.0
3	11	4	113.4	-115.8
3	13	4	104.1	-108.8
3	14	4	26.6	22.4
3	15	4	98.5	-102.2
3	17.	4	69.5	-73.6
3	19	4	68.1	-67.0
3	21	4	39.8	-60.3
4	0	4	162.4	-182.6
4	1	4	91.9	-89.5
4	2	4	116.2	-104.9
4	3	4	114.5	-98.9
4	4	4	28.9	14.5
4	5	4	102.9	95.4
4	7	4	151.5	146.0
4	8	4	132.4	-133.7
4	9	4	96.8	89.5
4	10	4	125.7	-128.8
4	11	4	58.6	66.9
4	13	4	26.1	33.7
4	14	4	53.8	57.9
4	15	4	47.1	44.2
4	17	4	63.9	61.2
4	18	4	34.7	-27.2
4	19	4	50.2	49.2
4	20	4	33.9	-34.3
4	21	4	58.9	39.2
5	0	4	65.1	-39.8
5	2	4	175.1	-188.1
5	3	4	78.5	-64.5
5	4	4	214.6	-225.8
5	5	4	43.4	-30.4
5	6	4	221.9	-227.4
5	7	4	50.2	45.5
5	8	4	131.5	-133.1
5	9	4	122.3	125.2
5	10	4	60.8	-52.6
5	11	4	68.7	71.4
5	12	4	56.9	-50.9
5	14	4	46.8	-40.9
5	15	4	38.4	33.3
5	16	4	53.8	-54.3
5	18	4	34.2	-30.7
5	19	4	58.3	46.4
5	20	4	19.0	-3.1
5	21	4	44.9	47.3
6	0	4	171.7	175.5
6	1	4	81.0	63.0
6	2	4	107.5	113.1
6	3	4	57.7	-56.1
6	4	4	115.6	127.7
6	5	4	38.7	-35.6
6	6	4	174.5	207.5
6	7	4	48.2	37.6
6	8	4	145.0	150.5
6	9	4	86.1	78.4
6	10	4	77.9	73.3
6	12	4	36.4	-36.6
6	16	4	37.8	35.2
6	18	4	41.2	36.5
6	19	4	42.9	36.3
6	19	4	37.0	36.3
7	0	4	108.3	86.4
7	1	4	34.7	-31.2
7	2	4	116.4	131.4
7	3	4	57.5	-52.4
7	4	4	169.4	208.7
7	6	4	177.3	224.6
7	7	4	104.3	110.8
7	8	4	128.2	120.7
7	9	4	60.3	67.4
7	10	4	67.9	68.0
7	12	4	52.1	47.9
7	14	4	54.3	47.1
7	15	4	66.5	78.4
7	16	4	45.7	37.8
7	17	4	83.5	77.1
7	19	4	50.7	52.3
8	1	4	81.0	-71.4
8	3	4	108.0	-102.9
8	4	4	78.2	-82.6
8	6	4	103.2	-91.0
8	8	4	89.7	-83.4
8	9	4	23.5	-28.5
8	10	4	24.3	14.4
8	11	4	95.9	-99.0
8	12	4	26.4	21.4
8	13	4	97.6	-87.5
8	15	4	60.3	-56.0
8	16	4	37.0	-33.2
8	17	4	55.2	-46.1
8	18	4	39.2	-31.8
8	19	4	39.8	-42.6
9	0	4	76.5	77.2
9	1	4	17.9	-18.6
9	2	4	36.7	17.6
9	3	4	65.6	-54.9
9	5	4	81.3	-94.7
9	7	4	86.1	-90.4
9	9	4	59.4	-59.2
9	10	4	43.7	33.2
9	11	4	58.3	-55.7
9	13	4	109.1	-103.1
9	15	4	116.7	-113.3
9	16	4	25.5	29.3
9	17	4	115.3	-93.3
9	19	4	65.9	-65.6
8	21	4	31.3	-33.5
10	0	4	88.6	-83.1
10	1	4	116.7	111.4
10	2	4	111.4	-113.6
10	3	4	130.5	131.4
10	4	4	85.2	-82.9
10	5	4	48.0	45.7
10	6	4	80.2	-74.6
10	7	4	65.4	-72.4
10	9	4	35.3	-33.5
10	11	4	84.1	81.9
10	12	4	60.5	-47.4
10	13	4	105.7	91.9
10	14	4	38.1	-32.2
10	15	4	58.9	51.7
11	0	4	235.3	-242.9
11	1	4	35.9	25.7
11	3	4	21.3	23.7
11	4	4	65.6	-70.3
11	5	4	22.4	24.4
11	6	4	51.9	-51.0
11	7	4	41.5	39.0
11	8	4	96.5	-91.2
11	9	4	36.1	33.8
11	10	4	105.7	-108.8
11	12	4	122.0	-115.5
11	14	4	53.3	-44.7
12	0	4	57.7	66.4
12	1	4	49.1	40.4
12	2	4	93.9	87.0
12	4	4	100.4	123.2
12	6	4	99.9	107.8
12	8	4	25.5	26.2
12	9	4	26.1	31.7
12	10	4	53.5	46.0
12	12	4	38.4	36.3
12	14	4	69.5	64.6
12	15	4	43.1	34.0
12	16	4	57.2	46.0
13	0	4	110.8	104.4
13	1	4	46.3	36.2
13	2	4	90.6	93.1
13	3	4	52.9	51.5
13	4	4	110.6	129.5
13	5	4	34.7	39.8
13	6	4	100.7	107.6
13	8	4	64.5	60.7
13	9	4	26.6	33.7
13	10	4	76.8	62.4
13	11	4	86.3	93.5
13	12	4	26.9	35.5
13	13	4	70.1	67.6
13	18	4	16.5	17.1
13	19	4	36.4	43.3
14	0	4	72.9	-83.4
14	1	4	34.2	-34.1
14	2	4	34.5	-33.1
14	7	4	26.4	-29.4
14	8	4	26.6	-23.4
14	9	4	27.2	-25.5
14	11	4	46.8	-46.4
14	13	4	81.9	-70.1
14	15	4	65.1	-65.2
15	0	4	35.9	37.3
15	3	4	25.5	0.5
15	7	4	66.1	-68.0
15	9	4	90.6	-120.6
15	11	4	54.7	-97.1
15	13	4	55.8	-59.0
15	17	4	42.6	-38.0
16	1	4	45.4	-50.4
16	2	4	37.3	-37.1
16	3	4	106.4	-125.9
16	4	4	53.5	-65.6
16	6	4	97.9	-94.1
16	7	4	105.7	107.3
16	8	4	38.4	-39.1
16	9	4	85.8	89.1
16	17	4	37.8	38.8
17	0	4	65.9	-67.6
17	2	4	97.4	-106.1
17	4	4	108.9	-113.4
17	6	4	109.1	-111.1
17	8	4	81.0	-83.4
17	11	4	43.4	40.9
17	13	4	31.3	27.4
17	14	4	28.9	-26.0
17	16	4	38.9	-40.3
18	0	4	72.1	97.6
18	1	4	27.2	33.1
18	2	4	60.8	68.4
18	3	4	27.2	40.8
18	4	4	47.1	55.4
18	5	4	27.2	11.7
18	6	4	46.8	47.2
18	7	4	26.6	-27.5

-cont'd-

TABLE 11 -cont'd-

H	K	L	|Fo|	Fc
18	8	4	45.7	36.8
18	10	4	86.3	69.4
18	12	4	44.5	38.4
18	13	4	40.9	30.4
19	0	4	115.6	119.1
19	2	4	71.8	74.2
19	4	4	60.3	59.8
19	5	4	53.5	49.8
19	6	4	59.1	56.3
19	8	4	50.7	52.6
19	10	4	52.4	52.6
19	12	4	45.7	39.7
19	13	4	26.1	23.2
19	14	4	41.7	33.2
19	15	4	44.5	47.7
20	1	4	26.6	-34.7
20	3	4	26.4	-32.2
20	7	4	24.7	-24.4
20	12	4	31.3	-27.8
20	13	4	31.3	-24.1
21	3	4	61.9	-58.8
21	5	4	69.3	-59.2
21	6	4	23.8	33.9
21	7	4	22.9	-22.8
21	11	4	25.0	-24.1
21	13	4	48.2	-64.3
22	0	4	76.5	-72.7
22	1	4	24.1	30.3
22	2	4	63.3	-58.3
22	8	4	34.5	-26.3
22	10	4	50.2	-54.2
22	11	4	14.3	18.9
22	12	4	19.6	-27.6
23	0	4	62.6	-61.5
23	2	4	85.2	-76.2
23	4	4	73.2	-70.8
23	6	4	61.9	-62.9
23	8	4	59.1	-55.4
23	10	4	33.4	-40.5
24	0	4	59.4	59.7
24	1	4	19.6	-22.1
24	2	4	38.9	33.0
24	3	4	19.0	-28.5
24	4	4	18.2	21.4
24	6	4	28.5	25.9
24	7	4	26.1	27.3
24	8	4	37.0	38.2
25	0	4	28.9	23.7
25	2	4	32.5	32.8
25	4	4	49.4	55.6
25	6	4	41.2	47.9
0	2	5	212.7	157.0
0	4	5	70.2	54.6
0	6	5	33.2	-41.1
0	8	5	119.5	-139.1
0	10	5	32.6	-30.9
0	12	5	29.8	-20.1
0	16	5	48.2	-42.6
0	18	5	43.7	-40.6
0	20	5	28.2	-27.5
1	1	5	235.3	229.2
1	2	5	84.0	-84.5
1	3	5	76.0	71.0
1	4	5	35.5	-30.1
1	5	5	80.1	79.4
1	6	5	16.7	-14.7
1	7	5	75.8	75.1
1	8	5	101.9	-117.8
1	9	5	68.1	76.2
1	10	5	126.6	-138.2
1	11	5	95.1	108.7
1	12	5	121.6	-132.2
1	13	5	60.5	62.1
1	15	5	27.9	27.9
1	16	5	39.3	-47.8
1	18	5	75.8	-72.4
1	20	5	84.9	-80.3
2	2	5	167.7	-150.0
2	3	5	21.1	-24.5
2	4	5	70.8	-58.4
2	5	5	21.7	-25.0
2	6	5	66.1	55.7
2	7	5	32.3	-30.3
2	8	5	90.2	89.7
2	9	5	89.6	-83.2
2	11	5	69.9	-62.0
2	13	5	60.5	-56.0
2	16	5	27.6	19.8
3	1	5	257.0	-227.9
3	2	5	23.5	-16.0
3	3	5	222.3	-282.7
3	4	5	117.4	-116.7
3	5	5	191.8	-205.7
3	6	5	17.3	-14.4
3	7	5	177.4	-193.5
3	8	5	91.9	79.8
3	9	5	114.5	-116.3
3	10	5	74.3	70.6
3	11	5	89.9	-95.1
3	13	5	98.1	-85.1
3	14	5	48.2	-53.0
3	15	5	39.6	-40.8
3	16	5	47.9	-49.8
3	17	5	65.5	-63.1
4	1	5	108.1	91.7
4	5	5	74.9	61.3
4	7	5	51.7	52.9
4	8	5	36.1	33.4
4	9	5	31.7	23.7
4	10	5	23.8	27.5
4	13	5	61.1	58.6
4	18	5	42.6	38.7
4	20	5	46.7	46.6
5	1	5	185.0	141.5
5	2	5	74.9	70.3
5	3	5	68.4	68.0
5	4	5	83.4	75.9
5	5	5	84.3	84.1
5	6	5	108.4	113.7
5	7	5	56.9	55.8
5	8	5	127.5	127.1
5	10	5	54.3	55.6
5	11	5	57.2	57.2
5	12	5	59.6	59.6
5	14	5	105.1	121.6
5	15	5	27.9	29.7
5	16	5	116.6	123.0
5	17	5	26.1	20.6
5	18	5	87.8	86.4
5	20	5	48.8	46.2
6	1	5	50.5	43.6
6	2	5	56.6	-52.9
6	3	5	16.4	-15.1
6	4	5	85.2	-87.8
6	5	5	82.5	-79.2
6	9	5	57.5	55.7
6	11	5	58.1	47.0
6	12	5	71.4	-73.3
6	13	5	27.6	-30.2
6	14	5	39.6	-30.9
6	18	5	41.1	-30.1
6	20	5	39.3	-36.2
7	3	5	121.3	146.4
7	4	5	82.6	-87.4
7	5	5	202.6	228.9
7	6	5	109.0	-109.5
7	7	5	121.0	136.1
7	8	5	110.2	-120.8
7	9	5	48.2	52.0
7	12	5	27.3	-31.7
7	14	5	79.6	-91.7
7	15	5	27.6	37.5
7	16	5	100.7	-101.4
7	17	5	25.2	28.1
7	18	5	104.0	-93.8
7	20	5	52.8	-50.6
8	2	5	165.4	162.7
8	3	5	37.5	-35.2
8	4	5	121.0	-78.8
8	5	5	81.9	-78.8
8	6	5	37.3	-35.1
8	7	5	74.9	-85.0
8	8	5	74.9	-88.6
8	9	5	34.9	-42.2
8	10	5	25.8	-23.5
8	11	5	26.7	23.6
8	12	5	73.1	82.7
8	14	5	56.1	58.4
8	17	5	55.2	-48.5
9	1	5	168.6	-182.2
9	2	5	107.8	111.5
9	3	5	178.0	-202.1
9	5	5	156.0	-161.5
9	7	5	154.2	-154.6
9	8	5	54.9	-59.0
9	9	5	84.9	-95.1
9	10	5	74.9	-81.5
9	11	5	72.2	-83.9
9	12	5	39.3	-44.5
9	13	5	74.3	-87.7
9	14	5	27.9	27.5
9	16	5	25.8	25.9
9	20	5	23.5	-24.1
10	1	5	58.1	63.9
10	3	5	37.0	36.0
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10	5	5	64.3	62.7
10	8	5	35.8	44.5
10	9	5	37.0	39.1
10	10	5	27.0	23.3
10	16	5	24.9	25.5
10	17	5	32.6	30.1
11	1	5	31.1	29.2
11	2	5	31.4	27.1
11	3	5	87.5	81.9
11	4	5	51.7	51.7
11	5	5	95.4	95.6
11	6	5	42.6	40.8
11	7	5	67.0	56.4
11	8	5	58.4	56.6
11	9	5	26.7	26.8
11	10	5	87.2	100.8
11	11	5	48.5	53.1
11	12	5	109.0	117.3
11	14	5	66.0	85.7
11	16	5	64.3	56.8
12	1	5	52.0	-39.9
12	2	5	40.5	-34.1
12	3	5	47.6	41.9
12	4	5	48.5	-47.3
12	5	5	24.0	20.0
12	7	5	26.1	-34.7
12	9	5	27.3	-30.2
12	12	5	62.5	-52.2
12	14	5	65.2	-59.8
13	1	5	171.9	189.5
13	2	5	55.2	44.7
13	3	5	86.6	80.7
13	8	5	110.2	-116.0
13	9	5	111.6	125.3
13	9	5	105.1	125.3
13	11	5	105.1	103.0
13	12	5	73.4	-50.1
13	13	5	60.2	54.1
13	14	5	63.1	-45.7
13	16	5	44.0	-42.0
13	18	5	51.7	-54.7
14	2	5	57.5	-60.7
14	3	5	82.5	-89.7
14	4	5	45.8	-38.0
14	5	5	96.6	-101.3
14	6	5	47.0	43.3
14	7	5	47.9	-36.9
14	8	5	62.5	55.2
14	10	5	39.6	35.9
14	13	5	58.4	-49.7
14	15	5	55.8	-46.1
14	18	5	31.1	32.4
15	1	5	116.3	-152.8
15	3	5	108.1	-133.9
15	5	5	61.3	-93.1
15	7	5	108.7	-113.2
15	9	5	125.7	-105.7
15	11	5	66.7	-69.6
15	13	5	56.1	-49.0
15	15	5	30.0	-31.4
15	17	5	30.0	-30.6
16	1	5	72.6	74.1
16	2	5	54.9	54.2
16	3	5	47.9	49.0
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16	11	5	59.0	55.6
16	12	5	35.5	36.7
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16	15	5	48.8	36.9
16	17	5	26.7	-32.3
17	1	5	62.5	61.6
17	3	5	48.5	39.0
17	4	5	39.6	42.7
17	6	5	48.5	47.3
17	8	5	47.6	50.5
17	10	5	74.3	71.2
17	12	5	71.7	71.1
17	14	5	59.9	57.7
17	16	5	50.5	55.5
18	8	5	59.9	-49.7
19	1	5	27.9	27.6
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19	3	5	73.1	79.8
19	4	5	67.3	-62.0
19	5	5	109.0	105.1
19	9	5	42.6	41.6
19	10	5	40.5	-36.6
19	12	5	56.6	-55.9
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21	7	5	89.0	-76.6
21	9	5	71.4	-56.3
21	11	5	44.3	-37.7
22	1	5	41.7	44.0
22	8	5	38.7	34.3
22	9	5	43.4	40.3
22	9	5	27.0	40.3
22	11	5	17.6	26.0
23	1	5	21.7	-11.9
23	2	5	21.7	27.9
23	3	5	47.6	25.3
23	4	5	41.4	49.4
23	5	5	28.2	32.0
23	10	5	9.4	25.2
24	1	5	33.2	32.7
24	1	5	19.0	32.7
25	1	5	54.0	59.2
25	2	5	21.4	20.7
25	3	5	47.9	45.8
25	5	5	22.9	23.8
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0	10	6	22.7	-23.9
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1	0	6	163.0	-218.3
1	1	6	22.4	-5.1
1	2	6	287.9	-232.7
1	3	6	50.5	-41.6
1	4	6	190.4	-181.4
1	5	6	62.2	-59.1
1	6	6	80.3	-92.6
1	7	6	18.1	-17.8
1	8	6	88.9	-85.7
1	9	6	52.2	-56.0
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1	11	6	48.2	-48.4
1	12	6	116.5	-116.4
1	13	6	64.3	-76.0
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1	15	6	66.0	-68.6
1	16	6	26.4	-23.5
1	17	6	35.6	-34.0
1	18	6	23.2	18.2
1	19	6	36.1	-29.1
1	21	6	18.1	-24.6
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3	1	6	48.5	43.3
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3	7	6	94.8	97.4
3	8	6	45.6	-44.6
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3	10	6	32.7	-31.6
3	11	6	134.4	150.9
3	12	6	25.5	22.6
3	13	6	109.1	102.9
3	14	6	37.9	42.2
3	15	6	103.9	110.6
3	17	6	70.6	75.6
3	19	6	64.9	57.8
3	20	6	17.2	-18.7
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4	3	6	39.9	-40.6
4	4	6	68.9	-77.4
4	5	6	16.6	-17.9
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4	20	6	23.5	23.0
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5	1	6	37.1	39.9
5	2	6	128.3	123.0
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5	4	6	240.0	247.9
5	6	6	258.3	271.7
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5	10	6	58.5	59.3
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5	15	6	26.7	-32.3
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5	19	6	48.2	-46.2
5	21	6	22.4	-34.6
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6	3	6	28.4	26.7
6	5	6	45.0	-47.8
6	6	6	64.9	-61.9
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6	19	6	18.9	-24.5
7	0	6	189.8	-187.2
7	1	6	16.6	-11.1
7	2	6	151.3	-154.3
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7	5	6	27.3	-29.9
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7	8	6	176.0	-156.0
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7	10	6	151.6	-137.0
7	11	6	63.1	-58.0
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7	13	6	66.0	-53.7
7	15	6	37.0	-36.2
7	17	6	46.7	-50.1
7	18	6	36.7	-29.0
7	19	6	57.7	-63.4
7	20	6	24.1	-27.0
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8	2	6	31.6	-34.4
8	3	6	42.2	39.6
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8	11	6	26.1	23.1
8	13	6	27.0	26.9
8	18	6	35.3	34.8
8	19	6	24.4	20.1
9	0	6	27.0	-28.6
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9	3	6	98.2	106.0
9	4	6	61.9	-63.9
9	5	6	88.4	77.5
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9	8	6	41.9	32.3
9	9	6	50.2	46.2
9	10	6	36.4	38.4
9	11	6	83.8	102.1
9	12	6	26.7	-18.3
9	13	6	84.9	99.6
9	14	6	59.1	-53.7
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9	16	6	23.8	-29.4
9	17	6	114.5	93.0
9	19	6	64.0	67.9
10	0	6	84.4	-90.9
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11	5	6	33.3	-32.7
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11	8	6	76.9	78.0
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11	11	6	26.7	-27.4
11	12	6	89.2	111.4
11	13	6	45.6	-46.8
11	14	6	62.6	61.4
11	15	6	41.9	-49.4
11	17	6	34.4	-35.2
11	19	6	16.9	-19.2
12	0	6	45.9	48.8
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12	6	6	50.2	-55.3
12	10	6	46.5	42.7
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13	3	6	34.7	29.4
13	4	6	78.9	-96.0
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17	0	6	66.0	67.1
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18	14	6	14.9	3.7
19	0	6	118.0	-98.7
19	2	6	74.3	-76.1
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19	13	6	40.1	-43.5
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21	0	6	41.6	-27.4
21	2	6	33.6	-17.0
21	3	6	91.2	81.3
21	5	6	59.7	58.5
21	11	6	37.3	42.1
22	10	6	25.3	27.7
23	0	6	109.4	93.0
23	2	6	85.5	75.8
23	4	6	55.9	64.9
23	6	6	69.1	64.8
23	8	6	59.7	58.2
24	3	6	39.3	39.6
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1	1	7	143.4	-148.4
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1	9	7	63.8	-62.3
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1	18	7	63.8	62.1
1	20	7	42.1	43.3
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2	5	7	65.8	-66.2
2	6	7	33.5	-24.7
2	7	7	51.4	-57.9
2	10	7	44.7	44.5
2	12	7	28.1	26.5
2	13	7	28.7	23.9
3	1	7	222.5	191.0
3	2	7	188.0	176.2
3	3	7	229.9	244.9
3	4	7	130.5	120.8
3	5	7	187.7	211.1
3	6	7	48.5	-52.8
3	7	7	125.4	127.3
3	8	7	95.1	-95.0
3	9	7	101.5	101.5
3	10	7	52.0	-41.1
3	11	7	86.5	86.0
3	12	7	49.2	56.6
3	13	7	71.2	73.8
3	14	7	65.1	64.3
3	15	7	70.5	73.7
3	18	7	23.6	-19.1
4	1	7	69.2	61.1
4	3	7	39.6	44.0
4	5	7	38.0	-32.8
4	6	7	54.2	49.3
4	9	7	55.9	56.7
4	11	7	73.1	69.9
4	13	7	29.0	-26.1
4	14	7	29.0	27.6
5	1	7	61.0	-52.5
5	2	7	124.2	-98.8
5	3	7	133.7	-133.3
5	4	7	96.7	-87.9
5	5	7	91.3	-79.3
5	6	7	67.3	-64.6
5	7	7	39.2	-28.5
5	8	7	23.9	-18.1
5	9	7	25.6	-26.8
5	10	7	84.5	-98.7
5	11	7	55.9	-61.2
5	12	7	95.1	-107.8
5	13	7	41.2	-37.1
5	14	7	76.9	-92.5
5	15	7	49.2	-50.6
5	16	7	81.7	-83.0
5	18	7	72.5	-81.6
5	20	7	51.1	-59.9
6	1	7	46.0	-50.1
6	2	7	47.2	54.8
6	3	7	45.6	43.4
6	4	7	34.1	26.9
6	5	7	46.6	55.3
6	6	7	44.3	-36.8
6	8	7	65.4	-70.6
6	9	7	45.0	-43.8
6	1	7	39.9	-41.2
6	12	7	40.9	34.5
6	14	7	29.0	-27.6
6	16	7	26.8	-27.1
6	18	7	31.2	-29.3
7	1	7	70.9	-69.1
7	2	7	88.8	80.4
7	3	7	82.7	-75.8
7	4	7	86.2	69.6
7	5	7	122.6	-137.8
7	6	7	46.3	41.1
7	7	7	119.1	-139.2
7	8	7	36.0	40.8
7	9	7	65.4	-65.2
7	10	7	73.4	76.5
7	12	7	65.1	64.0
7	14	7	76.3	77.1
7	15	7	27.8	-27.1
7	16	7	87.5	88.0
7	17	7	34.1	-28.1
7	18	7	68.0	70.8
7	20	7	33.8	53.8
8	1	7	20.1	-20.4
8	2	7	20.7	-19.3
8	3	7	47.6	-50.2
8	4	7	38.3	-34.6
8	5	7	46.0	-49.9
8	6	7	41.8	41.9
8	7	7	25.2	-20.1
8	8	7	26.2	23.6
9	1	7	184.2	204.0
9	2	7	49.4	-56.9
9	3	7	124.5	144.2
9	4	7	46.6	-40.8
9	5	7	99.9	108.5
9	7	7	113.6	116.3

-cont'd-

TABLE 11 -cont'd-

H	K	L	|Fo|	Fc
9	8	7	66.1	68.9
9	9	7	139.5	166.3
9	10	7	28.4	19.8
9	11	7	92.0	106.1
9	17	7	22.3	21.7
9	18	7	33.5	11.5
10	1	7	40.3	38.1
10	2	7	33.2	-36.0
10	3	7	41.5	40.7
10	5	7	25.2	-23.5
10	6	7	25.9	23.3
10	7	7	26.8	-24.3
10	10	7	28.7	27.0
10	11	7	41.2	48.9
10	13	7	28.4	35.2
10	17	7	30.0	-33.2
11	1	7	77.6	-70.9
11	3	7	56.5	-51.5
11	5	7	26.2	-29.0
11	6	7	81.1	-90.9
11	7	7	61.9	-60.8
11	8	7	80.1	-93.1
11	9	7	76.3	-78.0
11	10	7	71.6	-85.3
11	1	7	24.6	-70.9
11	12	7	76.3	-69.9
11	14	7	71.2	-69.8
11	16	7	72.5	-71.2
11	17	7	19.8	-22.9
11	18	7	55.2	-63.6
12	1	7	68.3	72.6
12	4	7	60.0	-23.3
12	8	7	49.8	-13.5
13	1	7	140.5	-164.5
13	3	7	61.3	-67.8
13	6	7	49.4	42.6
13	7	7	28.7	-29.0
13	8	7	76.9	76.4
13	9	7	50.4	-46.8
13	10	7	76.9	79.7
13	11	7	85.5	-89.0
13	12	7	61.9	60.0
13	13	7	75.0	-75.0
13	14	7	35.1	35.0
13	16	7	44.3	41.3
13	17	7	27.8	33.4
14	1	7	27.8	-28.7
14	2	7	28.1	23.9
15	1	7	90.7	99.2
15	3	7	108.2	125.9
15	5	7	127.1	156.9
15	7	7	77.2	85.3
15	9	7	49.4	44.9
15	11	7	53.9	47.4
15	13	7	67.6	62.8
15	14	7	30.7	28.1
15	15	7	57.2	54.8
17	1	7	29.0	-28.7
17	3	7	58.1	-47.0
17	5	7	40.9	-36.8
17	6	7	49.4	-51.2
17	8	7	77.9	-65.3
17	10	7	67.3	-67.2
17	11	7	33.8	-24.2
17	12	7	63.2	-60.8
17	13	7	49.2	-45.9
17	14	7	48.5	-48.9
17	15	7	21.0	-29.7
19	1	7	39.6	-31.1
19	3	7	61.9	-48.7
19	4	7	27.2	25.2
19	5	7	85.2	-85.1
19	6	7	26.2	22.5
19	7	7	84.5	-95.9
19	9	7	56.8	-44.2
19	10	7	21.7	20.9
19	12	7	48.8	50.4
20	5	7	35.7	-34.6
20	7	7	23.6	-24.0
21	1	7	86.5	76.4
19	1	7	39.6	-31.1
19	3	7	61.9	-48.7
19	4	7	27.2	25.2
19	5	7	85.2	-85.1
19	6	7	26.2	22.5
19	7	7	84.5	-95.9
19	9	7	56.8	-44.2
19	10	7	21.7	20.9
19	12	7	48.8	50.4
20	5	7	35.7	-34.6
20	7	7	23.6	-24.0
21	1	7	86.5	76.4
21	3	7	59.7	50.1
21	5	7	73.4	80.3
21	7	7	76.6	84.2
21	9	7	59.7	69.0
21	11	7	29.4	35.5
23	2	7	39.6	-40.3
23	4	7	32.9	-34.4
23	5	7	34.5	-31.9
23	6	7	22.0	-23.8
23	7	7	33.2	-37.9
0	2	8	106.9	-103.1
0	4	8	61.4	-57.7
0	6	8	82.0	-85.1
0	8	8	48.2	-44.7
0	10	8	46.9	-36.9
0	16	8	39.1	-44.2
1	0	8	32.0	83.1
1	2	8	173.7	145.1
1	3	8	64.4	51.0
1	4	8	160.2	179.0
1	5	8	18.5	22.5
1	6	8	102.9	113.4

H	K	L	|Fo|	Fc
1	8	8	53.9	57.8
1	10	8	66.8	73.9
1	11	8	40.1	40.8
1	12	8	88.0	93.0
1	13	8	66.8	63.2
1	14	8	59.7	64.3
1	15	8	65.1	69.4
1	16	8	39.1	35.5
1	17	8	36.4	32.0
2	0	8	14.9	11.1
2	1	8	37.4	34.3
2	2	8	39.4	31.5
2	3	8	102.9	76.7
2	4	8	38.1	36.1
2	5	8	42.5	37.5
2	6	8	20.9	17.3
2	12	8	29.4	28.0
2	13	8	66.8	72.9
2	15	8	64.8	61.6
2	20	8	18.9	-7.3
3	0	8	42.8	38.9
3	4	8	35.7	-33.9
3	5	8	43.9	-36.1
3	7	8	80.0	-88.6
3	8	8	55.3	45.3
3	9	8	87.0	-101.9
3	10	8	27.7	30.8
3	11	8	75.9	-83.3
3	13	8	73.2	-85.9
3	15	8	70.8	-77.3
3	17	8	71.9	-73.4
3	18	8	39.1	32.3
3	19	8	53.6	-54.2
4	0	8	39.4	36.1
4	1	8	21.5	-22.1
4	2	8	36.1	27.7
4	4	8	53.6	55.3
4	6	8	44.2	42.8
4	7	8	33.4	-31.6
4	8	8	24.9	35.6
4	9	8	59.4	-66.4
4	14	8	29.4	30.8
4	17	8	35.4	-28.0
4	19	8	31.7	-33.2
5	0	8	139.3	-123.5
5	1	8	29.7	-26.5
5	2	8	140.4	-127.3
5	3	8	80.0	-86.1
5	4	8	142.4	-134.0
5	6	8	139.7	-140.1
5	7	8	84.3	97.9
5	8	8	128.9	-141.0
5	9	8	90.0	102.6
5	10	8	69.1	-69.7
6	6	8	53.3	-55.5
6	7	8	35.4	34.1
6	9	8	39.1	36.9
6	10	8	28.7	-25.6
6	11	8	29.4	-24.1
6	12	8	29.7	-29.7
7	0	8	101.2	108.6
7	2	8	100.2	124.5
7	3	8	53.0	59.7
7	4	8	103.2	126.8
7	5	8	52.6	45.6
7	6	8	107.9	106.7
7	7	8	36.7	28.4
7	8	8	97.9	105.2
7	9	8	28.0	27.4
7	10	8	82.0	92.9
7	11	8	51.2	53.7
7	13	8	29.7	47.6
7	15	8	39.1	36.2
7	16	8	25.6	21.8
7	17	8	40.1	38.4
7	18	8	39.8	34.7
7	19	8	33.4	40.1
8	0	8	75.5	72.0
8	1	8	21.9	-22.7
8	2	8	54.6	59.2
8	7	8	26.7	32.1
8	9	8	49.6	50.3
8	10	8	29.4	33.9
8	12	8	29.7	33.8
8	17	8	22.2	31.4
8	19	8	21.5	30.1
9	1	8	40.5	-29.6
9	3	8	103.2	-98.2
9	4	8	35.4	34.0
9	5	8	51.6	-52.4
9	6	8	26.7	19.8
9	7	8	39.1	-38.1
9	8	8	50.6	-59.8
9	10	8	29.7	-37.3
9	11	8	66.8	-64.4
9	12	8	82.3	3.4
9	14	8	48.2	41.8
9	15	8	78.9	-75.1
9	17	8	67.1	-75.2
10	0	8	55.3	56.0
10	2	8	24.9	21.7
10	5	8	26.7	-25.5
10	7	8	40.1	-41.4
10	8	8	29.0	29.1
10	9	8	29.4	-38.6
10	10	8	42.2	35.0
10	17	8	28.0	-22.9
11	0	8	173.4	-185.1
11	1	8	45.2	49.5
11	2	8	121.5	-151.6
11	3	8	60.0	56.6
11	4	8	38.4	-77.1
11	5	8	27.7	23.7
11	6	8	28.3	-23.0

H	K	L	|Fo|	Fc
11	8	8	72.2	-67.4
11	10	8	78.9	-88.0
11	11	8	29.7	36.4
11	12	8	100.5	-97.8
11	13	8	48.2	42.2
11	14	8	64.4	-51.2
11	15	8	34.4	37.9
11	17	8	25.3	24.4
12	0	8	66.8	-76.0
12	2	8	61.8	-65.0
12	4	8	28.3	-27.1
12	6	8	41.1	-38.3
12	8	8	51.6	-55.5
12	10	8	41.8	-42.7
12	12	8	28.3	-29.5
13	0	8	69.5	74.6
13	2	8	75.5	86.1
13	4	8	82.3	108.0
13	6	8	78.6	89.3
13	7	8	42.2	49.7
13	8	8	66.8	64.9
13	9	8	51.2	44.8
13	10	8	58.7	44.6
13	11	8	40.1	37.6
13	12	8	38.7	37.3
13	13	8	36.4	32.5
13	14	8	47.6	45.3
13	15	8	36.7	37.0
13	16	8	35.7	26.6
13	17	8	26.3	30.6
14	0	8	29.0	-28.7
14	1	8	29.0	-37.2
14	4	8	51.2	49.9
14	6	8	42.2	42.5
14	7	8	29.7	33.7
14	9	8	50.6	45.9
14	11	8	39.1	28.0
15	0	8	51.2	47.4
15	1	8	51.2	47.5
15	3	8	42.2	27.6
15	7	8	78.3	-79.8
15	9	8	110.7	-97.5
15	11	8	74.8	-60.3
15	13	8	50.9	-45.3
15	15	8	37.4	-35.9
16	0	8	59.7	55.2
16	2	8	42.2	35.6
16	9	8	27.3	-28.9
16	10	8	26.3	40.4
16	13	8	29.4	-22.0
17	0	8	84.0	-86.2
17	2	8	78.3	-89.0
17	4	8	82.7	-89.0
17	6	8	80.6	-84.8
17	0	8	81.3	-86.2
17	9	8	51.9	39.9
17	10	8	34.7	-27.2
17	12	8	36.1	-32.7
17	14	8	31.0	-33.1
18	4	8	48.9	-45.7
18	6	8	54.6	-43.6
18	8	8	44.2	-33.3
19	0	8	83.6	69.4
19	2	8	67.8	68.7
19	3	8	47.2	48.2
19	4	8	76.3	66.8
19	5	8	37.1	33.8
19	6	8	57.3	45.1
19	8	8	46.9	38.6
19	9	8	35.1	30.4
19	10	8	35.4	32.7
19	12	8	28.0	24.7
20	3	8	25.6	35.0
20	5	8	24.2	24.2
20	11	8	18.2	26.3
21	1	8	34.1	-27.6
21	3	8	73.9	-81.7
21	5	8	53.9	-46.8
21	6	8	20.9	28.0
22	3	8	35.7	-20.2
23	0	8	62.4	-68.7
23	2	8	50.2	-61.0
23	3	8	22.2	23.8
23	4	8	39.8	-42.6
23	6	8	48.9	-50.2
0	2	9	60.1	79.7
0	4	9	70.2	53.7
0	6	9	35.4	36.3
0	10	9	37.3	26.6
0	12	9	55.8	60.3
0	14	9	95.9	113.1
0	16	9	66.4	55.8
1	1	9	47.9	69.7
1	2	9	24.1	17.7
1	3	9	75.4	76.1
1	5	9	49.3	58.0
1	6	9	54.2	-62.6
1	7	9	44.6	41.1
1	8	9	67.5	-87.7
1	9	9	35.7	35.5
1	10	9	70.2	-72.7
1	11	9	38.7	33.8
1	12	9	48.6	-33.7
1	13	9	28.1	20.8
1	14	9	73.5	-80.1
1	16	9	55.8	-58.4
1	18	9	34.4	-31.4
2	1	9	48.6	61.4
2	2	9	35.1	23.2
2	3	9	85.0	74.8
2	4	9	29.7	22.3
2	5	9	89.7	97.3
2	6	9	36.0	31.0
2	7	9	59.6	74.4

H	K	L	|Fo|	Fc
2	8	9	63.8	-77.6
2	9	9	36.0	43.1
2	10	9	37.7	-35.9
2	13	9	28.1	23.5
2	15	9	26.4	32.4
3	1	9	126.4	-122.3
3	2	9	121.0	-111.6
3	3	9	157.8	-167.6
3	4	9	76.4	-80.9
3	5	9	100.6	-98.3
3	6	9	37.1	31.3
3	7	9	97.5	-100.1
3	8	9	64.5	73.5
3	9	9	63.2	-59.5
3	11	9	67.8	-78.3
3	12	9	28.1	-35.7
3	13	9	39.7	-39.6
3	15	9	37.3	-36.7
4	1	9	67.1	-68.3
4	2	9	71.1	-61.5
4	3	9	121.7	-108.3
4	4	9	46.7	-43.2
4	5	9	87.0	-97.2
4	6	9	21.8	14.3
4	7	9	62.2	-74.3
4	9	9	45.0	-40.7
4	11	9	39.3	-44.2
4	12	9	68.8	-74.5
4	13	9	27.8	-24.6
4	14	9	47.3	-44.0
5	1	9	77.1	64.6
5	2	9	75.7	77.8
5	3	9	80.0	80.2
5	4	9	77.7	72.0
5	5	9	42.7	38.8
5	6	9	22.5	19.5
5	7	9	24.1	18.4
5	8	9	25.1	25.8
5	9	9	26.4	19.8
5	10	9	61.2	57.4
5	11	9	55.8	52.1
5	12	9	69.1	72.9
5	13	9	55.8	52.1
5	14	9	66.4	71.6
5	16	9	47.9	43.8
5	18	9	44.3	52.4
6	1	9	42.0	36.7
6	2	9	38.7	31.2
6	5	9	54.9	-52.7
6	6	9	40.6	36.1
6	7	9	42.9	-37.4
6	8	9	63.5	68.6
6	10	9	73.1	89.5
6	11	9	28.1	38.1
6	12	9	39.7	45.8
6	14	9	38.0	39.9
6	16	9	40.3	38.8
6	18	9	34.0	39.7
7	1	9	40.6	40.0
7	2	9	80.7	-87.9
7	3	9	48.3	44.9
7	4	9	59.2	-72.8
7	5	9	99.2	98.8
7	7	9	114.1	117.0
7	9	9	54.6	61.7
7	10	9	48.3	-54.8
7	12	9	39.7	-44.2
7	14	9	64.8	-61.4
7	16	9	60.1	-46.7
7	17	9	34.4	38.6
7	18	9	45.0	-56.3
8	1	9	107.1	108.9
8	3	9	75.7	74.7
8	5	9	88.0	89.3
8	7	9	52.3	54.5
8	9	9	61.8	68.0
8	11	9	39.7	39.9
9	1	9	104.2	-135.7
9	2	9	91.3	105.1
9	3	9	96.3	-107.3
9	4	9	60.5	57.0
9	5	9	71.8	-58.1
9	6	9	45.3	-44.0
9	7	9	97.0	-91.6
9	8	9	47.6	-55.6
9	9	9	92.6	-97.7
9	10	9	28.1	-31.6
9	11	9	74.1	-80.7
10	1	9	88.6	-90.8
10	3	9	35.7	-36.8
10	6	9	53.6	-50.1
10	7	9	47.3	-50.6
10	8	9	48.3	-53.0
10	9	9	68.8	-69.0
10	11	9	62.2	-56.3
10	16	9	33.7	-33.7
11	1	9	57.5	51.0
11	3	9	26.1	28.8
11	6	9	27.4	34.7
11	7	9	27.8	34.8
11	8	9	74.4	87.5
11	9	9	56.3	59.4
11	10	9	68.5	67.6
11	11	9	27.4	24.5
11	12	9	46.0	47.5
11	14	9	40.3	37.3
11	16	9	40.3	43.6
11	17	9	26.1	28.2
12	1	9	53.2	-53.0
12	3	9	27.1	-23.2
12	6	9	55.8	52.6
12	8	9	39.7	45.7
12	10	9	27.4	24.9
12	13	9	24.1	-25.9

H	K	L	|Fo|	Fc
12	14	9	31.1	26.1
12	16	9	42.4	49.5
13	1	9	61.5	66.1
13	2	9	27.4	23.5
13	3	9	67.8	74.9
13	5	9	48.6	53.7
13	6	9	39.7	-34.7
13	8	9	62.5	-56.6
13	10	9	53.9	-45.4
13	11	9	57.9	46.7
13	12	9	42.7	-26.3
13	13	9	64.8	59.5
13	14	9	35.7	-33.9
13	15	9	17.5	19.0
13	16	9	18.2	-27.9
14	9	9	46.7	48.5
14	11	9	70.2	53.3
14	13	9	37.1	38.7
15	1	9	69.1	-80.0
15	3	9	62.8	-80.2
15	5	9	62.5	-74.4
15	7	9	54.6	-53.8
15	9	9	25.8	-24.4
15	11	9	40.6	-37.7
15	13	9	54.9	-63.2
15	15	9	20.5	-31.6
16	3	9	62.2	-59.9
16	5	9	72.4	-70.5
16	7	9	37.3	-37.4
16	9	9	42.7	3.4
16	13	9	29.5	-30.3
17	3	9	60.5	48.0
17	5	9	37.3	40.3
17	6	9	51.9	43.3
17	8	9	54.2	41.9
17	10	9	30.4	25.6
17	12	9	42.0	37.2
17	13	9	32.4	40.7
18	6	9	42.4	25.8
18	12	9	111.1	46.6
19	5	9	52.3	41.7
19	7	9	64.8	60.6
19	9	9	41.3	39.0
20	1	9	46.2	45.6
20	3	9	39.0	36.3
20	4	9	21.8	-20.8
20	5	9	51.9	55.7
20	7	9	38.0	37.0
20	9	9	25.8	32.2
21	1	9	50.9	-44.2
21	3	9	56.8	-48.8
21	5	9	52.3	-53.9
21	7	9	46.2	-59.1
22	2	9	24.5	-25.1
22	4	9	35.4	-37.2
22	6	9	20.8	-7.1
23	3	9	17.8	4.3
0	2	10	101.1	117.2
0	4	10	136.0	130.3
0	6	10	112.6	113.4
0	8	10	26.0	24.1
0	10	10	49.1	45.4
0	12	10	58.4	54.8
0	14	10	74.0	66.7
1	0	10	55.9	-73.7
1	1	10	31.4	-47.8
[illegible]	[illegible]	10	86.0	-97.2
1	3	10	85.5	-96.1
1	4	10	96.4	-98.1
1	6	10	50.6	-55.0
1	10	10	28.1	-36.8
1	11	10	40.7	-28.6
1	12	10	65.3	-61.7
1	13	10	49.8	-52.1
1	14	10	55.9	-46.7
1	15	10	45.9	-38.9
1	17	10	21.3	-18.5
2	0	10	31.4	-34.7
2	1	10	52.7	-64.6
2	3	10	88.1	-80.5
2	4	10	63.2	-56.5
2	5	10	42.2	-47.7
2	6	10	39.7	-35.8
2	11	10	58.1	-59.7
2	12	10	29.2	-31.9
2	13	10	81.5	-84.5
2	14	10	39.3	-35.0
2	15	10	52.7	-62.6
2	16	10	24.2	-20.1
2	17	10	30.0	-27.3
3	0	10	45.9	52.4
3	1	10	30.0	35.4
3	2	10	23.1	14.5
3	4	10	44.4	-44.4
3	5	10	21.7	19.5
3	6	10	46.9	-49.5
3	7	10	50.2	48.1
3	9	10	55.2	59.3
3	11	10	58.1	43.8
3	13	10	40.5	39.9
3	15	10	52.3	52.7
3	16	10	23.8	-11.5
3	17	10	36.1	29.7
4	2	10	51.2	-43.8
4	3	10	43.3	-25.8
4	4	10	89.1	-77.4
4	6	10	80.1	-85.3
4	7	10	67.9	71.2
4	8	10	59.9	-61.2
4	9	10	55.9	62.0
4	15	10	44.8	39.9
4	17	10	45.9	47.5
4	18	10	15.5	-25.2
5	0	10	49.8	49.4

H	K	L	|Fo|	Fc
5	1	10	32.9	25.7
5	2	10	44.4	29.2
5	3	10	46.5	44.2
5	4	10	94.2	77.6
5	6	10	108.6	105.2
5	7	10	58.4	-58.6
5	8	10	90.6	85.3
5	9	10	49.1	-53.6
5	10	10	28.9	31.8
5	18	10	14.4	29.9
6	0	10	107.2	107.1
6	2	10	83.0	80.9
6	3	10	31.4	25.8
6	4	10	93.5	71.8
6	5	10	24.5	-5.7
6	6	10	99.6	89.2
6	7	10	26.7	-25.6
6	8	10	73.7	78.1
6	10	10	71.1	79.1
6	18	10	17.7	24.0
7	0	10	49.8	-38.3
7	2	10	51.2	-56.2
7	3	10	23.4	-24.2
7	4	10	54.9	-46.8
7	5	10	25.2	-26.8
7	6	10	65.0	-71.0
7	7	10	63.2	-21.7
7	10	10	58.4	-57.2
7	17	10	24.9	-30.8
8	0	10	124.2	-122.9
8	2	10	59.5	-73.3
8	5	10	26.3	-25.1
8	7	10	27.7	-37.4
8	8	10	28.5	-31.0
8	9	10	58.2	-52.4
8	10	10	65.3	-75.1
8	11	10	28.9	-46.6
8	12	10	28.1	-34.4
8	13	10	27.1	-33.9
8	15	10	40.5	-35.6
8	17	10	35.7	-44.2
9	0	10	25.2	-29.6
9	9	10	41.1	51.0
9	11	10	28.5	34.7
9	15	10	49.8	39.8
9	17	10	32.9	49.4
10	0	10	53.1	-51.0
10	1	10	46.2	44.4
10	2	10	46.5	-46.6
10	3	10	38.2	40.4
10	4	10	27.4	-42.0
10	5	10	28.1	32.6
10	6	10	28.5	-34.7
10	7	10	28.9	35.6
10	8	10	29.2	-33.2
10	11	10	39.7	36.6
10	12	10	38.2	-33.7
10	13	10	51.2	40.2
10	14	10	33.2	-26.6
10	15	10	51.2	48.3
11	2	10	73.7	71.8
11	4	10	56.6	61.5
11	10	10	63.6	58.1
11	12	10	64.2	56.4
11	14	10	38.6	34.4
12	0	10	113.7	127.3
12	2	10	106.9	103.7
12	3	10	28.5	-42.3
12	4	10	57.8	65.6
12	6	10	41.1	36.7
12	7	10	29.2	30.9
12	8	10	50.2	48.7
12	10	10	78.7	74.1
12	12	10	56.3	52.0
12	14	10	20.5	21.2
13	0	10	64.6	-68.6
13	2	10	71.1	-69.6
13	4	10	58.4	-48.6
13	6	10	50.6	-48.8
13	8	10	40.1	-26.8
14	4	10	50.6	-51.3
14	6	10	40.5	-51.2
14	7	10	63.2	-64.2
14	9	10	71.1	-68.3
14	11	10	41.9	-38.8
15	7	10	47.7	53.6
15	9	10	50.8	39.3
15	11	10	44.8	43.5
16	0	10	40.5	-50.0
16	2	10	28.1	-40.7
16	4	10	39.3	-39.6
16	6	10	46.5	-42.8
16	8	10	35.7	-39.1
16	10	10	31.4	-27.0
16	11	10	35.0	34.2
17	0	10	67.5	70.9
17	2	10	27.4	35.6
17	4	10	46.2	45.9
17	6	10	50.8	44.6
17	8	10	40.5	48.2
17	10	10	34.6	31.5
18	2	10	52.0	45.6
18	4	10	66.7	70.2
18	8	10	42.2	42.6
19	2	10	33.9	-31.5
19	4	10	40.1	-38.2
19	6	10	36.8	-34.4
19	8	10	18.0	-20.5
20	3	10	36.8	-41.3
20	5	10	19.5	-24.1
21	3	10	50.6	51.9
21	6	10	12.6	-11.1
22	3	10	16.2	23.3

END.

(e.g. $[PN(NMe_3)_2]_4$) where π-bonding has been established P-N bond lengths of the order 1.65-1.75Å have been measured (Paddock, 1962).

A four-membered ring is formed by PNP and Pd which are approximately coplanar (Table 10). Angles of the ring sum up to 360°. The P-P distance is about 2.6Å. This is rather short compared with the sum of van der Waals radii. Some overlap of d-orbitals is not impossible. Around each phosphorus atom, the average valency angle is approximately 109.5°. The individual angle however ranges from about 95° to 120° (individual e.s.d. is about 0.8°). It is not surprising that the angles at phosphorus deviate from the tetrahedral arrangement as the nature and size of the groups attached to the phosphorus atoms will cause some strain to be introduced.

The average length of the aromatic carbon-carbon bonds in the four benzene rings involved is 1.398±0.006Å. This value is in good agreement with the accepted values of 1.397Å (Sutton et al, 1958), the average angles of the benzene rings is about 120°. The mean P-C aryl is 1.81±0.01Å. Comparison of the individual values of P-C aryl bond lengths with those recorded by other workers such as J.J. Daly, Sartell and Brockway, Erlich, and Owston, etc., are summarised in Table 33.

PART II

X-RAY STRUCTURE ANALYSIS OF ETHYL IODIDE ADDUCT OF BIS-(DIPHENYL-PHOSPHINO)-ETHYLAMINE

2.1. INTRODUCTION

Until recently, few attempts have been made to study in detail the nature of the bonding in the tervalent phosphorus-nitrogen system. The first structure reported in this thesis throws some light on the nature of this bonding. Yet since one of the principal atoms - phosphorus - exhibits more than one co-ordination, it would be instructive to study some other complexes of the ligand - bis(diphenyl phosphino)ethylamine. Therefore we undertook the study of the ethyl iodide adduct of the ligand, the formula of which can be written as - $[(C_6H_5)_2P.N.(C_2H_5)P(C_6H_5)_2C_2H_5]^+I^-$.

The differing electronic configuration of the two principal atoms involved, (P and N), should help in understanding the type of bonding one is likely to encounter in such PNP systems. The electronic configuration of phosphorus, $(1s)^2$ $(2s)^2$ $(2p)^6$ $(3s)^2$ $(3p)^3$ suggests the possibility of bonding with such orbitals as p, sp^3 or sp^2 when phosphorus is involved in three or four co-ordination to other atoms. Hence, one would expect in the resultant compounds, bond angles ranging from 90° through 109°28' to 120°. The exact values however depend on several other factors: the steric requirements, the bond pair - bond pair repulsion, the electro-negativity and the number of the substituent groups. Nitrogen with electronic configuration $1s^2$ $2s^2$ $2p^3$ is capable of forming sp^2 hybrids, so that when involved in bonding, the angles should tend towards 120°. However, it is more usual to find angles close to the tetrahedral - 109°, in which sp^3 hybridisation can be postulated. The formation of σ-bonds between phosphorus and nitrogen, which is considered to be sp^2 hybridised, and two σ-bonds between the same phosphorus and two other substituents gives rise to a situation where both phosphorus and nitrogen possess a lone pair of electrons. This leads to the problem as to which atom would be more capable of donating its lone pair or in other words, which atom has the greater base strength.

Considering the electronegativities of the two principal atoms (P and N), nitrogen with an electronegativity of 3. (Pauling, Huggins, 1953, and Sanderson, 1955), might be expected to be more basic than phosphorus with a value of 2; but, experiments have shown that the reverse is the case. Burg (1958), in the preparation of a 1 : 1 methyl iodide adduct of dimethyl-aminodimethyl-phosphine found that the methyl group was attached to phosphorus, indicating that the greater electron donor bonding power resides on phosphorus. Thus a phosphonium compound was obtained rather than an ammonium.

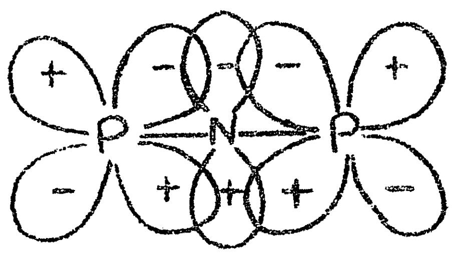
$Me_2P{-}N.Me_2 + MeI \rightarrow (Me_3P{-}N\ Me_2)^+I^-$.

The problem of quaternisation in PNP system might be similar to the above reported by Burg. Theoretically, one might consider the lone pair of electron on nitrogen in the PNP system to be completely delocalised over the whole system via the 3d orbitals : i.e. the p_z orbital containing the lone pair as being suitably positioned to allow an overlap with the diffuse vacant set of 3d orbitals on phosphorus, thus, resulting

resulting in $p_{\pi} = d_{\pi}$ back-bonding.

Such an overlap of orbitals can be shown
resulting in $p_{\pi} = d_{\pi}$ back-bonding.

Such an overlap of orbitals can be shown diagrammatically for a P=N=P system:



N.B. this diagram is not intended to convey an idea of a co-linear structure for the P=N=P skeleton.

Another problem which makes the P=N=P compounds different from some other phosphines is the question of how many phosphorus centres are involved in quarternisation. In compounds containing P-CH_2-P, the two phosphorus atoms have been reported quarternised, (Hewartson et al, 1962); but, the molecular weight determination as well as the n.m.r. studies (Payne et al, 1964) on P=N=P compounds point to the fact that only one of the two phosphorus atoms is involved in quarternisation.

Of late, there has been varied opinions on whether or not the bond in P-C(aryl)is affected by the conjugation in the benzene ring. Since this structure involves the two types of bonds, the P-C(aryl)and P-C(alkyl), it is of interest to compare the bond-lengths to see whether there is shortening of bond in P-C(aryl)which will in effect suggest that phosphorus interacts with the -bonding in the benzene ring to which it is attached.

2.2. CRYSTAL DATA
2.2. CRYSTAL DATA

The crystals of the ethyl-iodide adduct of bis-(diphenyl phosphino)-ethylamine were prepared as described in Part V of this thesis. The compound gave white needle-like crystals which were found suitable for X-Ray work after slow recrystallisation in nitromethane. The crystals of formula $[(C_6H_5)_2C_2H_5P.N.(C_2H_5).P(C_6H_5)_2]^+I^-$ (mol. wt. 569·1) are orthorhombic with $\underline{a}$ = 13·90 ± 0·03, $\underline{b}$ = 21·22 ± 0·05, $\underline{c}$ = 10·04 ± 0·03 Å; volume of unit cell, V = 2961·4 Å^3; measured density, ρ_m = 1·32 gm/cc (By floatation in KI solution); calculated density, ρ_c = 1·29 gm/cc - for 4 molecules per unit cell, F(000) = 1152, $\sum f_I^2$ = 2809 while $\sum f_{Rest}^2$ = 1537. The linear absorption coefficient for X-Rays (λ = 1·542 Å). μ = 166 cm^{-1}, M. Pt. = 157 ± 1°C.

2.3. SPACE GROUP DETERMINATION

Rotation, oscillation and moving-film photographic methods were used and Cu-Kα (λ = 1·542 Å) radiation was employed. The cell dimensions were determined from rotation and equitorial layer-line Weissenberg photographs. The space group was uniquely determined from the systematic halvings.

h00 absent when h = 2n + 1,

0k0 absent when k = 2n + 1,

00l absent when l = 2n + 1.

These conditions are satisfied by $P2_12_12_1$ (D_2^4, No. 19) space group. The multiple film technique, (Robertson, 1943), was employed.

2.4. INTENSITY DATA

Intensity data were obtained visually from the equitorial and equi-inclination upper-layer Weissenberg photographs taken from crystals rotated about the needle-axis (c-crystal axis). Small crystals of approximately square cross-section (0·020 x 0·021 cm^2) were used. No correction was made for absorption or spot shape, but the usual corrections were applied. The various layers hk0-hk6 were placed on the same scale by comparison of $\sum|F_o|$ and $\sum|F_c|$, and the scale obtained was adjusted to approach unity throughout the processes of structure-factor calculations.

2.5. STRUCTURE DETERMINATION

The position of the iodide ion was obtained from the Patterson projection $P(U,V)$, Fig. 1; and, from a three-dimensional Patterson function.

For an orthorhombic crystal, the expression for the Patterson function P(UVW) can be written as:-

$$P(UVW) = \frac{8}{V_c} \sum\sum\sum|F_{hkl}|^2 \cos 2\pi hU \cos 2\pi kV \cos 2\pi lW$$

Prior to each computation the coefficient $|F_{hkl}|^2$ in the above expression was modified by

$$MS = [\hat{f} \exp(B\sin^2\theta/\lambda^2)]^{-2}$$

The I.....I vectors to be expected in the space group $P2_12_12_1$, with one molecule/asymmetric unit, are shown in Table 12. The x and y co-ordinates of the iodide ion were obtained from the Patterson projection, while the Harker sections at U = ½, V = ½ and W = ½ on a 3-D Patterson map gave the co-ordinates x, y and z.

The peaks corresponding to the I.....I vectors are denoted

TABLE 12.

$P2_12_12_1$ - INTER-ATOMIC VECTORS.

ATOMIC POSITIONS	x, y, z	½-x, -y, ½+z	½+x, ½-y, -z	-x, ½+y, ½-z
x, y, z	-	½+2x, 2y, ½	½, ½+2y, 2z	2x, ½, ½+2z
½-x, -y, ½+z	½-2x, -2y, ½	-	-2x, ½, ½+2z	½, ½-2y, 2z
½+x, ½-y, -z	½, ½-2y, -2z	2x, ½, ½-2z	-	½+2x, -2y, ½
-x, ½+y, ½-z	-2x, ½, ½-2z	½, ½+2y, -2z	½-2x, 2y, ½	-

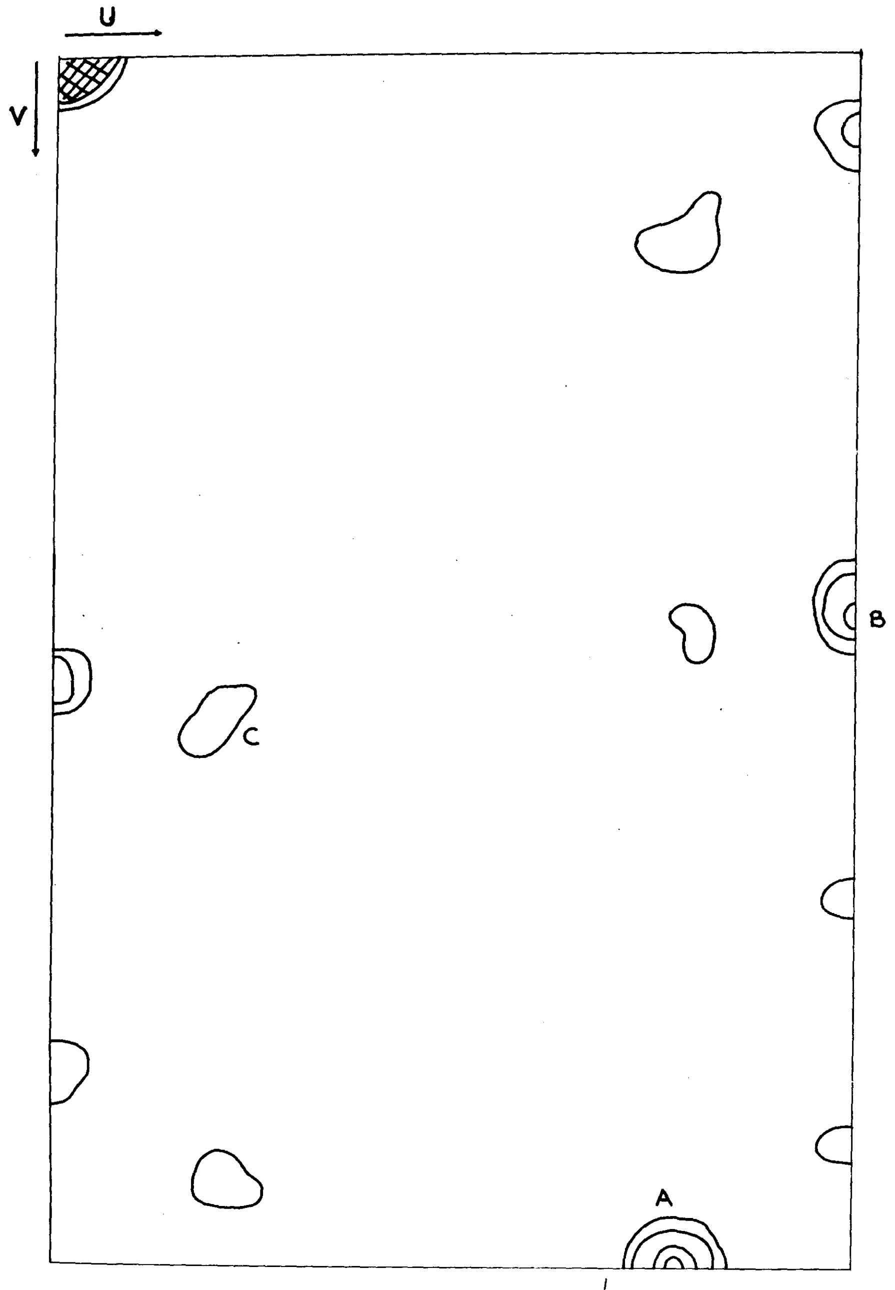


Fig. 1 Sharpened Patterson Projection P (U,V)

Contour scale equally arbitrary.

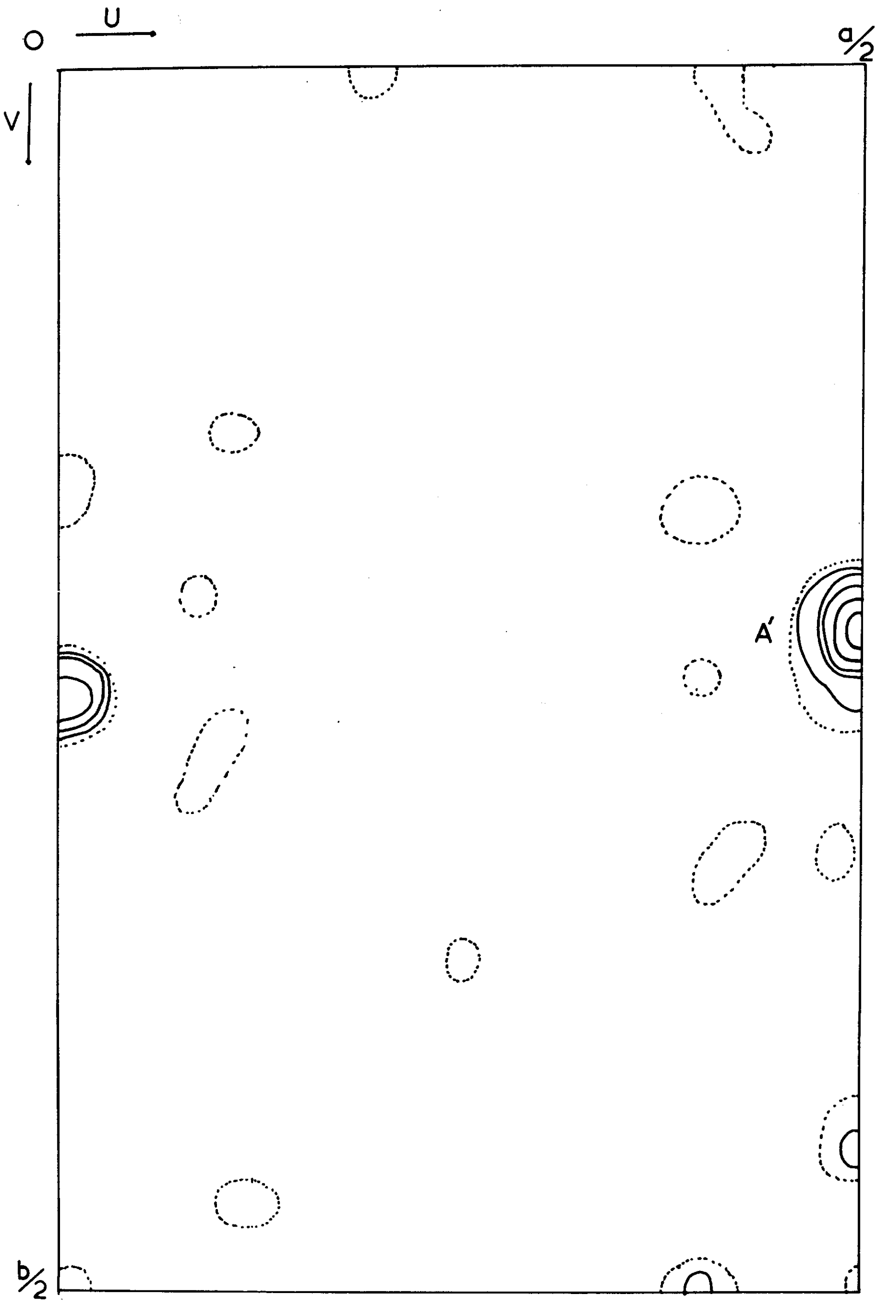


Fig 2. 3-D Sharpened Patterson Synthesis. Section to show I-I vector on P(½, V, W).
Contour scale equally arbitrary. 0 Å

by A^1, B^1 and C^1 in Figs. 2, 3 and 4. The co-ordinates determined from these are

$x/a = 0{\cdot}193$, $y/b = 0{\cdot}195$, $z/c = 0{\cdot}163$.

Structure Factors calculated for I^- alone with temperature factor, $B = 3{\cdot}3\ \mathring{A}^2$, gave an R-value of 39%. The first three-dimensional Fourier synthesis, for which the observed structure amplitudes and phase angles calculated for the iodide ion alone were employed, enabled approximate co-ordinates to be assigned to P(1), P(2) and nitrogen. These atoms were included in the next structure-factor calculations, with B = 4·1 for the phosphorus atoms and B = 4·5 for the nitrogen. The value of R diminished to 33·4%.

The second Fourier synthesis was computed with the improved phase constants in conjunction with the observed structure amplitudes as coefficients, the map obtained revealed almost the whole structure, apart from the ethyl group of the iodide ion. Thus, in the subsequent structure-factor calculations 30 atoms out of the 32 atoms (non-hydrogen) were included and the value of B = 4·7 was used for carbon atoms. R was 24·4%.

The subsequent three-dimensional Fourier synthesis showed all the atoms (except hydrogen). Calculation of a further set of structure factors, with each atom included as its appropriate chemical type yielded an agreement factor of 22·3%. During the course of refinement, however, two carbon atoms (the ethyl radical of the iodide ion), were discovered to have been badly positioned from the result of the previous Fourier synthesis. This error was later discovered to be due to diffraction ripples created on P(2) along the c-axis about

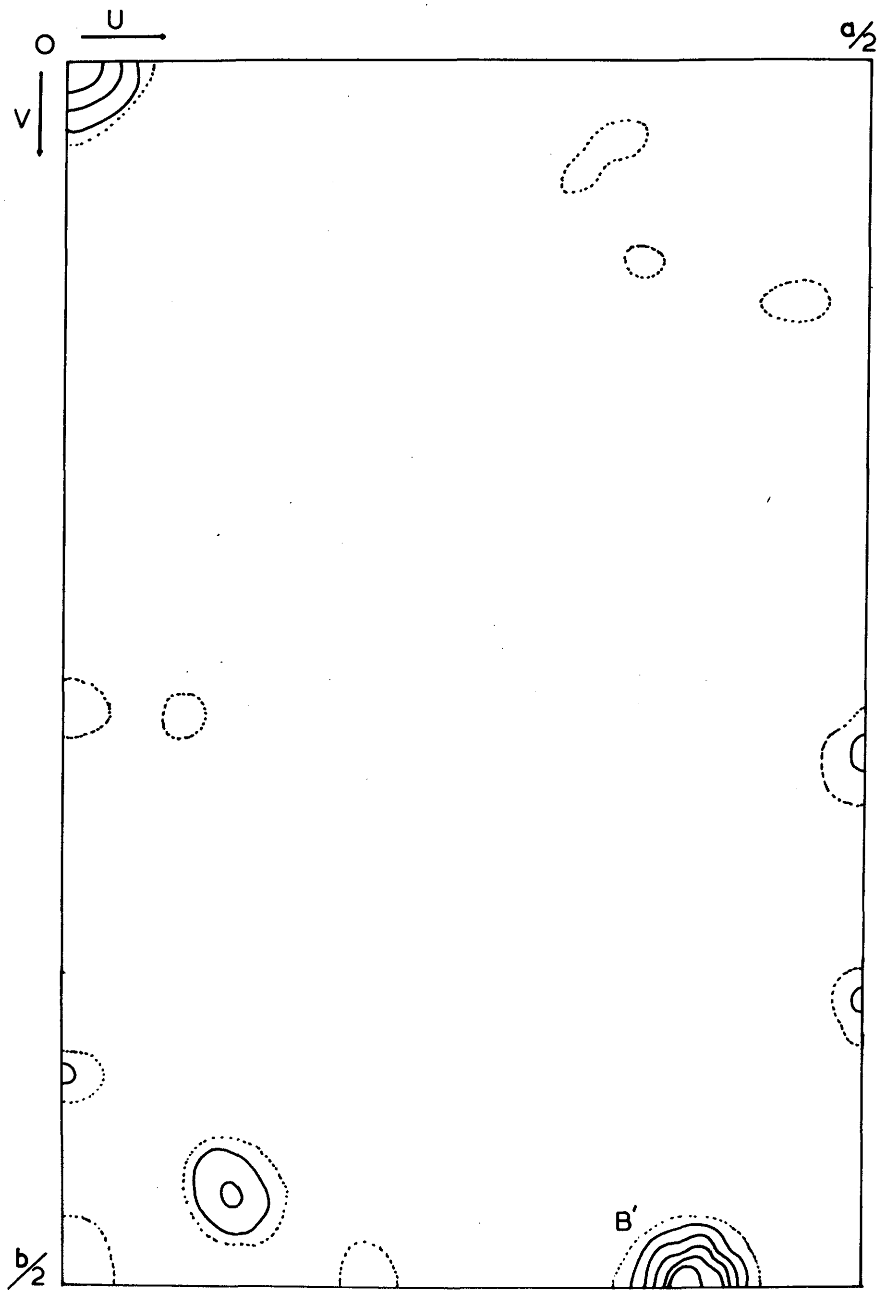


Fig 3. 3-D Patterson synthesis (sharpened). Section P(U, ½, W)

Contours at equal arbitrary intervals.

0 1 Å

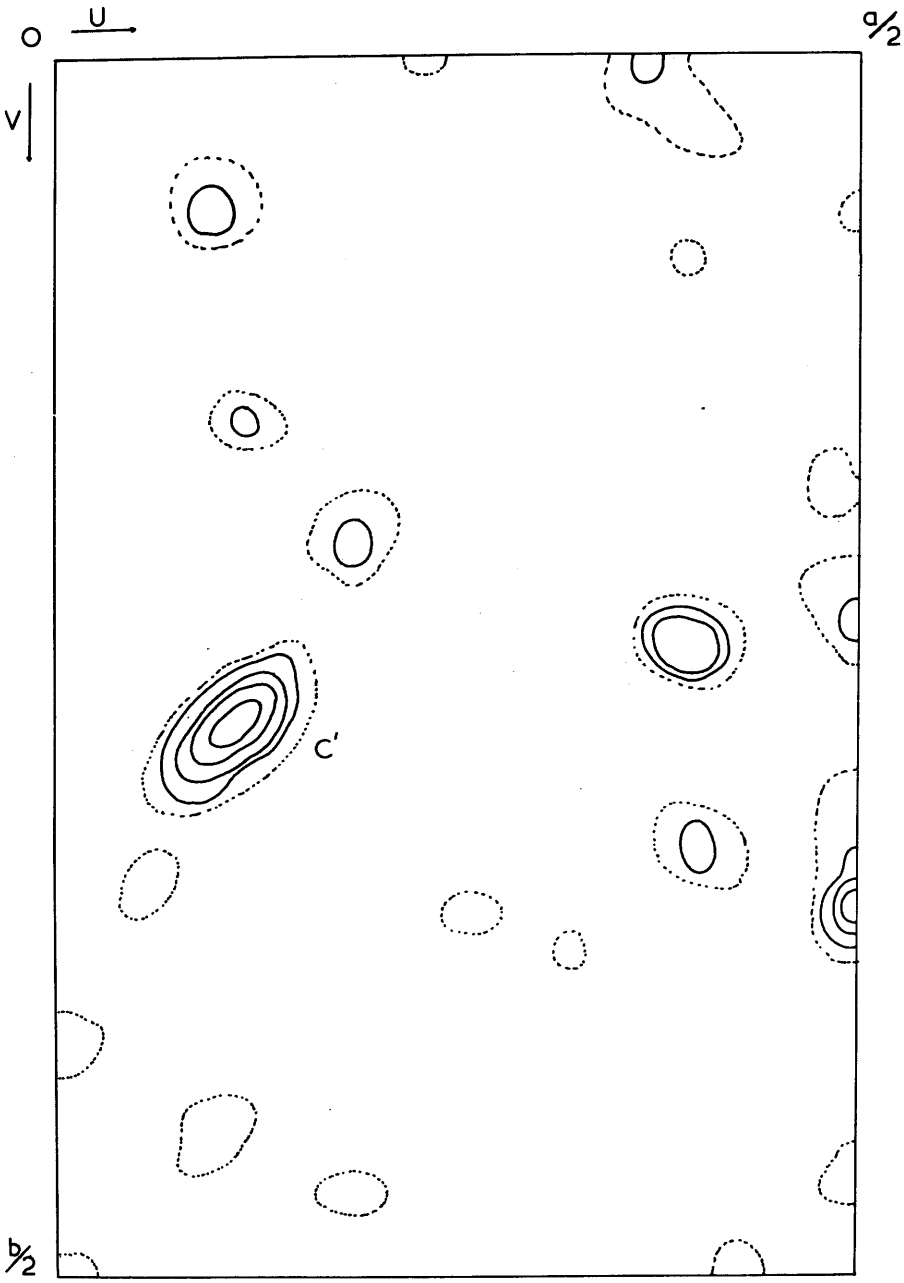


Fig 4. 3-D Sharpened Patterson synthesis. Section P(U,V,½).

Contours at equal arbitrary intervals.

which data were collected. The problem was solved by computing a difference Fourier synthesis in the region of the P(2) with structure-factor data calculated without the two carbon atoms inquestion. From the map obtained, the two atoms were located fairly accurately.

2.6. STRUCTURE REFINEMENT

Refinement was by the Least-squares method as described earlier in this thesis. Anisotropic temperature factors were assigned to iodine and phosphorus, while the temperature factors of the rest remain isotropic.

The weighting scheme used was -

$$\sqrt{w} = 1/[p_1 + |F_o| + p_2 |F_o|^2 + p_3|F_o|^3]^{\frac{1}{2}}$$

where $p_1 = 2 \times F$ min, $p_2 = 2\ F_o$ max., $p_3 = 0$. (Cruickshank's).

For most part of the refinement, the shift factor used were in the order 0·8, 0·9, 0·7 and 1·26. Convergence was attained after ten cycles of least-squares. The final value of R, excluding unobserved reflections was 13·0%. The course of the whole analysis is shown in Table 13. For the structure-factor calculations throughout, theoretical atomic scattering factors were used: those of Berghuis et al. (1955) for carbon and nitrogen, and the Thomas-Fermi values (1935) for phosphorus and iodine were chosen.

2.7. RESULTS

The final values of $|F_o|$, F_c, A_c and B_c are given in Table 14. The final positional parameters are listed in Table 15 while the corresponding standard deviations occupy Table 16.

TABLE 13.

COURSE OF ANALYSIS.

118 Reflections for the Patterson projection P(UV).

1221 " " " 3-D Patterson synthesis.

Found I^-

1st. Structure-factor calculations, $B_{I^-} = 3.3Å^2$

R = 39.0%

1100 Reflections for the 1st. 3-D Fourier synthesis.

Found I^- + 2P + N

2nd. Structure-factor calculations, $B_P = 4.1$, $B_N = 4.5Å^2$

R = 33.4%

1221 Reflections for the 2nd. 3-D Fourier synthesis.

Found I^- + 2P + 26C + N

3rd. Structure-factor calculations, $B_C = 4.7Å^2$

R = 24.4%

1221 Reflections for the 3rd. 3-D Fourier synthesis.

Found All the 32 atoms (non-hydrogen).

4th. Structure-factor calculations, temp. factors remain same.

R = 22.3%

1st. Cycle of S.F.L.S. Refinement, B_{I^-}, BP, (anisotropic).

R = 17.75%

2nd. Cycle of S.F.L.S. Refinement,

R = 16.60%

3rd. Cycle of S.F.L.S. Refinement,

R = 15.70%

- Cont'd -

TABLE 13. - Cont'd -

COURSE OF ANALYSIS.

4th. Cycle of S.F.L.S. Refinement,

R = 14.54%

5th. Cycle of S.F.L.S. Refinement, (Only 30 atoms included here).

R = 13.79%

6th. Cycle of S.F.L.S. Refinement,

R = 13.41%

7th. Cycle of S.F.L.S. Refinement, (All 32 atoms included).

R = 13.24%

8th. Cycle of S.F.L.S. Refinement,

R = 13.11%

9th. Cycle of S.F.L.S. Refinement,

R = 13.06%

10th. Cycle of S.F.L.S. Refinement, (Final data scaling).

Final R = 13.00%

TABLE 14.

H	K	L	|Fo|	|Fc|	Ac	Bc
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

TABLE 15.

FRACTIONAL ATOMIC COORDINATES.

ATOMS	(x/a)	(y/b)	(z/c)
I	0.6962	0.3638	-0.1660
P(1)	0.6983	0.1038	0.1208
P(2)	0.8097	0.2124	0.2323
N	0.6954	0.1875	0.1615
C(1)	0.6065	0.2273	0.1992
C(2)	0.5590	0.2215	0.3400
C(3)	0.7870	0.3444	0.1577
C(4)	0.7806	0.4121	0.2151
C(5)	0.7783	0.4270	0.3448
C(6)	0.7905	0.3878	0.4304
C(7)	0.8043	0.3115	0.4239
C(8)	0.8002	0.2963	0.2968
C(9)	0.6371	0.1088	-0.0296
C(10)	0.6319	0.1704	-0.1222
C(11)	0.5937	0.1681	-0.2591
C(12)	0.5535	0.1099	-0.3047
C(13)	0.5475	0.0628	-0.2285
C(14)	0.5893	0.0520	-0.1081
C(15)	0.8590	0.1686	0.3656
C(16)	0.9573	0.1535	0.3731

- Cont'd -

TABLE 15 -Cont'd-

FRACTIONAL ATOMIC COORDINATES.

ATOMS	(x/a)	(y/b)	(z/c)
C(17)	0.9971	0.1251	0.4973
C(18)	0.9373	0.1090	0.6055
C(19)	0.8250	0.1143	0.6038
C(20)	0.7932	0.1489	0.4815
C(21)	0.4972	0.0664	0.2037
C(22)	0.6078	0.0651	0.2221
C(23)	0.6451	0.0292	0.3427
C(24)	0.5804	-0.0047	0.4308
C(25)	0.4735	-0.0044	0.4042
C(26)	0.4389	0.0326	0.2991
C(27)	0.8989	0.2083	0.0978
C(28)	0.8995	0.1852	-0.0252

TABLE 16.

STANDARD DEVIATIONS IN ATOMIC COORDINATES (in Å)

ATOMS	σ(x)	σ(y)	σ(z)
I	0.003	0.003	0.004
P(1)	0.008	0.008	0.010
P(2)	0.009	0.009	0.012
N	0.030	0.027	0.035
C(1)	0.032	0.033	0.042
C(2)	0.035	0.036	0.047
C(3)	0.042	0.056	0.050
C(4)	0.041	0.041	0.047
C(5)	0.038	0.039	0.049
C(6)	0.042	0.055	0.050
C(7)	0.042	0.040	0.047
C(8)	0.042	0.039	0.046
C(9)	0.030	0.031	0.040
C(10)	0.037	0.040	0.046
C(11)	0.034	0.036	0.043
C(12)	0.042	0.044	0.052
C(13)	0.042	0.060	0.054
C(14)	0.031	0.031	0.039
C(15)	0.026	0.028	0.038
C(16)	0.043	0.047	0.053

- Cont'd -

The final temperature-factor parameters are recorded in Table 17. Intramolecular bonded distances, intramolecular non-bonded < 6 Å, and intermolecular distances < 4 Å are compiled in Tables 18, 19 and 20. Table 21 lists interbond angles.

2.8. DISCUSSION

The structure of the ethyl-iodide adduct of bis-(diphenyl-phosphine)-ethylamine has been established. The adduct is a phosphonium compound, quarternisation taking place at one P-atom only. Results show that P(1) and P(2) differ significantly in their configuration P(2) is the quaternary phosphorus occupying the centre of a tetrahedron with mean bond angle of about $109\cdot5 \pm 0\cdot71°$. The bonds around P(1) corresponding to a substantially sp^3 hybridised atom have mean bond-angle of $102 \pm 0\cdot70°$ and would seem to involve a large amount of p-character.

The mean P-C (aryl) is $1\cdot81 \pm 0\cdot02$ Å, while P-C (alkyl) is $1\cdot81 \pm 0\cdot05$ Å. These values are within the range recorded in other compounds of this class (Table 33). These values do not suggest any π-bond formation in P-C (aryl). This point is discussed further in the summary (Part IV).

The P(2)-N distances, $1\cdot75 \pm 0\cdot03$ Å, agrees quite well with the value of $1\cdot72$ Å recorded in the previous work but differs significantly from the other P-N distance [P(1)-N] of $1\cdot88 \pm 0\cdot03$ Å. This difference confirms the chemical distinction between the two phosphorus atoms. Since the sum of the single-bond covalent radii ($1\cdot84$ Å) is quite close to

TABLE 17.

FINAL ANISOTROPIC THERMAL PARAMETERS (Uij).

ATOMS						
I	0.073	0.070	0.075	0.045	0.042	0.064
P(1)	0.022	0.028	0.030	-0.003	-0.018	-0.000
P(2)	0.019	0.048	0.042	-0.025	0.015	-0.022

FINAL ISOTROPIC THERMAL PARAMETERS (Uij), (for Nitrogen and Carbon atoms).

N	0.044	C(10)	0.050	C(20)	0.066
C(1)	0.037	C(11)	0.039	C(21)	0.029
C(2)	0.047	C(12)	0.063	C(22)	0.012
C(3)	0.095	C(13)	0.091	C(23)	0.035
C(4)	0.056	C(14)	0.028	C(24)	0.062
C(5)	0.050	C(15)	0.020	C(25)	0.057
C(6)	0.092	C(16)	0.061	C(26)	0.035
C(7)	0.056	C(17)	0.061	C(27)	0.112
C(8)	0.054	C(18)	0.079	C(28)	0.141
C(9)	0.028	C(19)	0.043		

TABLE 12.

Interatomic Bond Lengths in Å, with estimated Standard Deviations.

P(1)	-	N	1.88(0.03)	C(12)	-	C(13)	1.26(0.07)
P(1)	-	C(9)	1.74(0.04)	C(13)	-	C(14)	1.36(0.06)
P(1)	-	C(22)	1.81(0.03)	C(14)	-	C(9)	1.59(0.05)
P(2)	-	N	1.75(0.03)	C(15)	-	C(16)	1.41(0.05)
P(2)	-	C(8)	1.90(0.04)	C(16)	-	C(17)	1.49(0.07)
P(2)	-	C(15)	1.77(0.04)	C(17)	-	C(18)	1.41(0.07)
P(2)	-	C(27)	1.81(0.05)	C(18)	-	C(19)	1.57(0.06)
C(3)	-	C(4)	1.55(0.07)	C(19)	-	C(20)	1.50(0.06)
C(4)	-	C(5)	1.34(0.07)	C(20)	-	C(15)	1.54(0.06)
C(5)	-	C(6)	1.30(0.07)	C(21)	-	C(22)	1.55(0.04)
C(6)	-	C(7)	1.63(0.07)	C(22)	-	C(23)	1.52(0.05)
C(7)	-	C(8)	1.32(0.07)	C(23)	-	C(24)	1.45(0.06)
C(8)	-	C(3)	1.60(0.07)	C(24)	-	C(25)	1.51(0.06)
C(9)	-	C(10)	1.61(0.05)	C(25)	-	C(26)	1.40(0.06)
C(10)	-	C(11)	1.47(0.06)	C(26)	-	C(21)	1.45(0.05)
C(11)	-	C(12)	1.43(0.06)	C(27)	-	C(28)	1.56(0.07)

TABLE 19.

INTRA-MOLECULAR NON-BONDED DISTANCES.

P(1)	...	C(23)	2.84	N	...	C(21)	3.77
P(1)	...	P(2)	2.99	N	...	C(23)	3.77
P(1)	...	C(1)	3.01	N	...	C(7)	3.82
P(1)	...	C(21)	3.02	C(1)	...	C(8)	3.20
P(1)	...	C(27)	3.57	C(1)	...	C(22)	3.45
P(1)	...	C(15)	3.58	C(1)	...	C(3)	3.54
P(1)	...	C(28)	3.60	C(1)	...	C(21)	3.74
P(1)	...	C(2)	3.82	C(1)	...	C(7)	3.93
P(1)	...	C(20)	3.96	C(2)	...	C(22)	3.55
P(2)	...	C(16)	2.77	C(2)	...	C(21)	3.63
P(2)	...	C(7)	2.81	C(2)	...	C(8)	3.73
P(2)	...	C(20)	2.84	C(2)	...	C(20)	3.85
P(2)	...	C(1)	2.86	C(2)	...	C(7)	3.99
P(2)	...	C(3)	2.88	C(3)	...	C(5)	2.54
P(2)	...	C(28)	2.92	C(3)	...	C(7)	2.63
P(2)	...	C(2)	3.65	C(3)	...	C(6)	2.94
N	...	C(2)	2.54	C(3)	...	C(27)	3.33
N	...	C(22)	2.90	C(4)	...	C(6)	2.40
N	...	C(15)	2.90	C(4)	...	C(8)	2.67
N	...	C(8)	2.93	C(4)	...	C(7)	3.01
N	...	C(27)	2.99	C(5)	...	C(7)	2.54
N	...	C(20)	3.34	C(5)	...	C(8)	2.81
N	...	C(28)	3.53	C(6)	...	C(8)	2.42
N	...	C(3)	3.55	C(7)	...	C(15)	3.16

- Cont'd -

TABLE 19 -Cont'd-

INTRA-MOLECULAR NON-BONDED DISTANCES.

C(7)	...	C(20)	3.50	C(12)	...	C(19)	3.92
C(7)	...	C(16)	3.98	C(15)	...	C(27)	2.89
C(8)	...	C(15)	2.91	C(15)	...	C(28)	3.99
C(8)	...	C(27)	3.06	C(16)	...	C(20)	2.54
C(8)	...	C(20)	3.62	C(16)	...	C(27)	3.09
C(8)	...	C(16)	3.80	C(20)	...	C(23)	3.55
C(9)	...	C(13)	2.52	C(21)	...	C(25)	2.56
C(9)	...	C(11)	2.67	C(21)	...	C(23)	2.58
C(9)	...	C(12)	2.99	C(21)	...	C(24)	2.95
C(10)	...	C(12)	2.51	C(22)	...	C(26)	2.56
C(10)	...	C(14)	2.55	C(22)	...	C(24)	2.58
C(10)	...	C(13)	2.79	C(22)	...	C(25)	3.01
C(11)	...	C(13)	2.37	C(23)	...	C(25)	2.57
C(11)	...	C(14)	2.88	C(23)	...	C(26)	2.89
C(11)	...	C(19)	3.70	C(24)	...	C(26)	2.48
C(12)	...	C(14)	2.40				

TABLE 20.

INTER-MOLECULAR DISTANCES < 4Å

I	...	C(3)v	3.59	C(11)	...	C(20)vii	3.83
I	...	C(16)ii	3.94	C(12)	...	C(24)vii	3.62
P(1)	...	C(25)iii	3.83	C(12)	...	C(25)vii	3.91
C(1)	...	C(28)v	3.85	C(12)	...	C(4)ii	3.93
C(2)	...	C(17)vi	3.80	C(13)	...	C(24)vii	3.73
C(4)	...	C(26)viii	3.93	C(13)	...	C(4)ii	3.77
C(5)	...	C(12)i	3.86	C(18)	...	C(22)viii	3.93
C(5)	...	C(13)i	3.93	C(18)	...	C(21)viii	3.94
C(5)	...	C(25)vi	3.98	C(18)	...	C(23)viii	3.95
C(6)	...	C(26)vi	3.71	C(18)	...	C(26)viii	3.97
C(6)	...	C(25)vi	3.85	C(18)	...	C(25)viii	3.97
C(6)	...	C(12)i	3.86	C(19)	...	C(23)viii	3.89
C(7)	...	C(12)i	3.99	C(22)	...	C(25)iii	3.60
C(9)	...	C(28)v	3.99	C(24)	...	C(26)iv	3.75
C(10)	...	C(28)v	3.85				

THE ENVIRONMENT OF IODINE < 6Å.

I	...	P(2)	5.37	I	...	C(27)	5.15
I	...	C(1)	4.84	I	...	C(10)	4.22
I	...	C(3)	3.51	I	...	N	5.12

The subscripts refer to the following positions:

i	$1+x, y, z$	v	$-\frac{1}{2}+x, \frac{1}{2}-y, -z$
ii	$-1+x, y, z$	vi	$\frac{1}{2}+x, \frac{1}{2}-y, 1-z$
iii	$1\frac{1}{2}-x, -y, -\frac{1}{2}+z$	vii	$-\frac{1}{2}+x, \frac{1}{2}-y, 1-z$
iv	$1\frac{1}{2}-x, -y, \frac{1}{2}+z$	viii	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$

TABLE 21.

INTERBOND ANGLES (°).

I - P(2)	- N	72		C(7) - C(8)	- C(3)	130
I - C(1)	- C(2)	147		C(8) - C(3)	- C(4)	105
I - C(3)	- P(2)	113		C(9) - C(10)	- C(11)	122
I - C(3)	- C(4)	102		C(10) - C(11)	- C(12)	118
I - C(27)	- C(28)	84		C(11) - C(12)	- C(13)	121
I - C(10)	- C(11)	91		C(12) - C(13)	- C(14)	130
P(1) - N	- P(2)	111		C(13) - C(14)	- C(9)	120
I - N	- P(1)	118		C(14) - C(9)	- C(10)	108
N - P(2)	- C(27)	112		C(15) - C(16)	- C(17)	120
C(27) - P(2)	- C(15)	104		C(16) - C(17)	- C(18)	122
C(15) - P(2)	- C(8)	105		C(17) - C(18)	- C(19)	124
C(8) - P(2)	- N	109		C(18) - C(19)	- C(20)	110
C(8) - P(2)	- C(27)	113		C(19) - C(20)	- C(15)	125
N - P(2)	- C(15)	114		C(20) - C(15)	- C(16)	118
N - P(1)	- C(22)	103		C(21) - C(22)	- C(23)	116
N - P(1)	- C(9)	102		C(22) - C(23)	- C(24)	121
C(22) - P(1)	- C(9)	100		C(23) - C(24)	- C(25)	120
C(3) - C(4)	- C(5)	125		C(24) - C(25)	- C(26)	118
C(4) - C(5)	- C(6)	122		C(25) - C(26)	- C(21)	126
C(5) - C(6)	- C(7)	132		C(26) - C(21)	- C(22)	118
C(6) - C(7)	- C(8)	106				

ETHYLIODIDE ADDUCT OF BIS-(DIPHENYL-PHOSPHINO)-ETHYLAMINE.

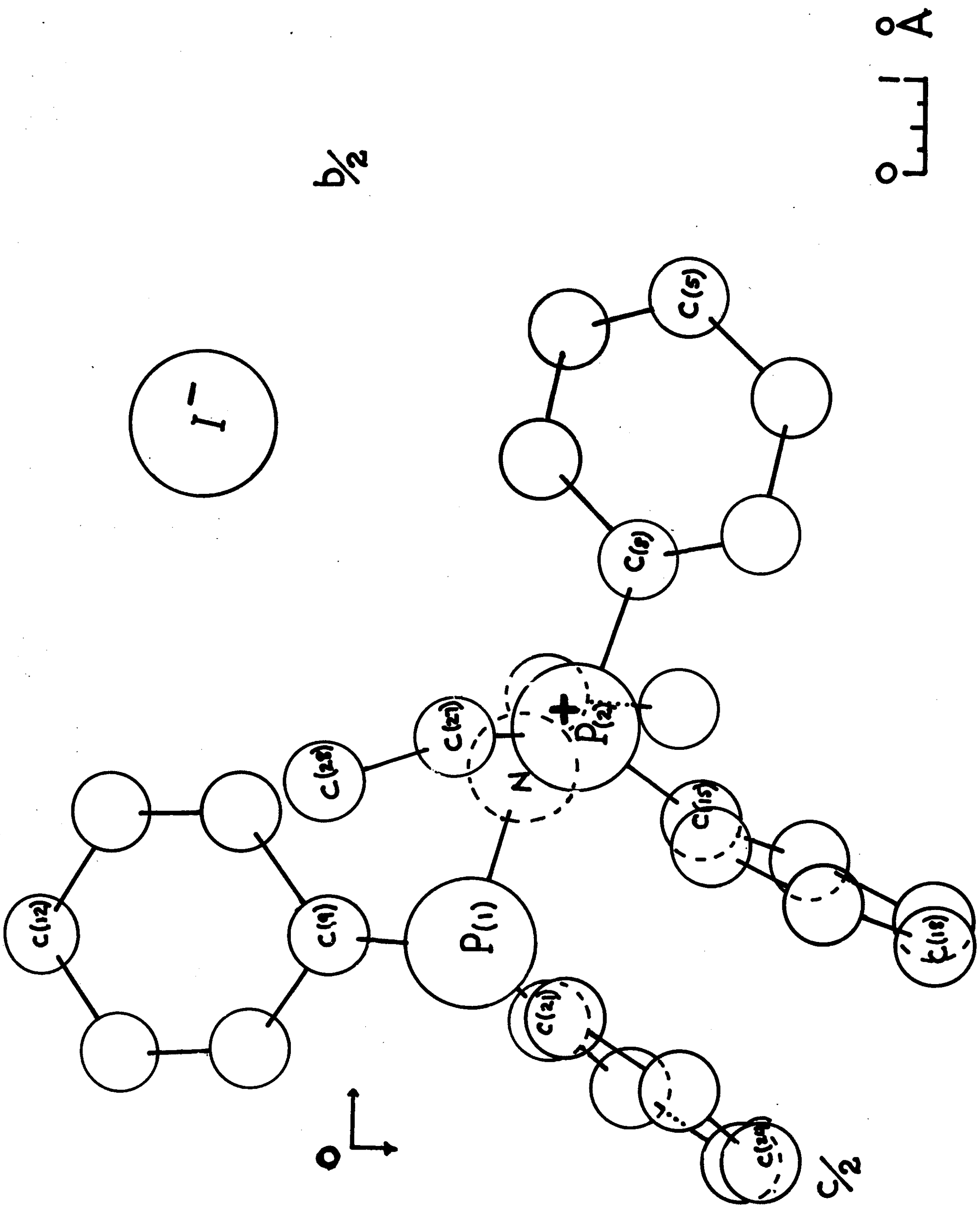


Fig. 5. Atomic arrangements as viewed down the a-axis.

$1{\cdot}88 \pm 0{\cdot}03$ Å, this value is probably the first example of a true P-N single bond reported for this class of compounds. The non-linearity of the P-N-P skeleton is established, the angle $P\hat{N}P$ being $111{\cdot}14 \pm 1{\cdot}6°$. This value is smaller than any reported in the phosphonitrilic systems (Paddock, 1962) which supports the statement made in Part I that the nitrogen in the P-N-P system is in a different environment from that in the other systems so far investigated.

The closest approach between $P(2)^+$ and I^- is $5{\cdot}37 \pm 0{\cdot}01$ Å. Investigation of the surroundings of the iodide ion revealed that P(1) is even further away from I^- (at >6 Å) and that N is at $5{\cdot}11 \pm 0{\cdot}03$ Å. The structures of several quaternary nitrogen compounds containing $N^+ \ldots I^-$ have been studied and all the shortest $N^+ \ldots I^-$ distances reported are less than 5 Å. In the crystal structure analyses of caracurine II dimethiodide and macusine-A iodide (McPhail et al. 1961, 1963) the shortest $N^+ \ldots I^-$ distances are 4·42, 4·52 and 4·58 Å. McKay et al. (1955) also reported a value of 4·38 Å in morphine hydriodide. Hence all the evidence supports the view that quaternisation occurs at one of the phosphorus atoms and not at the nitrogen atom of the P-N-P system.

It seems that size and shape are the factors controlling the packing of the molecule rather than charge.

The closest contacts between I^- and the carbon atoms are 3·51 and 4·13 Å, which agree well with the shortest $C \ldots I^-$ distances of 3·66, 3·87 and 3·96 Å in caracurine II dimethiodide (McPhail and Robertson, 1961); 3·74 and 3·94 Å reported in hunterburnine-β methiodide (Asher, 1963).

ETHYLIODIDE ADDUCT OF BIS-(DIPHENYL-PHOSPHINO)-ETHYLAMINE.

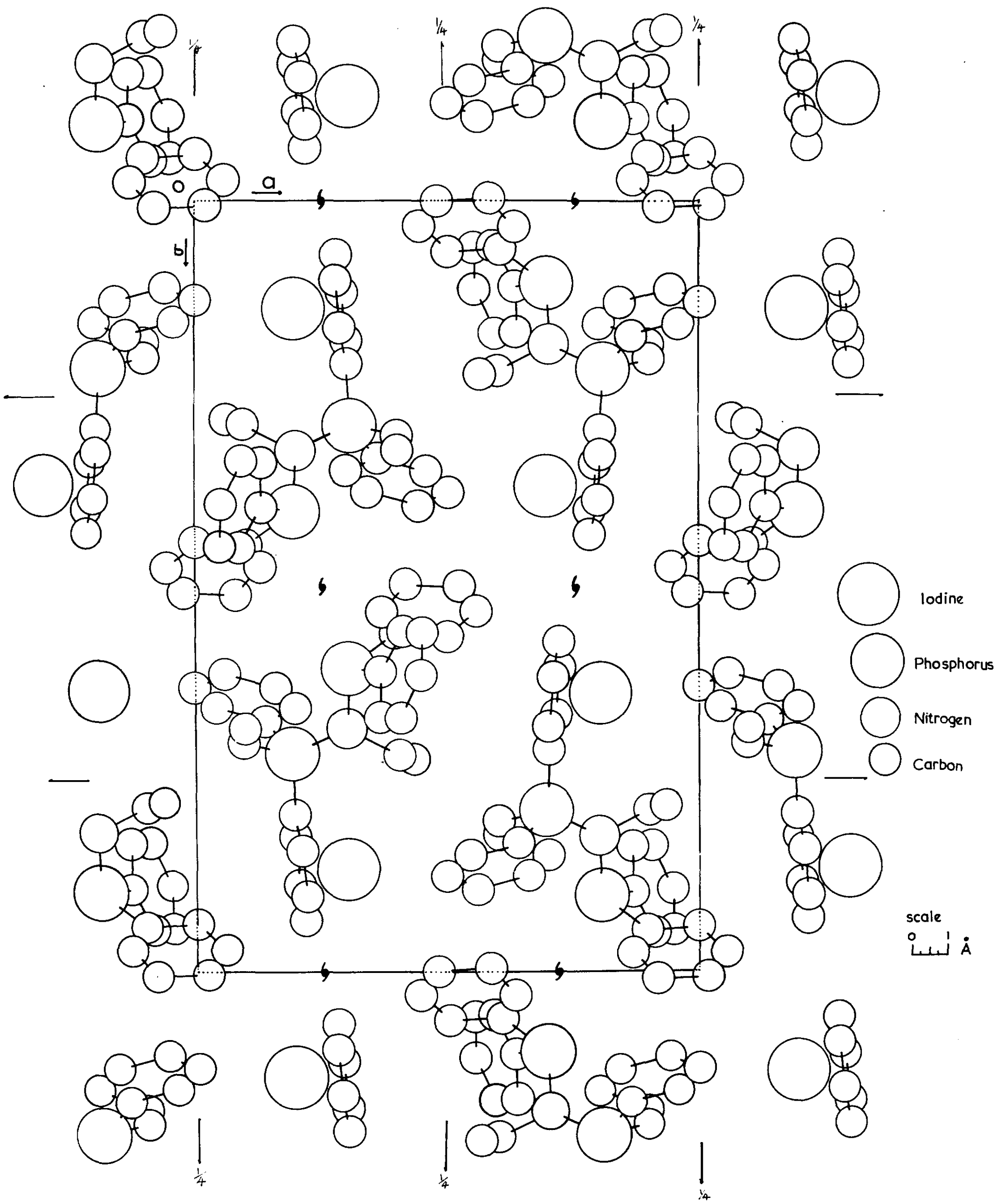


Fig. 6. Packing of the molecules in projection down the c-axis.

In view of the relatively high standard deviations (Table16) an extensive discussion of the bond-lengths between light atoms will not be attempted. However, the values obtained are in general agreement with normally accepted values. The average carbon (sp^3)-carbon (sp^3) bond length is 1·56 Å; this is similar to the accepted value of 1·547 Å in diamond. The mean bond angle of the benzene rings is about 120°, but the average aromatic carbon-carbon bond length is 1·47 Å which is much longer than the expected value of 1·397 Å (Sutton et al., 1958).

PART III

X-RAY STRUCTURE ANALYSIS OF BIS-(DIPHENYL-PHOSPHINO)-ETHYLAMINE-MOLYBDENUM-TETRACARBONYL

INTRODUCTION

Theoretical Concept of bonding in Bis-(diphenyl-phosphino)ethylamine-molybdenum-tetracarbonyl:

The bonding in this complex may be viewed as one which involves two major components. On one hand, the bond formation between the phosphine ligand, and the metal molybdenum; and, on the other hand, the bond between the metal and the carbonyl group. Each of these involves mainly the formation of σ - bond and probably accompanied by π-bond formation due to back - co-ordination.

In the case of a metal-carbonyl formation, a σ - bond is formed by a dative overlap of the filled carbon σ - orbital with an empty metal σ - orbital. (Fig. 1a). In order to stabilise the σ - bond, there is dissipation of the excess negative charge from the d_{π}-orbital of the metal into an empty anti-bonding p-orbital of the carbon. Thus a d_{π}-p_{π} back-bonding, (Fig. 1b), accompanies the formation of a σ - bond

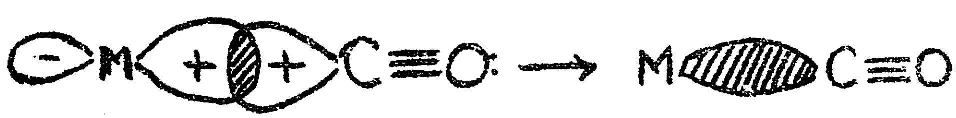


Fig. 1a. The formation of M-C σ - bond.

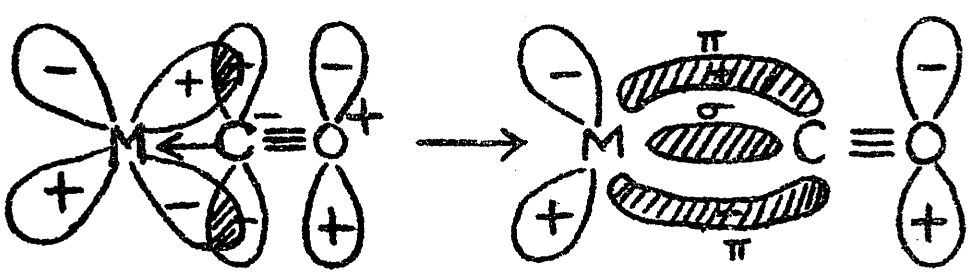


Fig. 1b M-C σ - bond and π-bond formation.

Diagrammetric representation of the whole mechanism can be made in terms of the Valence Bond Theory (Cotton et al., 1962).

$M - C \equiv O \longleftrightarrow M = C = O$.

[illegible] is seen to lower the C–O bond order and this should result in the increase in C–O carbonyl bond length compared with its value in free CO. The above mechanism gives both Mo–C and C–O partial double bond character, thus up to a point the effect of σ – bond formation strengthens the π-bonding and vice versa.

The mechanism becomes more complicated if the metal carbonyl is complexed to some other electron donors. Up till now it is still not possible to detect σ – π synergic bonding in complexes with P, As or S by infra red; but, it is generally assumed that some π-bonding is associated with these poor π-electron donors. Poilblanc and Bigorgne (1962) working on the triphenyl-phosphine-molybdenum tricarbonyl found that the carbonyl frequency which occurs at 1980 cm^{-1} in molybdenum hexacarbonyl is lowered to 1835 cm^{-1} and 1934 cm^{-1} in the triphenyl phosphine complex. The decrease in the value of frequency is due to the strong π-bonding between the metal ion and the carbon of the carbonyl group. This in effect will reduce the C–O bond order and results in C–O bond lengthening. The extent to which this order is lowered is dependent on the nature of the substituents attached to phosphorus. Electronegativity is the chief factor influencing the substituent groups. The C–O stretching frequency in $PF_3Ni(CO)_3$ was found almost same as that in $Ni(CO)_4$. (Bigorgue and Zelwer, 1960).

If the theory of delocalisation of electrons in PNP system is correct, and, assuming that the phosphorus does not interact with the π-bonding in the conjugated system (benzene) to which it is attached, it is reasonable to assume that the bonding between the ligand – PNP – and the metal – molybdenum – is similar to that between carbonyl group and the metal. Donation of electrons by the phosphorus atom to the central metal atom will result in a σ-bond formation, Fig. 2a. A transfer of the excess negative charge on the metal into the empty d-orbital of phosphorus will result in a d_π-d_π back bonding which helps to strengthen the σ-bond formation and vice versa. In a PNP-molybdenum carbonyl complex, the presence of a CO group (a better π-bonder) will reduce the amount of π-bonding in the Mo-P bond. This effect will be transmitted into the PNP system and the resultant P-N bond order is increased. If the above operation is correct, one expects to have shorter average P-N bond length in $PNPMo(CO)_4$ than in $PNPPdCl_2$, say.

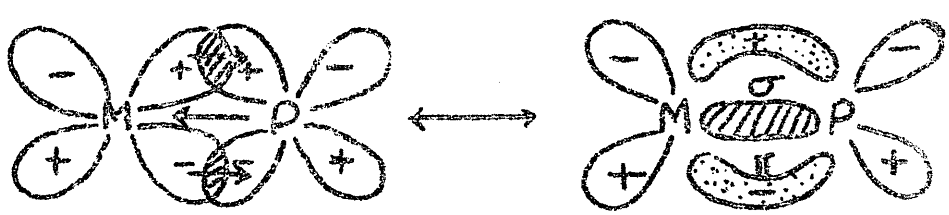


Fig. 2a. Formation of Mo-P σ-bond and d_π-d_π back bonding.

The existence of π-bonding in Mo-P would result in the lowering of C-O bond order which would necessitate lower stretching frequency. Payne and Walker (1965) recorded a value of 1873 cm^{-1} for the C-O stretching frequency of the carbonyl in $PNPEtMo(CO)_4$; this value is lower than the value 1980 cm^{-1} recorded for the C-O stretching frequency in molybdenum hexacarbonyl. Thus one expects the C-O bond length in $PNPEtMo(CO)_4$ to be longer than the value in molybdenum hexacarbonyl or in free CO.

Other factors which could be in favour or against the π-bonding in Mo-P include effective overlapping of the d-orbitals. This overlap to some extent is governed by the Mo-P distance and P-Mo-P bond angle. The same could be said of the PNP skeleton in this complex. It is necessary therefore to collect more information to substantiate the lowering or the increasing of all the bond orders discussed. The establishment of the structure and stereochemistry of bis-(diphenyl-phosphino)ethylamine-molybdenum-tetracarbonyl would thus be of assistance in the understanding of the various bondings involved - hence the X-Ray crystal structure analysis was undertaken.

3.2. CRYSTAL DATA

The crystals of bis-(diphenyl-phosphine)-ethylamine-molybdenum-tetracarbonyl,

$[(C_6H_5)_2.P.N.(C_2H_5).P.(C_6H_5)_2Mo(CO)_4]$ (mol. wt. 621·4) are orthorhombic. The unit cell dimensions are $\underline{a}$ = 16·9 ± 0·03, $\underline{b}$ = 17·21 ± 0·04, $\underline{c}$ = 20·16 ± 0·04 Å and the volume of the unit cell = 5791 Å^3; ρ_m = 1·45 g/cm^3 (by floatation in KI solution); ρ_{cal} = 1·42 g/cc, Z = 8. F(000) = 2528; μ for CuKα - radiation (λ = 1·542 Å) is 70·0 cm^{-1}.

All atoms occupy a general eight-fold set of positions.

$\sum f^2_{Mo}$ = 1176 ; $\sum f^2_{Rest}$ = 1860 ; M.Pt. = 207 ± 1°C.

3.3. SPACE GROUP DETERMINATION

The space group was uniquely determined from the following systematic absences:-

hk0	:	when	h+k	is odd
h0l	:	"	l	is odd
0kl	:	"	k	is odd
h00	:	"	h	is odd
0k0	:	"	k	is odd
00l	:	"	l	is odd

These conditions are satisfied by the space group Pbcn (D^{14}_{2h}), No. 60).

3.4. INTENSITY DATA

The crystal system was found from oscillation photographs, and the unit cell parameters were determined from rotation and moving film photographs. The reciprocal lattice was employed by recording the intensities of the h0l to h7l layers with a a Weissenberg camera. Intensities were estimated visually using the step-wedge technique and after the normal Lorentz, polarisation and Tunell factors had been applied, 1700 non-zero independent structure amplitudes were evaluated.

3.5. STRUCTURE DETERMINATION

A trial set of co-ordinates for the molybdenum atom was obtained from a sharpened three-dimentional Patterson synthesis. The Mo...Mo vectors expected by the application of the Pbcn symmetry are given in Table (22). From such a Patterson map, Mo...Mo vector peak is expected at $\frac{1}{2} - 2x$, $\frac{1}{2} - 2y$, $\frac{1}{2}$; this peak marked A in Fig.1 was found on section at V = 40/240. The values of x and y were first worked out from this double weight peak. Also Mo...Mo vector peaks expected at 0, - 2y, $\frac{1}{2}$; and at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2} - 2z$ were found on sections at V = 80/240 and V = 120/240 respectively. These are marked B and C in Figs. 2 and 3. From these vector peaks the x, y and z co-ordinates of Mo atom were worked out and these values were confirmed by the co-ordinates derived from the single weight peak at 2x, 2y, 2z on section at V = 80/240 (Fig.3). The co-ordinates obtained for the molybdenum atom in this way were:

$$x/a = 0.321, \; y/b = 0.324, \; z/c = 0.186.$$

Since these co-ordinates are in general positions they should give a satisfactory phase determination of the structure factor. The first set of structure factors calculated using these values for the co-ordinates gave an R-value of 50%.

The probable signs given by the molybdenum atom were used with the observed structure amplitude as coefficients to comput

TABLE 22.

Pbcn – INTER-ATOMIC VECTORS.

	x, y, z	$\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$	$\frac{1}{2}+x, \frac{1}{2}-y, -z$	$-x, y, \frac{1}{2}-z$
x, y, z	–	$\frac{1}{2}+2x, \frac{1}{2}+2y, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}+2y, -2z$	$2x, 0, \frac{1}{2}+2z$
$\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$	$\frac{1}{2}-2x, \frac{1}{2}-2y, \frac{1}{2}$	–	$-2x, 0, \frac{1}{2}+2z$	$\frac{1}{2}, \frac{1}{2}-2y, 2z$
$\frac{1}{2}+x, \frac{1}{2}-y, -z$	$\frac{1}{2}, \frac{1}{2}-2y, -2z$	$2x, 0, \frac{1}{2}-2z$	–	$\frac{1}{2}+2x, \frac{1}{2}-2y, \frac{1}{2}$
$-x, y, \frac{1}{2}-z$	$-2x, 0, \frac{1}{2}-2z$	$\frac{1}{2}, \frac{1}{2}+2y, -2z$	$\frac{1}{2}-2x, \frac{1}{2}+2y, \frac{1}{2}$	–
$-x, -y, -z$	$-2x, -2y, -2z$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-2z$	$\frac{1}{2}-2x, \frac{1}{2}, 0$	$0, -2y, \frac{1}{2}$
$\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-2z$	$2x, 2y, -2z$	$0, 2y, \frac{1}{2}$	$\frac{1}{2}+2x, \frac{1}{2}, 0$
$\frac{1}{2}-x, \frac{1}{2}+y, z$	$\frac{1}{2}-2x, \frac{1}{2}, 0$	$0, 2y, \frac{1}{2}$	$-2x, 2y, 2z$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+2z$
$x, -y, \frac{1}{2}+z$	$0, -2y, \frac{1}{2}$	$\frac{1}{2}+2x, \frac{1}{2}, 0$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+2z$	$2x, -2y, 2z$

	$-x, -y, -z$	$\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z$	$\frac{1}{2}-x, \frac{1}{2}+y, z$	$x, -y, \frac{1}{2}+z$
x, y, z	$2x, 2y, 2z$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+2z$	$\frac{1}{2}+2x, \frac{1}{2}, 0$	$0, 2y, \frac{1}{2}$
$\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}+2z$	$-2x, -2y, 2z$	$0, -2y, \frac{1}{2}$	$\frac{1}{2}-2x, \frac{1}{2}, 0$
$\frac{1}{2}+2x, \frac{1}{2}-y, -z$	$\frac{1}{2}+2x, \frac{1}{2}, 0$	$0, -2y, \frac{1}{2}$	$2x, -2y, -2z$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-2z$
$-x, y, \frac{1}{2}-z$	$0, 2y, \frac{1}{2}$	$\frac{1}{2}-2x, \frac{1}{2}, 0$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}-2z$	$-2x, 2y, -2z$
$-x, -y, -z$	–	$\frac{1}{2}-2x, \frac{1}{2}-2y, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}-2y, -2z$	$-2x, 0, \frac{1}{2}-2z$
$\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z$	$\frac{1}{2}+2x, \frac{1}{2}+2y, \frac{1}{2}$	–	$2x, 0, \frac{1}{2}-2z$	$\frac{1}{2}, \frac{1}{2}+2y, -2z$
$\frac{1}{2}-x, \frac{1}{2}+y, z$	$\frac{1}{2}, \frac{1}{2}+2y, 2z$	$-2x, 0, \frac{1}{2}+2z$	–	$\frac{1}{2}, \frac{1}{2}+2y, -2z$
$x, -y, \frac{1}{2}+z$	$2x, 0, \frac{1}{2}+2z$	$\frac{1}{2}, \frac{1}{2}-2y, 2z$	$\frac{1}{2}+2x, \frac{1}{2}-2y, \frac{1}{2}$	–

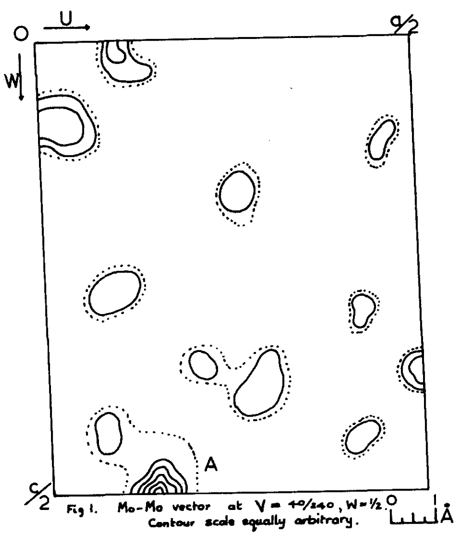


Fig 1. Mo-Mo vector at $V = 40/240$, $W = 1/2$.
Contour scale equally arbitrary.

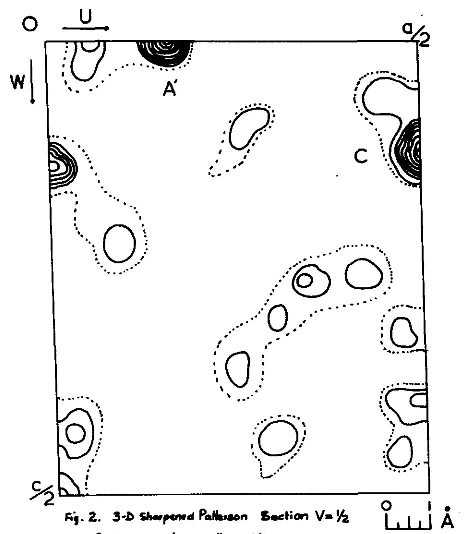


Fig. 2. 3-D Sharpened Patterson Section $V = 1/2$
Contour scale equally arbitrary.

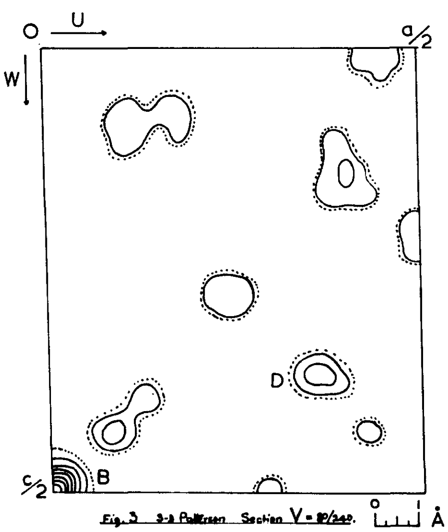


Fig. 3 3-D Patterson Section $V = 80/240$.
Contour scale equally arbitrary.

the first 3-D Fourier synthesis. The outcome was a host of diffraction ripples around molybdenum, phosphorus and the fourth oxygen, O(4), which initially coalesced with its carbon, C(6). However, two peaks were prominent and equidistant from the molybdenum atom; the distances calculated justified Mo-P bond lengths. Therefore, these two peaks were included with Mo in the next round of structure-factor calculations. R fell to 39%.

With these more reliable signs the second Fourier synthesis was computed with all the 1700 non-zero terms. The map obtained revealed the benzene rings attached to the two phosphorus atoms, the PNP skeleton and the probable positions of the first three carbonyl groups. In the midst of diffraction ripples still left, only the 24-carbon atoms of the phenyl groups could be located with some precision. Hence only 27 out of the 38 non-hydrogen atoms of the complex were included in the third round of phase determining process. The reliability-factor at this stage was 29·4%. The third Fourier synthesis computed gave the positions of all the atoms. R-factor was down to 24·4%.

At this stage, it was decided that refinement of atomic parameters by the least-squares method might prove better and faster than by Fourier syntheses.

3.6. STRUCTURE REFINEMENT

The block-diagonal elements of the least-squares programme were used. The weighting scheme and the shift-factors adopted are same as before. Anisotropic temperature factors were assigned to the Molybdenum, phosphorus and oxygen atoms while

TABLE 23.

COURSE OF ANALYSIS.

1700 Reflections for the 3-D Patterson synthesis.

Found Molybdenum atom.

1st. Structure-factor calculations, $B_{Mo} = 4.10Å^2$ (the temp. factor)

R = 50%

1020 Reflections for the 1st. 3-D Fourier synthesis.

Found Mo + 2P

2nd. Structure-factor calculations, $B_P = 4.00Å^2$

R = 39%

1700 Reflections for the 2nd. 3-D Fourier synthesis.

Found Mo + 2P + 24C

3rd. Structure-factor calculations, $B_C = 3.50Å^2$

R = 29.4%

1700 Reflections for the 3rd. 3-D Fourier synthesis.

Found All the 38 atoms (non-hydrogen).

4th. Structure-factor calculations, $B_{O/N} = 3.50Å^2$

R = 24.4%

1st. Cycle of S.F.L.S. Refinement, B_{Mo}(anisotropic).

R = 16.6%

2nd. Cycle of S.F.L.S. Refinement,

R = 11.79%

3rd. Cycle of S.F.L.S. Refinement, B_{Mo}, B_P, B_O, B_N(anisotropic).

R = 10.47%

4th. Cycle of S.F.L.S. Refinement,
R = 10.04%

5th. Cycle of S.F.L.S. Refinement,
R = 10.00%

6th. Cycle of S.F.L.S. Refinement, Data rescaled.
Final R = 9.45%

the remaining atoms were given isotropic temperature factors. Convergence was attained after six cycles of Least-squares. The final agreement was 9·45%. The whole course of analysis is as shown on Table 23.

3.7. RESULTS

The final scaled observed and calculated structure amplitudes are compiled in Table 24. Table 25 contains the atomic co-ordinates and their corresponding standard deviations are listed in Table 26. The thermal vibrations occupy Table 27. The inter-atomic bond-lengths with their respective standard deviations are compiled in Table 28. Inter-atomic bond angles are recorded in Table 29 with their corresponding standard deviations. Intra-molecular and inter-molecular distances <4 Å are listed in Tables 30 and 31 respectively. Table 32 consists of the deviation of atoms from some selected mean planes, and some important dihedral angles.

TABLE 24.

H	K	L	|Fo|	Fc
0	0	2	269.4	-369.2
0	0	4	13.6	14.6
0	0	6	341.6	334.2
0	0	8	304.6	-318.3
0	0	10	235.3	226.6
0	0	12	23.2	27.2
0	0	14	207.8	-199.2
0	0	16	261.8	257.7
0	0	18	143.1	-136.0
0	0	24	45.2	-38.1
1	0	2	260.9	-316.7
1	0	4	125.0	114.2
1	0	6	149.8	-135.0
1	0	8	63.4	48.0
1	0	10	177.0	146.2
1	0	12	247.7	-271.8
1	0	14	170.1	157.5
1	0	16	49.2	46.0
1	0	18	132.6	-130.9
1	0	20	53.0	54.9
1	0	22	54.3	-50.3
1	0	24	20.8	20.8
2	0	0	331.7	-570.3
2	0	2	268.4	296.1
2	0	4	49.7	33.1
2	0	6	15.5	15.9
2	0	8	46.7	46.7
2	0	10	120.0	-113.8
2	0	12	38.4	28.4
2	0	14	171.5	162.1
2	0	16	298.2	-210.1
2	0	18	72.7	75.0
3	0	2	183.9	168.9
3	0	4	74.6	-76.2
3	0	6	149.8	141.3
3	0	8	30.5	-30.0
3	0	10	76.1	71.2
3	0	12	105.0	95.1
3	0	14	91.0	-78.3
3	0	18	24.2	21.3
3	0	24	28.3	-24.2
4	0	0	320.7	-323.6
4	0	2	158.0	-179.7
4	0	4	171.7	-155.7
4	0	6	88.7	-68.4
4	0	8	220.2	210.8
4	0	10	160.2	-159.5
4	0	12	20.0	11.7
4	0	14	66.2	-66.6
4	0	16	41.0	38.6
4	0	18	42.0	38.6
4	0	22	61.2	-61.9
4	0	24	68.8	63.7
5	0	2	216.4	187.6
5	0	4	88.5	-88.4
5	0	6	189.0	188.1
5	0	8	59.6	48.7
5	0	10	131.4	-118.6
5	0	12	130.2	125.4
5	0	14	49.2	-45.1
5	0	18	24.2	30.7
5	0	24	24.4	28.5
6	0	0	51.3	48.3
6	0	2	65.4	-71.1
6	0	4	58.7	-49.9
6	0	6	201.9	189.8
6	0	8	280.9	-275.8
6	0	10	140.9	142.7
6	0	16	59.0	56.8
6	0	18	53.8	-60.1
6	0	22	102.5	105.8
6	0	24	106.2	-111.1
7	0	2	215.0	-198.9
7	0	4	297.5	273.8
7	0	6	295.5	-316.7
7	0	8	81.2	-65.4
7	0	10	142.9	137.2
7	0	12	155.0	-164.8
7	0	14	43.8	42.1
7	0	18	50.5	-56.2
7	0	20	126.4	111.2
7	0	22	79.6	-69.1
7	0	24	37.5	-30.3
8	0	0	149.9	-101.7
8	0	2	72.2	66.0
8	0	6	218.7	-223.5
8	0	8	313.3	336.1
8	0	10	133.5	-139.4
8	0	12	22.6	23.8
8	0	14	23.8	23.8
8	0	16	75.1	-71.0
8	0	18	46.8	51.6
8	0	22	107.5	-113.9
8	0	24	55.6	79.9
9	0	2	35.7	-25.3
9	0	4	137.0	-127.5
9	0	6	122.9	108.7
9	0	8	29.2	29.0
9	0	10	155.7	-154.6
9	0	18	27.9	33.2
9	0	20	61.8	-62.4
9	0	22	31.0	31.5
10	0	4	28.0	23.6
10	0	6	75.7	71.1
10	0	8	158.2	-158.2
10	0	10	32.3	30.8
10	0	14	75.1	75.6
10	0	16	41.0	-44.7
10	0	18	29.3	-26.8
10	0	22	38.5	40.9
11	0	2	145.6	124.3
11	0	4	115.4	-99.4
11	0	6	34.5	30.6
11	0	10	52.8	52.3
11	0	12	99.7	97.5
11	0	14	48.2	-50.3
11	0	18	41.4	44.6
12	0	0	274.9	258.4
12	0	2	97.8	-86.6
12	0	6	53.7	55.9
12	0	8	62.3	-69.5
12	0	10	51.1	53.2
12	0	14	111.7	-114.7
12	0	16	104.1	116.8
12	0	18	31.0	-34.0
12	0	20	15.0	9.6
13	0	2	157.6	-132.1
13	0	4	102.1	103.7
13	0	6	33.5	-34.9
13	0	10	42.0	38.8
13	0	12	58.5	-64.6
13	0	14	81.3	86.3
13	0	18	44.3	-55.2
13	0	20	46.2	43.9
14	0	0	173.0	-172.3
14	0	2	109.2	108.1
14	0	8	86.7	77.8
14	0	10	47.9	-51.1
14	0	14	81.3	79.8
14	0	16	94.2	-109.0
14	0	18	57.0	54.5
16	0	0	96.4	97.6
16	0	2	53.8	-55.3
16	0	14	46.1	-46.0
16	0	16	45.2	51.3
17	0	2	23.2	-19.4
17	0	4	25.1	-18.8
17	0	6	38.6	37.1
17	0	10	28.0	-23.7
18	0	6	53.8	53.9
18	0	8	76.4	-67.5
18	0	10	27.3	31.8
19	0	2	36.3	-33.7
19	0	4	78.9	79.3
19	0	6	71.2	-69.1
19	0	8	16.2	-18.6
19	0	10	60.7	61.3
19	0	12	32.7	-41.3
20	0	0	44.0	-39.8
20	0	2	27.5	25.7
20	0	6	63.0	-60.3
20	0	8	81.1	87.5
21	0	2	24.2	22.9
21	0	4	47.3	-51.0
7	1	22	30.0	27.0
7	1	24	21.7	-18.0
8	1	1	53.1	57.4
8	1	2	68.0	-57.9
8	1	3	69.1	-74.4
8	1	4	139.7	135.1
8	1	5	109.7	107.5
8	1	6	44.9	-44.9
8	1	7	39.7	-35.7
8	1	8	25.2	14.9
8	1	9	46.8	-52.5
8	1	10	47.0	48.9
8	1	11	85.3	87.5
8	1	12	40.3	-50.9
8	1	13	54.6	-56.9
8	1	15	40.0	35.1
8	1	17	30.8	24.6
8	1	18	24.5	-15.6
8	1	19	42.5	-45.8
8	1	20	26.9	27.5
8	1	21	47.1	42.7
8	1	22	30.7	-32.2
8	1	23	20.9	-20.3
9	1	1	117.6	-103.0
9	1	2	23.0	15.9
9	1	3	69.6	65.1
9	1	4	19.4	-12.4
9	1	5	87.0	95.5
9	1	6	59.5	-63.2
9	1	7	106.4	-119.2
9	1	8	66.9	67.3
9	1	9	111.1	128.2
9	1	10	87.7	-102.2
9	1	11	37.6	-36.0
9	1	13	24.9	-21.1
9	1	14	25.3	26.2
9	1	15	71.9	82.0
9	1	16	50.5	-46.6
9	1	17	55.2	-62.1
9	1	18	23.8	21.2
9	1	19	22.5	18.8
9	1	21	29.7	31.9
9	1	22	32.4	-40.1
9	1	23	41.7	-52.1
10	1	1	20.0	-18.5
10	1	2	50.8	69.8
10	1	3	154.3	156.1
10	1	4	65.7	-60.8
10	1	5	157.1	-156.5
10	1	6	56.7	94.4
10	1	7	54.4	50.8
10	1	9	51.3	53.0
10	1	10	50.9	-46.6
10	1	11	122.7	-145.9
10	1	12	50.0	53.7
10	1	13	73.8	90.5
10	1	15	25.3	-24.6
10	1	16	24.8	22.7
10	1	17	34.0	-44.1
10	1	18	32.3	29.8
10	1	19	85.4	89.3
10	1	20	33.7	-42.7
10	1	21	63.1	-70.4
10	1	22	23.3	24.7
11	1	0	48.0	41.2
11	1	1	117.7	111.3
11	1	3	67.3	-62.8
11	1	5	91.6	-94.4
11	1	6	70.6	71.6
11	1	7	138.2	146.4
11	1	8	67.4	-66.5
11	1	9	87.0	-98.3
11	1	10	52.5	47.5
11	1	11	38.1	42.5
11	1	12	25.3	22.5
11	1	13	25.4	32.2
11	1	15	55.5	-62.2
11	1	16	24.1	18.2
11	1	17	54.0	56.0
11	1	18	26.5	-24.0
11	1	19	34.5	-34.6
11	1	20	19.5	-14.8
11	1	21	18.5	-16.1
11	1	22	19.0	23.1
12	1	1	16.2	14.1
12	1	2	23.0	-17.1
12	1	3	82.9	-73.1
12	1	4	54.8	51.7
12	1	5	94.7	96.9
12	1	6	49.8	-44.7
12	1	7	48.7	-47.0
12	1	9	27.4	-23.5
12	1	10	60.8	66.2
12	1	11	55.6	64.3
12	1	12	18.0	-18.3
12	1	13	43.6	-49.0
12	1	15	29.4	24.9
12	1	18	28.4	-25.9
12	1	19	44.3	-39.0
12	1	20	41.4	42.1
12	1	21	39.4	46.5
13	1	0	34.0	23.6
13	1	8	52.4	53.5
13	1	9	35.9	38.1
13	1	12	30.6	33.1
13	1	14	23.8	-26.0
14	1	2	46.8	-39.7
14	1	3	25.1	-13.6
14	1	10	25.1	-23.2
14	1	11	24.7	20.3
14	1	19	17.8	-13.9
15	1	0	58.4	-51.2
15	1	1	50.8	-41.9
15	1	3	33.1	26.4
15	1	5	33.1	33.2
15	1	7	35.6	-34.8
15	1	9	33.1	29.3
15	1	11	23.6	-24.8
15	1	13	21.8	-24.7
15	1	14	41.1	37.7
15	1	15	40.5	44.8
15	1	16	36.8	-40.8
15	1	17	41.5	-39.7
15	1	18	17.0	16.0
16	1	1	33.8	-25.6
16	1	2	43.6	40.2
16	1	3	66.5	62.1
16	1	4	51.9	-54.7
16	1	5	58.9	-61.7
16	1	6	24.7	19.2
16	1	7	24.3	25.9
16	1	8	23.9	-20.7
16	1	9	25.6	20.7
16	1	10	24.9	-23.4
16	1	11	55.9	-55.6
16	1	12	49.0	47.5
0	2	1	212.6	408.5
0	2	2	128.6	139.4
0	2	3	86.7	-84.4
0	2	4	77.1	67.6
0	2	5	60.7	-75.1
0	2	6	20.0	-17.8
0	2	7	71.4	76.4
0	2	9	93.5	-93.7
0	2	10	100.4	-97.9
0	2	11	53.7	45.8
0	2	12	54.2	44.7
0	2	13	100.6	102.7
0	2	15	211.5	-202.8
0	2	16	38.1	-35.7
0	2	17	134.0	139.4
0	2	18	64.8	72.6
0	2	19	32.3	-31.6
0	2	22	74.9	-69.9
0	2	23	25.7	15.8
0	2	24	72.7	65.9
0	2	25	49.8	-49.1
1	2	1	139.3	180.1
1	2	2	41.3	54.9
1	2	3	201.7	-223.6
1	2	4	197.9	-232.7
1	2	5	211.4	241.5
1	2	6	227.4	198.5
1	2	7	51.9	47.9
1	2	8	49.5	-36.5
1	2	9	88.3	-82.2
1	2	10	65.8	-63.2
1	2	11	69.2	70.2
1	2	12	72.5	74.4
1	2	13	171.8	-177.9
1	2	14	81.0	-77.6
1	2	15	30.0	23.7
1	2	16	36.1	37.2
1	2	17	63.9	65.3
1	2	18	22.9	-21.3
1	2	19	55.9	-58.5
1	2	20	67.0	-65.6
1	2	21	52.3	46.8
1	2	22	28.2	20.1
1	2	23	25.6	-25.9
2	2	0	89.6	-96.4
2	2	1	164.9	-220.9
2	2	3	18.1	21.2
2	2	4	28.3	26.2
2	2	5	148.0	-143.4
2	2	6	120.5	128.5
2	2	8	140.9	-135.6
2	2	9	64.2	63.5
2	2	10	60.6	64.5
2	2	11	97.6	-100.2
2	2	12	51.8	-49.6
2	2	13	47.5	-48.2
2	2	14	20.4	22.6
2	2	15	190.7	186.0
2	2	16	22.1	-22.8
2	2	17	121.6	-123.8
2	2	18	39.7	-35.3
2	2	22	59.4	51.2
2	2	24	58.2	-53.8
2	2	25	30.4	31.4
3	2	1	114.9	-117.8
3	2	3	100.6	97.8
3	2	4	148.1	154.9
3	2	5	66.3	64.1
3	2	6	97.9	-97.0
3	2	7	38.4	34.5
3	2	9	64.1	-60.3
3	2	10	46.9	44.3
3	2	11	55.7	-52.0
3	2	12	26.4	-16.4
3	2	13	30.5	22.7
3	2	15	40.8	-38.3
3	2	16	28.1	-31.8
3	2	17	28.7	-27.3
3	2	22	39.0	-39.9
4	2	0	216.1	240.9
4	2	1	130.6	133.0
4	2	2	170.7	-174.6
4	2	3	80.0	62.0
4	2	4	79.2	-76.4
4	2	6	69.3	-76.0
4	2	7	142.6	-140.0
4	2	8	30.3	22.2
4	2	9	144.1	115.2
4	2	10	35.8	-31.1
4	2	11	31.3	-20.9
4	2	12	38.2	40.0
4	2	14	72.7	-74.5
4	2	15	43.6	-38.1
4	2	16	89.7	89.6
4	2	21	50.7	47.3
4	2	22	27.0	-20.6
4	2	23	66.2	-57.8
4	2	25	16.8	20.5
5	2	2	125.1	-122.9
5	2	3	24.7	-10.6
5	2	4	128.9	121.8
5	2	5	171.2	-180.1
5	2	6	14.3	-17.5
5	2	8	63.6	58.2
5	2	9	41.1	40.6
5	2	10	25.0	27.7
5	2	11	59.0	-72.3
5	2	12	67.9	-74.2
5	2	13	41.1	37.2
5	2	14	114.7	103.9
5	2	15	44.2	-45.7
5	2	18	32.3	-23.8
5	2	19	54.9	54.8
5	2	20	30.5	29.1
5	2	21	83.5	-79.3
5	2	25	22.7	33.6
6	2	0	230.7	-217.5
6	2	1	139.7	140.0
6	2	2	144.5	149.3
6	2	4	39.6	-32.9
6	2	5	22.6	-22.6
6	2	6	30.5	-34.7
6	2	7	319.2	350.3
6	2	8	29.0	19.7
6	2	9	175.8	-180.7
6	2	10	26.1	-29.3
6	2	11	36.7	27.4
6	2	12	28.6	27.3
6	2	14	123.3	122.9
6	2	15	44.8	-39.5
6	2	16	94.0	-92.3
6	2	17	64.3	75.4
6	2	18	50.7	52.2
6	2	19	31.2	-32.7
6	2	21	62.2	-52.2
6	2	23	90.8	100.5
7	2	1	45.1	43.6
7	2	3	60.8	-64.4
7	2	4	81.4	-169.2
7	2	5	90.4	152.3
7	2	6	56.4	59.3
7	2	7	121.3	-121.1
7	2	8	30.6	-30.7
7	2	9	93.3	-90.6
7	2	11	107.7	112.0
7	2	12	105.5	112.5
7	2	13	61.1	-63.0
7	2	14	97.3	-99.0
7	2	15	45.4	48.3
7	2	18	44.9	42.8
7	2	19	74.9	-78.0
7	2	20	50.1	-48.4
7	2	21	101.4	90.0
7	2	22	37.8	32.1
8	2	0	92.0	91.5
8	2	1	88.1	-75.4
8	2	2	97.5	-103.8
8	2	5	79.0	82.3
8	2	6	34.8	36.2
8	2	7	179.9	-199.8
8	2	9	173.2	172.6
8	2	14	84.5	-85.7
8	2	15	32.3	27.2
8	2	16	56.1	54.5
8	2	17	39.2	-42.0
8	2	18	31.1	-30.7
8	2	21	50.7	49.9
8	2	23	80.8	-78.0
9	2	2	48.2	-36.3
9	2	3	29.9	34.5
9	2	4	35.2	36.9
9	2	5	91.2	-84.6
9	2	7	71.4	66.7
9	2	9	83.7	79.0
9	2	10	49.6	-55.3
9	2	11	43.1	-36.9
9	2	12	54.2	-60.4
9	2	13	39.1	36.1
9	2	19	35.0	27.7
9	2	21	55.6	-52.2
10	2	0	38.9	-22.2
10	2	1	51.5	-39.4
10	2	5	43.0	-44.3
10	2	6	30.5	33.7
10	2	7	65.6	71.3
10	2	8	67.3	-77.1
10	2	9	60.0	-58.0
10	2	12	35.0	-31.4
10	2	14	39.7	44.3
10	2	15	32.2	30.1
10	2	16	34.6	-44.2
11	2	1	59.8	-48.8
11	2	3	56.0	55.2
11	2	4	56.8	52.3
11	2	5	28.8	-17.8
11	2	6	46.4	-39.8
11	2	7	30.0	23.2
11	2	8	30.5	-34.0
11	2	10	54.8	55.7
11	2	11	28.7	-26.0
11	2	13	72.4	71.6
11	2	17	41.3	-46.8
11	2	20	47.5	46.4
12	2	0	41.3	25.7
12	2	1	148.2	126.0
12	2	2	51.0	45.2
12	2	3	29.7	-25.1
12	2	5	30.3	-26.7
12	2	6	68.7	-61.3
12	2	8	223.4	120.0
12	2	9	32.0	-27.5
12	2	10	64.5	-62.1
12	2	12	45.8	40.3
12	2	13	32.1	30.9
12	2	15	71.5	-72.9
12	2	17	64.4	64.2
12	2	18	27.8	25.4
13	2	1	75.4	61.7
13	2	3	111.1	-94.2
13	2	4	88.4	-78.3
13	2	5	63.1	55.3
13	2	6	84.1	79.2
13	2	8	32.3	31.4
13	2	10	39.7	-37.6
13	2	11	45.6	49.4
13	2	12	59.6	54.8
13	2	13	88.2	-90.6
13	2	17	50.6	46.6
13	2	19	34.4	-37.7
13	2	20	50.5	-51.5
14	2	1	139.7	-126.9
14	2	3	32.0	26.9
14	2	6	88.6	87.5
14	2	7	45.8	-43.7
14	2	8	85.7	-86.1
14	2	9	45.6	46.5
14	2	10	55.3	53.0
14	2	11	44.4	-44.5
14	2	15	95.9	102.3
14	2	17	73.0	-69.0
14	2	19	26.9	29.5
15	2	1	45.8	-40.6
15	2	3	64.8	57.0
15	2	4	64.8	66.2
15	2	6	51.0	-49.4
15	2	10	43.5	39.4
15	2	11	42.3	-42.2
15	2	12	40.8	-35.5
15	2	13	55.2	59.2
15	2	17	33.9	-33.8
16	2	1	66.6	71.3
16	2	6	38.4	-36.3
16	2	15	54.6	-53.2
17	2	1	37.9	29.4
17	2	3	21.7	-22.5
18	2	0	57.7	-59.1
18	2	7	61.3	62.3
18	2	8	43.7	6.5
1	3	1	106.6	-120.6
1	3	2	191.2	206.6
1	3	3	43.1	-38.0
1	3	4	62.0	50.5
1	3	5	59.9	-53.4
1	3	6	165.4	-164.5
1	3	7	65.8	56.9
1	3	8	87.5	95.4
1	3	9	75.4	70.8
1	3	10	35.7	-25.1
1	3	11	29.6	-27.8

-cont'd-

TABLE 24 -cont'd-

H	K	L	|Fo|	Fc
1	3	12	18.1	-16.3
1	3	14	88.6	82.5
1	3	16	83.1	-76.3
1	3	17	35.5	-37.6
1	3	18	32.1	31.8
1	3	22	33.8	-33.8
1	3	24	45.9	46.0
2	3	1	61.9	-73.1
2	3	2	236.9	259.0
2	3	3	279.1	-314.3
2	3	4	301.5	-304.9
2	3	5	247.3	226.9
2	3	6	295.8	266.9
2	3	7	57.4	-46.9
2	3	8	24.5	-28.7
2	3	9	15.2	11.6
2	3	10	125.6	-126.9
2	3	11	32.3	27.4
2	3	12	56.8	178.6
2	3	14	103.0	-101.2
2	3	15	26.0	21.0
2	3	18	90.8	72.1
2	3	20	83.1	-69.3
2	3	22	54.8	37.4
3	3	0	121.5	138.1
3	3	1	178.8	178.2
3	3	2	297.6	-318.1
3	3	3	139.7	128.2
3	3	4	91.1	-64.7
3	3	5	22.0	-22.7
3	3	6	253.3	247.3
3	3	7	16.7	5.9
3	3	8	218.3	-199.2
3	3	10	59.4	91.3
3	3	11	24.9	-25.7
3	3	14	145.7	-140.8
3	3	16	140.0	141.6
3	3	18	86.1	-76.5
3	3	22	96.6	82.5
3	3	24	90.7	-95.2
4	3	1	73.2	-51.5
4	3	2	82.8	-91.4
4	3	3	106.4	-92.1
4	3	4	335.5	333.3
4	3	6	178.0	-158.2
4	3	7	17.5	-22.2
4	3	8	37.2	39.4
4	3	9	50.0	-45.2
4	3	10	143.1	147.5
4	3	11	25.6	26.3
4	3	12	102.4	-189.5
4	3	14	132.4	131.0
4	3	15	26.6	-24.2
4	3	18	90.6	-88.5
4	3	20	108.8	103.2
4	3	22	64.7	-57.0
5	3	0	160.5	-198.1
5	3	1	123.7	108.1
5	3	2	135.3	139.9
5	3	3	56.5	-52.4
5	3	5	13.6	16.1
5	3	6	144.6	-141.6
5	3	7	45.2	-38.5
5	3	8	151.1	151.5
5	3	9	26.6	-31.5
5	3	10	112.1	-113.5
5	3	14	85.2	76.7
5	3	15	26.9	30.6
5	3	16	89.9	-84.4
5	3	18	59.7	54.9
5	3	22	68.7	-66.1
5	3	24	70.6	63.1
6	3	1	77.1	79.7
6	3	2	106.6	96.7
6	3	3	59.5	-54.7
6	3	4	148.6	-149.3
6	3	5	86.6	-79.1
6	3	6	18.7	20.5
6	3	7	37.5	35.7
6	3	10	87.3	-82.7
6	3	12	49.4	50.1
6	3	13	21.0	-20.3
6	3	14	43.4	-35.0
6	3	16	32.0	-30.3
6	3	18	27.4	28.3
6	3	20	41.3	-37.3
6	3	21	33.3	-25.1
6	3	22	24.6	26.0
7	3	0	24.6	-22.8
7	3	1	20.2	-7.9
7	3	2	39.7	42.3
7	3	3	33.1	-33.8
7	3	5	84.3	-85.0
7	3	7	67.9	60.6
7	3	9	32.0	-23.0
7	3	10	19.2	4.7
7	3	12	29.4	31.4
7	3	13	21.5	-22.9
7	3	15	31.8	27.5
8	3	2	43.2	39.3
8	3	3	94.9	97.3
8	3	4	127.0	-124.6
8	3	9	47.4	-42.1
8	3	10	71.8	-71.0
8	3	12	64.3	61.6
8	3	13	51.6	53.4
8	3	14	54.9	-53.1
8	3	16	34.2	35.3
8	3	20	60.8	-54.7
8	3	22	36.5	29.6
9	3	0	159.9	164.5
9	3	2	161.7	-162.8
9	3	3	24.5	24.5
9	3	4	39.4	35.3
9	3	6	101.5	101.7
9	3	7	33.0	-32.4
9	3	8	152.3	-139.2
9	3	9	40.5	33.8
9	3	10	132.1	125.1
9	3	14	75.8	-77.3
9	3	15	27.8	-28.9
9	3	16	94.1	91.5
9	3	18	64.7	-55.2
9	3	21	19.9	19.4
9	3	22	29.3	30.6
10	3	1	34.1	30.7
10	3	2	142.0	-141.4
10	3	3	29.3	34.5
10	3	4	168.6	187.7
10	3	6	93.0	-90.3
10	3	7	22.0	22.5
10	3	9	21.1	20.7
10	3	10	116.1	121.1
10	3	11	31.2	-39.2
10	3	12	98.3	-101.9
10	3	14	91.1	88.4
10	3	18	60.3	-55.1
10	3	20	82.9	78.6
10	3	22	57.9	-51.6
11	3	0	130.4	-125.3
11	3	1	23.8	-22.3
11	3	2	138.6	130.4
11	3	3	28.0	29.1
11	3	4	24.5	18.3
11	3	6	98.0	-95.6
11	3	8	108.8	113.7
11	3	9	37.9	42.9
11	3	10	74.5	-78.0
11	3	14	80.3	82.1
11	3	15	46.7	42.9
11	3	16	89.2	-92.8
11	3	17	35.1	-32.2
11	3	18	56.8	50.5
12	3	2	62.3	66.5
12	3	4	100.0	-105.1
12	3	6	72.5	77.5
12	3	10	32.0	-32.7
12	3	12	70.1	76.3
12	3	14	49.0	-50.4
12	3	18	37.1	28.2
12	3	20	35.2	-33.3
13	3	1	72.6	78.2
13	3	3	26.8	-21.2
13	3	14	29.7	-31.1
13	3	15	28.3	-25.5
13	3	16	26.7	31.7
14	3	3	39.0	-36.5
14	3	10	38.6	-38.6
14	3	18	16.3	14.3
15	3	0	39.3	31.1
15	3	1	27.8	-26.7
15	3	2	50.7	-49.8
15	3	6	27.6	28.8
15	3	7	24.5	32.2
15	3	8	38.4	-75.3
15	3	9	34.5	-30.8
15	3	10	45.4	42.9
15	3	14	17.9	-20.7
15	3	16	39.5	37.7
15	3	17	12.8	-16.3
15	3	18	19.0	-24.2
16	3	1	27.5	-24.7
16	3	2	54.8	-53.1
16	3	4	89.8	86.3
16	3	6	46.3	-50.3
16	3	9	22.6	-27.3
16	3	10	46.8	47.0
16	3	12	65.2	-57.3
16	3	14	33.4	33.5
17	3	0	52.8	-58.5
17	3	1	26.3	25.9
17	3	2	67.8	60.3
17	3	6	61.5	-58.4
17	3	7	34.8	-34.5
17	3	8	74.1	74.9
17	3	10	54.2	-53.7
17	3	14	39.4	40.0
18	3	2	39.7	36.7
18	3	4	60.1	-63.8
18	3	6	39.5	37.6
18	3	10	27.0	-30.0
18	3	12	46.0	51.7
19	3	0	25.2	22.4
19	3	1	21.8	-16.1
19	3	2	21.6	-21.5
19	3	6	34.1	37.7
19	3	7	26.7	28.4
19	3	8	20.6	-25.5
19	3	10	25.7	28.8
21	3	0	22.4	28.5
21	3	2	21.5	-26.7
0	4	1	158.2	-142.3
0	4	2	8.2	0.8
0	4	3	119.4	112.3
0	4	4	233.0	234.5
0	4	5	145.2	128.0
0	4	6	103.9	-97.9
0	4	7	359.5	-320.5
0	4	8	60.4	64.6
0	4	9	278.2	307.0
0	4	10	87.9	94.8
0	4	11	80.6	-77.4
0	4	13	38.3	-35.4
0	4	14	42.7	44.0
0	4	15	59.4	51.0
0	4	16	55.4	-52.3
0	4	17	27.2	-34.4
0	4	19	44.4	43.0
0	4	21	110.1	94.7
0	4	22	42.5	-37.1
0	4	23	108.2	-102.9
0	4	24	23.2	25.8
0	4	25	65.6	22.0
1	4	1	35.5	-22.7
1	4	2	121.5	-140.3
1	4	3	203.2	175.3
1	4	4	41.6	-40.6
1	4	5	260.7	-265.1
1	4	6	83.0	77.1
1	4	7	48.6	37.1
1	4	9	98.1	101.1
1	4	11	153.0	-164.2
1	4	12	48.0	45.1
1	4	13	121.4	127.9
1	4	14	24.7	-30.3
1	4	15	36.5	-40.8
1	4	16	40.7	-41.4
1	4	19	119.1	99.9
1	4	21	121.4	-118.6
1	4	23	29.5	30.3
1	4	25	38.7	43.3
2	4	0	75.5	-73.7
2	4	3	43.1	-43.9
2	4	4	47.8	-41.1
2	4	5	121.7	-122.0
2	4	6	37.6	-29.3
2	4	7	263.0	260.0
2	4	8	47.4	36.7
2	4	9	188.6	-187.6
2	4	11	24.5	29.2
2	4	12	46.8	-42.6
2	4	14	40.6	-43.3
2	4	15	30.0	31.1
2	4	16	40.9	44.8
2	4	21	68.9	-52.7
2	4	23	90.3	79.5
2	4	24	17.6	-22.1
2	4	25	38.8	-50.6
3	4	1	63.5	-67.0
3	4	4	58.7	-60.9
3	4	5	23.6	26.5
3	4	6	41.4	35.2
3	4	7	84.7	-80.8
3	4	8	17.9	25.3
3	4	9	71.3	-60.0
3	4	13	34.0	34.8
3	4	17	40.6	-48.3
3	4	19	31.2	-40.7
3	4	21	47.1	44.2
3	4	25	12.2	-20.6
4	4	0	130.1	-98.0
4	4	1	180.1	221.2
4	4	3	63.7	-47.4
4	4	7	136.0	-126.8
4	4	8	136.4	-124.7
4	4	9	37.9	35.8
4	4	13	51.0	50.5
4	4	15	122.1	-143.1
4	4	17	44.8	44.7
4	4	22	28.6	21.9
4	4	23	27.7	-33.7
5	4	1	141.0	129.0
5	4	3	222.3	-256.2
5	4	4	85.1	79.5
5	4	5	50.6	60.8
5	4	6	77.0	-69.6
5	4	7	37.1	36.2
5	4	8	16.0	-20.9
5	4	9	44.6	-46.9
5	4	10	37.7	31.4
5	4	11	110.8	102.4
5	4	12	21.5	-16.3
5	4	13	171.0	-155.3
5	4	14	36.7	38.6
5	4	17	69.0	68.4
5	4	19	64.9	-64.5
5	4	20	60.2	52.8
5	4	22	21.4	-25.5
5	4	23	15.7	-22.5
6	4	0	31.8	34.0
6	4	1	244.2	-233.3
6	4	2	93.8	77.4
6	4	3	68.9	72.3
6	4	4	15.4	-15.9
6	4	5	24.5	19.9
6	4	6	61.2	-62.6
6	4	7	17.5	10.7
6	4	8	104.1	91.7
6	4	9	63.1	64.1
6	4	11	74.8	-66.7
6	4	13	94.0	-90.1
6	4	14	30.5	41.6
6	4	15	191.3	198.3
6	4	16	22.4	-24.0
6	4	17	120.0	-116.6
6	4	18	38.1	53.1
6	4	19	33.6	36.3
6	4	22	26.5	-25.9
6	4	24	38.1	42.6
7	4	1	120.0	-112.3
7	4	3	244.7	246.5
7	4	4	78.7	-67.5
7	4	5	95.6	-95.6
7	4	6	38.3	37.8
7	4	7	51.0	47.7
7	4	8	36.9	33.8
7	4	9	21.7	17.1
7	4	10	50.9	-50.3
7	4	11	126.6	-131.0
7	4	12	38.8	35.8
7	4	13	158.8	166.7
7	4	14	38.0	-35.5
7	4	17	70.2	-76.7
7	4	19	101.7	99.5
7	4	20	39.0	-38.1
7	4	21	30.9	-37.1
7	4	22	25.0	22.3
8	4	0	104.6	109.2
8	4	1	270.9	243.0
8	4	3	22.7	-28.8
8	4	4	36.8	31.9
8	4	5	23.9	-30.0
8	4	6	49.3	48.6
8	4	7	62.4	61.9
8	4	8	49.4	-49.8
8	4	9	19.4	-24.0
8	4	11	62.1	53.2
8	4	13	103.4	102.1
8	4	14	44.5	-47.1
8	4	15	120.2	-128.7
8	4	16	35.3	41.0
8	4	17	127.0	118.9
8	4	19	31.8	-34.8
8	4	22	29.2	31.5
9	4	1	88.4	87.5
9	4	3	122.5	-119.6
9	4	4	25.0	26.1
9	4	5	75.8	75.5
9	4	6	45.4	-39.6
9	4	11	62.3	63.8
9	4	12	30.9	-31.7
9	4	13	70.2	-75.4
9	4	15	31.6	29.6
9	4	17	47.9	52.7
9	4	19	38.4	-40.2
10	4	1	51.6	-46.8
10	4	3	33.7	32.7
10	4	5	54.4	-59.8
10	4	7	90.3	91.9
10	4	9	47.1	-47.8
10	4	15	46.8	48.5
10	4	17	41.4	-42.2
10	4	21	22.2	-28.5
11	4	2	24.0	-23.0
11	4	3	41.9	-46.5
11	4	5	67.4	78.4
11	4	7	55.6	-57.3
11	4	9	44.6	-48.6
11	4	11	44.6	48.7
11	4	21	43.9	40.8
12	4	0	110.5	-102.7
12	4	5	56.3	59.5
12	4	7	168.8	-180.2
12	4	8	54.0	59.3
12	4	9	112.6	116.5
12	4	10	22.4	-20.3
12	4	11	22.4	-33.2
12	4	13	31.1	-43.2
12	4	14	37.1	40.5
12	4	16	31.1	-33.3
12	4	17	36.8	-37.5
13	4	2	55.1	65.6
13	4	3	86.9	84.1
13	4	5	196.8	-150.2
13	4	7	63.0	63.1
13	4	9	63.4	66.2
13	4	11	104.7	-100.9
13	4	12	40.7	35.2
13	4	13	60.0	61.9
13	4	14	35.4	-36.4
13	4	19	62.2	69.5
13	4	20	15.4	-20.8
14	4	0	38.4	42.2
14	4	1	38.5	40.5
14	4	2	38.5	-40.3
14	4	3	38.6	-35.5
14	4	5	54.8	-64.7
14	4	7	144.4	144.3
14	4	8	38.6	-39.9
14	4	9	118.8	-108.8
14	4	10	37.8	38.5
14	4	14	33.1	-31.7
14	4	16	45.2	41.3
14	4	17	27.6	30.9
15	4	2	31.7	-30.1
15	4	3	35.4	-39.8
15	4	4	31.6	26.3
15	4	5	97.6	100.0
15	4	6	27.1	-21.5
15	4	9	52.3	-57.1
15	4	11	64.0	70.8
15	4	12	33.7	-34.8
15	4	13	26.1	-32.9
15	4	14	30.0	29.4
16	4	0	31.2	-32.4
16	4	6	37.0	-42.6
16	4	7	63.1	-68.9
16	4	9	53.1	55.4
16	4	14	18.5	20.5
17	4	1	25.8	26.7
17	4	13	19.6	-22.2
18	4	1	51.4	-57.6
19	4	1	29.7	-36.7
19	4	3	46.0	52.1
19	4	5	35.8	-42.3
19	4	11	25.3	-40.6
20	4	1	55.0	71.0
20	4	3	23.7	-27.5
20	4	5	15.5	-15.5
20	4	7	15.3	28.0
1	5	1	36.4	32.7
1	5	2	90.9	-88.5
1	5	3	107.5	103.1
1	5	4	52.2	50.8
1	5	5	26.7	23.7
1	5	6	25.5	-17.3
1	5	7	72.4	-68.8
1	5	8	50.9	-53.4
1	5	9	102.6	82.4
1	5	10	44.3	43.6
1	5	11	42.8	-45.3
1	5	12	61.4	-59.2
1	5	14	25.1	-25.7
1	5	15	52.2	61.8
1	5	16	41.1	42.8
1	5	18	27.5	-22.5
1	5	23	35.1	-35.0
1	5	24	19.7	-20.5
2	5	1	129.2	-152.8
2	5	2	16.7	-11.9
2	5	3	178.8	194.6
2	5	4	124.1	132.9
2	5	5	161.5	-164.3
2	5	6	54.4	-55.6
2	5	7	35.6	34.6
2	5	8	17.8	-21.1
2	5	9	46.7	43.0
2	5	10	72.8	84.2
2	5	11	124.9	-119.4
2	5	12	94.7	-83.1
2	5	13	86.3	79.5
2	5	14	63.9	61.1
2	5	18	44.8	-46.0
2	5	19	88.1	83.2
2	5	20	39.7	41.9
2	5	21	62.0	-63.8
2	5	22	46.8	-46.1
2	5	23	40.0	40.1
2	5	25	16.3	15.8
3	5	0	255.2	-293.2
3	5	1	147.2	166.4
3	5	2	164.3	175.3
3	5	3	160.8	-153.6
3	5	5	89.6	-85.8
3	5	6	130.2	-123.5
3	5	7	164.0	185.7
3	5	8	158.4	162.1
3	5	9	180.7	-200.4
3	5	10	100.8	-88.3
3	5	11	98.6	102.7
3	5	13	37.4	32.6
3	5	14	36.1	29.6
3	5	15	86.4	-94.2
3	5	16	97.0	-94.5
3	5	17	69.4	67.1
3	5	18	31.6	35.0
3	5	19	37.9	-39.3
3	5	22	36.1	-39.0
3	5	23	69.9	65.1
3	5	24	40.7	39.8
3	5	25	31.9	-46.7
4	5	1	57.2	45.9
4	5	2	115.4	111.6
4	5	3	184.5	-185.7
4	5	4	40.8	-38.3
4	5	5	126.3	122.4
4	5	6	111.2	103.3
4	5	7	113.6	-122.8
4	5	8	34.8	30.8
4	5	9	66.1	-61.4
4	5	10	92.6	-89.5
4	5	11	107.1	104.8
4	5	12	47.6	41.4
4	5	13	102.8	-104.5
4	5	14	29.9	-26.9
4	5	15	65.4	70.2
4	5	17	38.8	37.7
4	5	18	49.8	49.9
4	5	19	72.0	-72.5
4	5	20	35.8	-37.0
4	5	21	77.5	77.2
4	5	22	43.2	40.3
4	5	23	26.7	-30.6
5	5	0	172.1	159.8
5	5	1	186.3	-193.5
5	5	3	72.0	66.1
5	5	5	36.9	30.2
5	5	6	45.2	38.8
5	5	7	150.8	-146.9
5	5	8	146.0	-146.6
5	5	9	163.3	169.3
5	5	10	112.3	103.8
5	5	11	72.2	-65.6
5	5	12	19.9	20.0
5	5	13	41.5	-37.0
5	5	15	58.3	59.2
5	5	16	89.5	89.5
5	5	17	70.9	-80.3
5	5	18	31.3	-34.1
5	5	19	37.1	39.3
5	5	22	24.0	26.6
5	5	23	40.2	-39.7
5	5	24	24.2	-28.7
6	5	2	30.3	-20.2
6	5	3	108.0	95.6
6	5	4	45.6	-36.2
6	5	5	42.4	-36.9
6	5	6	61.4	-44.0
6	5	7	23.2	15.1
6	5	8	34.3	35.3
6	5	9	31.1	32.8
6	5	10	49.6	45.5
6	5	11	39.3	-34.1
6	5	13	30.0	26.0
6	5	15	31.4	-29.6
6	5	20	21.7	28.4
6	5	21	20.0	-20.9
7	5	0	34.3	34.9
7	5	1	32.6	-17.8
7	5	2	53.2	-54.2

-cont'd-

TABLE 24 -cont'd-

H	K	L	|Fo|	Fc
7	5	4	27.0	30.2
7	5	6	39.2	37.4
7	5	7	36.8	25.1
7	5	10	39.2	30.5
7	5	11	40.7	-38.9
7	5	12	25.7	25.1
7	5	14	22.1	-16.2
7	5	16	22.4	33.4
8	5	2	89.1	-86.4
8	5	3	80.5	82.9
8	5	4	63.7	55.3
8	5	5	32.3	-26.0
8	5	6	79.9	-71.0
8	5	7	65.8	65.8
8	5	10	28.8	25.5
8	5	11	51.4	-44.0
8	5	12	52.8	-55.8
8	5	13	41.2	43.8
8	5	14	44.7	47.4
8	5	15	22.4	-25.6
8	5	18	41.8	-35.8
8	5	21	20.0	-20.2
9	5	0	176.7	-180.7
9	5	1	144.7	135.2
9	5	2	62.4	58.9
9	5	3	39.5	-35.7
9	5	4	19.7	19.0
9	5	5	18.4	-22.9
9	5	6	75.6	-66.6
9	5	7	54.9	50.7
9	5	8	107.2	109.4
9	5	9	68.1	-67.6
9	5	10	47.2	-43.5
9	5	11	21.6	22.0
9	5	12	22.0	-22.3
9	5	13	31.6	37.3
9	5	14	24.6	31.9
9	5	15	74.0	-84.5
9	5	16	69.2	-77.3
9	5	17	63.6	70.6
9	5	18	40.3	36.7
9	5	19	32.6	-29.5
9	5	22	18.2	-20.3
10	5	1	45.5	43.4
10	5	2	105.8	118.9
10	5	3	103.6	-107.4
10	5	4	105.9	-98.9
10	5	5	65.4	64.6
10	5	6	79.9	71.6
10	5	7	45.6	-49.2
10	5	8	39.0	-38.4
10	5	10	67.1	-66.4
10	5	11	88.4	82.1
10	5	12	65.2	62.6
10	5	13	70.9	-75.4
10	5	14	66.9	-61.4
10	5	15	34.7	37.3
10	5	18	47.0	45.3
10	5	19	37.4	-39.1
10	5	20	40.2	-40.5
10	5	21	23.1	25.5
10	5	22	20.2	25.6
11	5	0	143.9	138.3
11	5	1	109.2	-105.3
11	5	2	59.7	-54.7
11	5	3	49.2	48.3
11	5	5	46.1	41.3
11	5	6	36.3	40.2
11	5	7	21.3	-25.2
11	5	8	94.9	-92.8
11	5	9	38.0	40.1
11	5	10	55.8	66.7
11	5	14	55.9	-48.0
11	5	15	85.3	82.6
11	5	16	68.5	69.1
11	5	17	53.0	-49.8
11	5	18	33.5	-35.4
12	5	1	25.6	-29.7
12	5	2	57.5	-51.1
12	5	3	47.2	38.6
12	5	4	30.1	22.8
12	5	5	37.3	-37.8
12	5	6	21.7	-21.3
12	5	10	24.6	28.8
12	5	11	31.7	-38.4
12	5	12	31.4	-44.2
12	5	13	55.6	56.0
12	5	14	26.0	33.8
12	5	17	22.0	-22.9
12	5	18	28.3	-33.1
12	5	19	30.4	30.2
13	5	0	87.1	-84.6
13	5	1	37.7	37.5
13	5	2	43.7	49.1
13	5	16	17.8	-20.8
13	5	17	16.3	19.7
14	5	4	38.8	40.6
14	5	5	22.4	-30.6
14	5	6	27.5	-31.9
14	5	7	30.0	37.5
15	5	0	44.8	-40.2
15	5	5	38.5	-36.3
15	5	6	58.3	-57.7
15	5	7	37.8	36.3
15	5	8	43.1	42.3
15	5	9	47.2	-50.5
15	5	10	22.6	-27.9
15	5	16	16.5	-16.4
15	5	17	14.7	18.3
16	5	2	37.8	37.1
16	5	3	53.3	-54.2
16	5	4	48.3	-47.7

H	K	L	|Fo|	Fc
16	5	5	52.4	57.4
16	5	6	42.2	47.2
16	5	7	32.8	-42.2
16	5	9	27.9	-30.2
16	5	10	34.9	36.3
16	5	11	41.5	38.3
16	5	12	27.7	30.4
16	5	13	42.6	-38.4
16	5	15	24.7	27.9
17	5	0	56.9	44.7
17	5	1	28.4	-32.3
17	5	2	25.3	-32.0
17	5	3	22.9	17.1
17	5	5	22.3	25.3
17	5	6	26.8	29.5
17	5	7	70.9	-68.1
17	5	8	71.7	-68.5
17	5	9	64.5	61.6
17	5	10	26.8	28.0
17	5	11	25.1	-24.5
18	5	2	25.8	-23.6
18	5	3	20.9	25.2
18	5	4	27.6	26.8
18	5	5	42.7	-41.6
18	5	6	39.2	-36.7
18	5	10	33.7	34.5
18	5	11	24.9	-25.2
18	5	12	21.3	-20.9
19	5	7	38.5	43.2
19	5	8	38.7	42.8
19	5	9	16.2	-19.3
0	6	1	47.6	-45.3
0	6	2	47.1	44.0
0	6	3	37.2	-38.8
0	6	4	43.3	51.0
0	6	5	70.5	51.8
0	6	6	145.3	150.7
0	6	7	27.0	-26.8
0	6	8	253.5	-253.0
0	6	9	111.4	122.9
0	6	10	106.7	110.9
0	6	11	25.4	-33.8
0	6	12	27.8	18.9
0	6	13	55.6	64.8
0	6	15	77.9	-91.8
0	6	16	22.3	9.5
0	6	17	66.1	72.0
0	6	18	99.0	-96.2
0	6	20	17.3	-25.8
0	6	22	99.6	106.3
0	6	24	47.5	-87.4
1	6	1	89.1	84.2
1	6	2	32.7	-34.0
1	6	3	35.3	-32.2
1	6	4	233.5	252.6
1	6	5	90.1	84.6
1	6	6	211.4	-202.3
1	6	8	71.4	-71.3
1	6	9	59.0	51.9
1	6	10	191.8	183.2
1	6	11	52.7	49.7
1	6	12	143.8	-148.7
1	6	13	65.7	-57.7
1	6	14	35.6	27.7
1	6	15	36.9	38.5
1	6	18	87.2	-80.2
1	6	19	18.0	-19.5
1	6	22	124.2	-57.7
1	6	22	56.3	-57.7
1	6	24	21.5	-22.1
2	6	0	24.8	-27.5
2	6	1	121.2	-136.3
2	6	2	21.3	19.4
2	6	3	66.1	65.8
2	6	4	54.3	-42.1
2	6	5	34.5	32.7
2	6	6	178.6	-179.9
2	6	7	19.7	10.8
2	6	8	208.4	212.6
2	6	9	57.7	-46.7
2	6	10	88.8	-94.0
2	6	11	25.8	19.1
2	6	12	27.3	-19.2
2	6	13	51.0	-55.0
2	6	15	50.6	46.6
2	6	17	45.3	-40.5
2	6	18	61.6	57.1
2	6	19	25.4	22.3
2	6	22	91.0	-76.1
2	6	24	69.0	68.7
3	6	1	34.2	-35.7
3	6	2	32.8	40.5
3	6	3	96.4	97.4
3	6	4	11.6	6.5
3	6	5	12.5	4.9
3	6	6	48.3	35.9
3	6	8	50.7	49.9
3	6	9	41.8	45.2
3	6	10	84.9	-80.1
3	6	11	33.9	-31.4
3	6	13	47.4	46.3
3	6	14	50.8	52.3
3	6	17	47.2	-51.5
3	6	20	29.5	-29.8
3	6	24	24.6	26.8
4	6	0	167.5	-192.9
4	6	1	114.2	120.5
4	6	2	37.3	37.7
4	6	3	46.3	-40.3
4	6	4	19.3	18.3
4	6	5	55.6	53.4
4	6	6	20.2	-17.3

H	K	L	|Fo|	Fc
4	6	7	62.8	-68.5
4	6	8	60.1	-62.2
4	6	9	50.0	-40.0
4	6	10	14.8	23.3
4	6	12	16.3	-18.9
4	6	14	63.2	63.0
4	6	15	36.3	-30.7
4	6	16	55.3	-54.0
4	6	17	26.1	21.5
4	6	18	25.8	25.2
4	6	19	17.7	-24.1
4	6	22	31.4	27.8
4	6	23	36.2	-33.4
4	6	24	11.4	-14.8
5	6	1	14.4	8.9
5	6	2	38.7	99.3
5	6	3	64.0	-53.7
5	6	4	87.1	-103.1
5	6	5	77.4	-74.4
5	6	6	70.3	61.8
5	6	7	27.2	31.4
5	6	10	33.5	-22.8
5	6	11	27.7	-28.7
5	6	12	109.6	123.1
5	6	14	84.7	-73.1
5	6	18	82.4	72.0
5	6	20	50.9	-52.7
5	6	22	34.4	33.9
5	6	24	16.3	-18.1
6	6	0	275.7	317.1
6	6	1	40.5	-39.2
6	6	2	130.2	-148.1
6	6	3	28.9	-22.3
6	6	4	61.7	46.9
6	6	5	60.1	-62.9
6	6	6	88.8	96.9
6	6	7	82.1	80.1
6	6	8	91.6	-82.9
6	6	9	40.1	-39.1
6	6	10	100.2	111.7
6	6	11	42.1	44.9
6	6	14	125.7	-130.5
6	6	15	36.9	39.3
6	6	16	154.8	166.0
6	6	18	93.0	-81.0
6	6	21	35.7	-30.6
6	6	23	31.5	32.0
7	6	2	142.4	-160.1
7	6	4	110.4	95.1
7	6	5	23.6	16.8
7	6	6	79.8	-69.5
7	6	9	38.8	-39.3
7	6	10	65.8	50.5
7	6	11	31.0	29.9
7	6	12	136.2	-156.1
7	6	14	98.5	93.7
7	6	18	108.2	-96.6
7	6	19	33.1	-26.0
7	6	20	67.2	68.9
7	6	21	33.9	34.8
7	6	22	31.5	-30.2
8	6	0	233.3	-266.1
8	6	1	48.3	45.5
8	6	2	144.5	149.5
8	6	3	31.0	-31.3
8	6	4	43.7	48.6
8	6	5	25.2	22.8
8	6	6	21.2	-17.1
8	6	7	67.9	-62.0
8	6	8	57.3	41.0
8	6	9	75.4	70.9
8	6	10	56.6	-45.3
8	6	11	19.2	-17.2
8	6	13	18.3	21.3
8	6	14	107.1	108.4
8	6	15	20.2	-25.4
8	6	16	115.2	-118.5
8	6	18	50.8	53.4
8	6	21	24.1	23.9
8	6	23	23.6	-35.7
9	6	2	127.5	131.8
9	6	3	25.8	16.0
9	6	4	90.1	-87.2
9	6	7	46.2	46.8
9	6	12	98.2	93.9
9	6	14	73.9	-72.2
9	6	16	17.9	-19.6
9	6	18	61.7	52.7
9	6	20	27.2	-27.8
9	6	21	11.7	-15.3
10	6	1	38.3	-32.1
10	6	2	44.6	-37.0
10	6	3	42.1	44.3
10	6	4	16.2	-13.9
10	6	5	46.5	-45.9
10	6	6	60.0	-65.1
10	6	7	48.4	48.9
10	6	8	69.9	64.1
10	6	9	37.8	-39.3
10	6	14	51.8	-46.6
10	6	16	42.4	41.0
10	6	21	21.6	-27.8
11	6	3	41.3	-37.6
11	6	4	61.0	-61.5
11	6	5	47.3	46.2
11	6	6	84.8	88.3
11	6	7	47.1	-48.7
11	6	8	31.2	31.7
11	6	10	52.1	-46.8
11	6	16	37.0	32.1
11	6	21	24.0	-7.3
12	6	5	35.9	33.1

H	K	L	|Fo|	Fc
12	6	6	57.3	46.9
12	6	7	44.8	-41.1
12	6	8	108.9	-106.3
12	6	10	48.9	53.4
12	6	16	31.0	22.7
12	6	17	19.2	25.7
12	6	18	22.4	-41.9
13	6	2	60.3	-54.3
13	6	4	112.9	125.5
13	6	6	104.4	-96.6
13	6	10	80.0	83.9
13	6	12	91.6	-85.2
13	6	14	48.7	40.2
13	6	16	20.1	-24.0
13	6	18	26.1	-26.1
14	6	0	61.8	-60.1
14	6	1	22.6	-24.2
14	6	2	34.6	31.4
14	6	6	90.4	-87.9
14	6	7	26.0	30.0
14	6	8	100.4	104.4
14	6	10	70.6	-73.7
14	6	15	29.5	34.6
14	6	18	30.3	37.6
15	6	2	34.4	39.3
15	6	3	31.8	35.3
15	6	4	69.4	-74.8
15	6	10	73.0	-70.7
15	6	12	45.9	49.7
16	6	6	27.1	30.1
16	6	7	23.8	-27.8
16	6	8	65.6	-64.0
16	6	10	35.8	36.3
16	6	15	23.0	-23.8
17	6	2	20.5	17.7
17	6	14	13.1	-17.7
18	6	0	67.0	68.1
18	6	2	24.0	-26.4
18	6	10	11.0	14.1
19	6	2	46.2	-45.7
19	6	4	39.6	36.8
20	6	0	57.2	-60.9
20	6	2	35.1	38.0
1	7	0	33.8	46.5
1	7	1	69.0	71.5
1	7	3	33.8	-36.7
1	7	4	36.2	20.0
1	7	5	10.8	4.1
1	7	6	47.7	56.5
1	7	7	100.7	117.6
1	7	8	61.3	-67.6
1	7	9	96.3	-89.4
1	7	10	36.1	36.7
1	7	11	46.9	55.1
1	7	13	26.0	26.2
1	7	15	49.7	-55.2
1	7	17	83.8	77.0
1	7	18	30.7	-25.4
1	7	23	40.6	41.8
2	7	1	37.1	23.8
2	7	2	68.9	-76.0
2	7	3	155.2	-174.7
2	7	4	41.1	-41.5
2	7	5	154.6	154.8
2	7	6	61.6	-53.6
2	7	7	157.7	-148.2
2	7	8	34.0	35.1
2	7	9	65.1	-58.1
2	7	10	122.6	118.0
2	7	11	130.0	117.8
2	7	13	66.3	-56.0
2	7	15	73.9	80.6
2	7	17	40.6	40.8
2	7	18	49.1	-45.7
2	7	19	44.9	-42.9
2	7	20	26.2	29.4
2	7	21	86.8	76.6
3	7	0	141.7	-149.0
3	7	1	216.7	-227.1
3	7	2	22.8	21.8
3	7	3	65.7	72.8
3	7	4	21.5	22.4
3	7	5	92.8	100.2
3	7	6	99.9	-112.4
3	7	7	195.7	-217.1
3	7	8	104.6	99.1
3	7	9	172.5	166.4
3	7	10	22.9	-19.1
3	7	11	31.2	-31.5
3	7	13	53.0	-45.0
3	7	15	115.2	113.8
3	7	16	40.5	-40.5
3	7	17	128.2	-113.2
3	7	18	32.6	31.2
3	7	19	31.5	34.2
3	7	21	30.8	17.9
3	7	23	76.7	-77.8
3	7	24	23.5	24.5
4	7	1	62.0	-61.8
4	7	2	27.3	-22.2
4	7	3	161.8	174.2
4	7	4	21.4	18.7
4	7	5	189.9	-220.4
4	7	6	68.2	66.0
4	7	7	55.0	83.5
4	7	9	86.3	73.4
4	7	10	42.9	-41.0
4	7	11	135.4	-131.3
4	7	12	25.9	30.7
4	7	13	98.3	108.9
4	7	15	46.4	-46.8
4	7	16	20.3	20.3

H	K	L	|Fo|	Fc
4	7	17	28.6	-34.5
4	7	18	39.6	40.3
4	7	19	68.2	60.5
4	7	21	72.3	-66.2
4	7	23	24.7	24.9
5	7	0	20.9	30.2
5	7	1	130.6	144.0
5	7	2	23.6	-13.6
5	7	3	69.1	-63.6
5	7	5	64.7	-58.7
5	7	7	69.4	68.7
5	7	8	55.7	-47.8
5	7	9	114.2	-110.8
5	7	10	28.0	26.9
5	7	11	26.6	24.3
5	7	13	15.8	10.5
5	7	15	104.3	-101.9
5	7	16	28.7	32.0
5	7	17	74.8	70.3
5	7	19	19.3	-25.5
5	7	21	16.0	-17.5
5	7	22	31.4	31.9
5	7	23	46.0	49.7
6	7	1	49.5	48.7
6	7	2	19.0	-20.3
6	7	3	26.7	20.6
6	7	4	15.5	21.8
6	7	5	62.8	77.0
6	7	6	13.4	-16.9
6	7	7	12.7	-22.9
6	7	8	29.8	-38.9
6	7	10	17.8	15.4
6	7	11	38.5	44.7
6	7	12	22.1	-19.2
6	7	13	61.0	-55.1
6	7	23	21.4	-20.8
7	7	0	22.8	-9.6
7	7	1	19.9	-27.8
7	7	2	32.8	36.0
7	7	3	31.3	-36.6
7	7	7	42.6	39.8
7	7	8	19.8	23.4
7	7	9	63.6	-62.2
7	7	12	27.7	28.2
7	7	16	34.8	28.7
8	7	1	42.3	46.6
8	7	2	22.5	-28.4
8	7	3	99.1	-86.5
8	7	4	32.0	34.0
8	7	5	112.1	109.8
8	7	6	19.5	-15.2
8	7	8	25.4	-26.0
8	7	9	42.7	-40.2
8	7	11	69.9	72.6
8	7	12	23.0	-29.9
8	7	13	57.2	-57.6
8	7	14	14.8	12.5
8	7	17	36.6	38.4
8	7	18	29.6	-32.2
8	7	19	52.3	-47.8
8	7	21	34.4	37.0
9	7	0	40.2	-45.0
9	7	1	152.0	-144.5
9	7	2	54.2	49.1
9	7	3	81.4	78.9
9	7	5	76.4	70.3
9	7	6	17.8	-17.1
9	7	7	124.9	-132.8
9	7	9	126.4	127.9
9	7	11	28.2	-26.7
9	7	12	28.6	-33.0
9	7	13	23.4	-25.5
9	7	14	45.2	50.1
9	7	15	88.9	79.8
9	7	16	56.8	-49.6
9	7	17	66.0	-65.1
9	7	21	20.6	19.7
10	7	1	85.2	-93.7
10	7	2	77.5	79.5
10	7	3	113.0	106.2
10	7	4	36.2	-22.8
10	7	5	121.2	-118.7
10	7	7	31.2	27.2
10	7	8	27.5	27.4
10	7	9	39.6	40.5
10	7	10	36.6	-43.8
10	7	11	98.0	-101.8
10	7	12	28.7	29.6
10	7	13	88.5	84.0
10	7	14	32.5	-31.0
10	7	15	36.7	-47.1
10	7	17	47.6	-44.4
10	7	18	28.2	27.7
10	7	19	64.4	57.9
10	7	21	46.4	-56.4
11	7	0	94.0	98.0
11	7	1	135.9	126.8
11	7	2	47.1	-47.4
11	7	3	30.8	-28.7
11	7	5	35.2	-29.5
11	7	7	130.0	122.1
11	7	9	88.4	-101.1
11	7	10	16.6	17.6
11	7	11	46.8	52.0
11	7	13	36.0	35.3
11	7	14	49.9	-43.5
11	7	15	88.1	-80.4
11	7	16	43.2	43.3
11	7	17	72.1	68.9
12	7	1	31.8	30.1
12	7	2	22.6	-22.6
12	7	3	81.1	-83.1

END 10M 33S

TABLE 25.

BIS-(DIPHENYL-PHOSPHINO)-ETHYLAMINE-MOLYBDENUM-TETRACARBONYL.

FRACTIONAL ATOMIC COORDINATES.

ATOMS	(x/a)	(y/b)	(z/c)
Mo	0.3241	0.3283	0.1874
P(1)	0.2554	0.4269	0.1174
P(2)	0.2558	0.4362	0.2504
O(1)	0.4927	0.4053	0.1556
O(2)	0.3764	0.2139	0.0777
O(3)	0.4036	0.2321	0.3046
O(4)	0.1668	0.2311	0.2019
N	0.2094	0.4731	0.1807
C(1)	0.1710	0.5592	0.1756
C(2)	0.0791	0.5541	0.1912
C(3)	0.4305	0.3774	0.1693
C(4)	0.3577	0.2546	0.1173
C(5)	0.3735	0.2704	0.2629
C(6)	0.2233	0.2699	0.1982
C(7)	0.3491	0.5618	0.1060
C(8)	0.3159	0.4986	0.0756
C(9)	0.3391	0.4784	0.0087
C(10)	0.3972	0.5293	-0.0236
C(11)	0.4267	0.5927	0.0076

- Cont'd -

TABLE 25 - Cont'd -

FRACTIONAL ATOMIC COORDINATES.

ATOMS	(x/a)	(y/b)	(z/c)
C(12)	0.4020	0.6153	0.0712
C(13)	0.1803	0.4067	0.0552
C(14)	0.1704	0.3282	0.03338
C(15)	0.1168	0.3042	-0.0161
C(16)	0.0774	0.3660	-0.0490
C(17)	0.0853	0.4455	-0.0310
C(18)	0.1368	0.4650	0.0205
C(19)	0.3006	0.5174	0.2934
C(20)	0.2542	0.5722	0.3311
C(21)	0.2917	0.6339	0.3591
C(22)	0.3741	0.6487	0.3507
C(23)	0.4198	0.5994	0.3171
C(24)	0.3858	0.5327	0.2860
C(25)	0.1830	0.4078	0.3124
C(26)	0.2148	0.3922	0.3761
C(27)	0.1648	0.3559	0.4250
C(28)	0.0930	0.3474	0.4156
C(29)	0.0525	0.3574	0.3494
C(30)	0.1041	0.3883	0.2953

TABLE 26.

STANDARD DEVIATIONS IN ATOMIC COORDINATES (in Å)

ATOMS	σ(x)	σ(y)	σ(z)
Mo	0.002	0.002	0.001
P(1)	0.005	0.008	0.004
P(2)	0.005	0.008	0.004
O(1)	0.016	0.021	0.016
O(2)	0.020	0.024	0.017
O(3)	0.021	0.024	0.016
O(4)	0.016	0.022	0.016
N	0.015	0.022	0.013
C(1)	0.021	0.032	0.019
C(2)	0.028	0.034	0.024
C(3)	0.019	0.027	0.017
C(4)	0.022	0.028	0.020
C(5)	0.021	0.031	0.021
C(6)	0.020	0.029	0.018
C(7)	0.017	0.027	0.017
C(8)	0.018	0.029	0.017
C(9)	0.018	0.028	0.017
C(10)	0.023	0.030	0.021
C(11)	0.024	0.032	0.022

- Cont'd -

TABLE 26 - Cont'd -

STANDARD DEVIATIONS IN ATOMIC COORDINATES (in Å)

ATOMS	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
C(12)	0.022	0.030	0.021
C133)	0.019	0.027	0.018
C(14)	0.024	0.030	0.023
C(15)	0.024	0.032	0.023
C(16)	0.020	0.029	0.019
C(17)	0.021	0.029	0.020
C(18)	0.022	0.029	0.021
C(19)	0.016	0.027	0.016
C(20)	0.021	0.032	0.020
C(21)	0.025	0.035	0.025
C(22)	0.028	0.036	0.029
C(23)	0.025	0.032	0.022
C(24)	0.019	0.027.	0.019
C(25)	0.018	0.029	0.018
C(26)	0.026	0.033	0.025
C(27)	0.029	0.038	0.028
C(28)	0.031	0.035	0.030
C(29)	0.032	0.038	0.031
C(30)	0.027	0.034	0.025

TABLE 27.

FINAL ANISOTROPIC THERMAL PARAMETERS (Uij).

ATOMS	(U11)	(U22)	(U33)	(2U23)	(2U31)	(2U12)
Mo	0.034	0.039	0.022	0.004	0.000	0.007
P(1)	0.031	0.041	0.018	-0.004	-0.000	-0.001
P(2)	0.035	0.020	0.020	-0.000	0.009	0.008
O(1)	0.055	0.089	0.064	0.001	0.014	-0.005
O(2)	0.119	0.091	0.057	-0.075	0.018	0.033
O(3)	0.107	0.108	0.066	0.102	-0.070	0.008
O(4)	0.066	0.023	0.069	-0.055	0.024	-0.024
N	0.039	0.063	0.023	-0.001	0.001	0.033

FINAL ISOTROPIC THERMAL PARAMETERS (Uij).
(for Carbon atoms).

C(1)	0.042	C(11)	0.055	C(21)	0.066
C(2)	0.072	C(12)	0.051	C(22)	0.077
C(3)	0.034	C(13)	0.036	C(23)	0.057
C(4)	0.045	C(14)	0.056	C(24)	0.040
C(5)	0.049	C(15)	0.059	C(25)	0.038
C(6)	0.041	C(16)	0.044	C(26)	0.069
C(7)	0.031	C(17)	0.048	C(27)	0.077
C(8)	0.034	C(18)	0.050	C(28)	0.080
C(9)	0.032	C(19)	0.029	C(29)	0.088
C(10)	0.052	C(20)	0.048	C(30)	0.071

DISCUSSION

The final results of this analysis establish the molecular structure and the relative stereochemistry of bis-(diphenyl-phosphino)-ethylamine molybdenum tetracarbonyl. The character of the P-N-P ligand is confirmed as bidentate with the two phosphorus atoms occupying cis-position. The coordination about the molybdenum atom is distorted octahedral, the distortion arising from the bridging nitrogen atom in the P-N-P ligand, which restricts the position which coordinating phosphorus atoms can take up. The P-$\hat{Mo}$-P angle is 64.8 ± 0.18°, other angles at molybdenum centre range from 86° to 100° (Table 29).

Each of the phosphorus atoms is approximately tetrahedrally bonded with an average valency angle of 109.5 ± 0.30° (Table 29). The mean P-C(aryl) bond lengths is 1.81 ± 0.01Å. It is noteworthy that the four independent P-C(aryl) bond lengths give approximately the same values-varying from 1.80 to 1.81Å (Table 28). The mean P-N bond length (1.71 ± 0.01Å) compares quite favourably with the P-N bond length (1.72 ± 0.01Å) in palladium complex (Part 1) and does not differ significantly from the value of 1.75 ± 0.03Å for the bond distance between nitrogen and the four-coordinated phosphorus in the ethyl iodide adduct (Part II). The P-$\hat{N}$-P angle 103.8 ± 1° in this compound (PNP-Mo-tetracarbonyl) is intermediate between the value of 97.7 ± 0.7° obtained in the palladium complex (Part I) and the value of 111.1 ± 1.6° registered in the ethyl iodide adduct

BIS-(DIPHENYL-PHOSPHINO)-ETHYLAMINE MOLYBDENUM TETRACARBONYL.

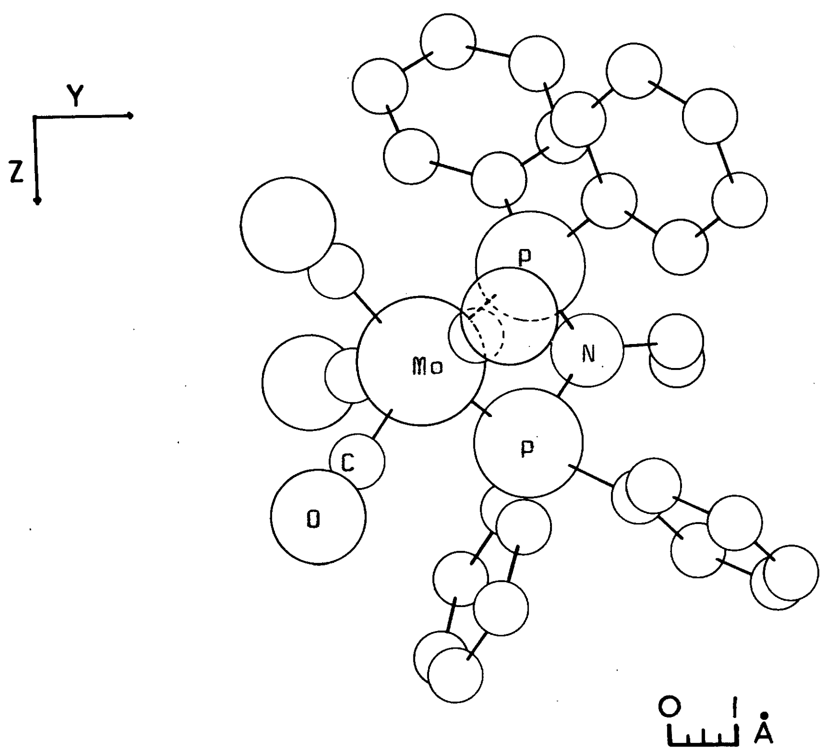
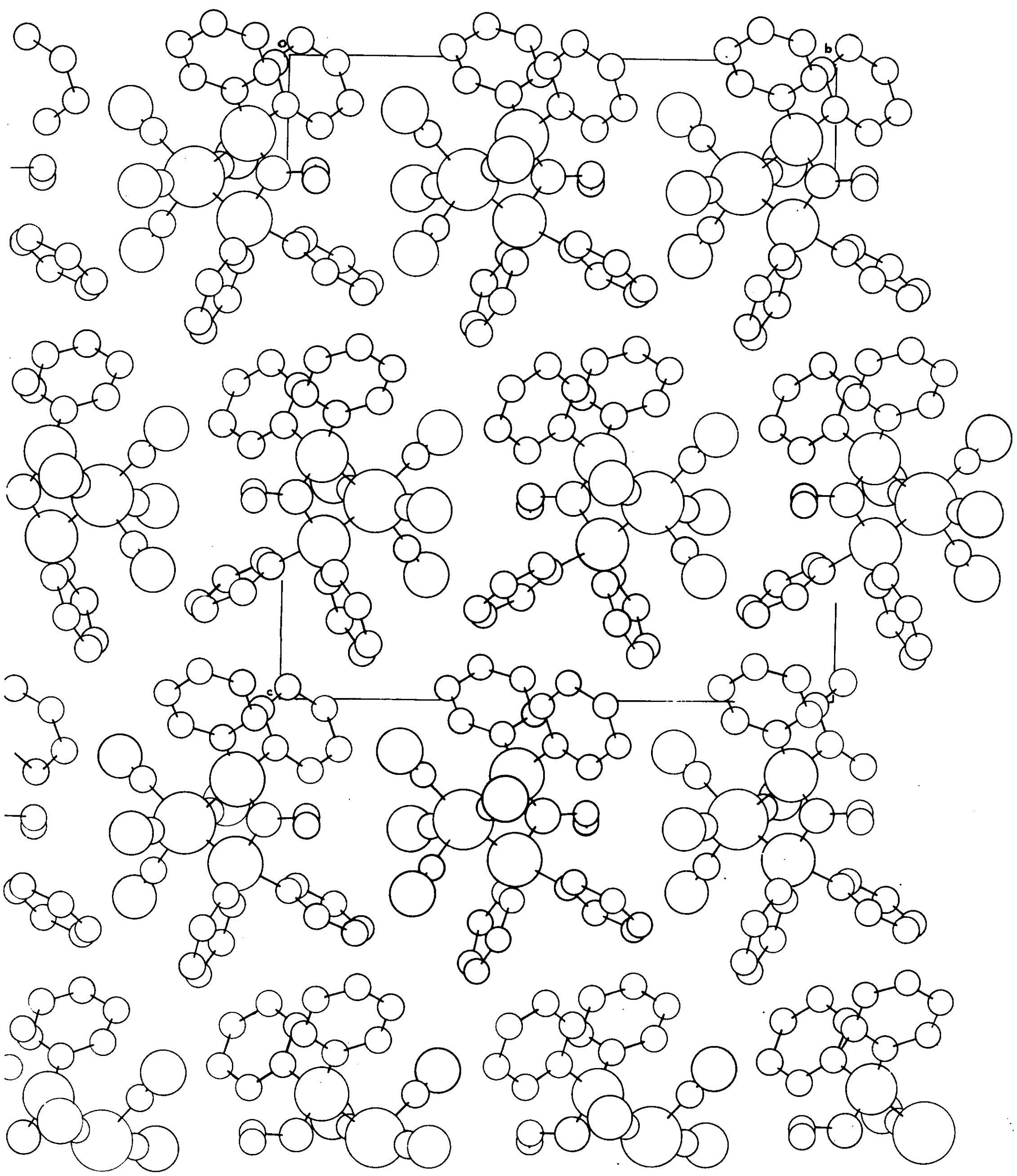


Fig. I. Atomic arrangements as viewed down the a-axis.

BIS-(DIPHENYL-PHOSPHINO)-ETHYLAMINE MOLYBDENUM TETRACARBONYL.



Scale 0 1 2 Å

Fig. 4. Packing of the molecules in projection down the a-axis.

BIS-(DIPHENYL-PHOSPHINO)-ETHYLAMINE MOLYBDENUM TETRACARBONYL.

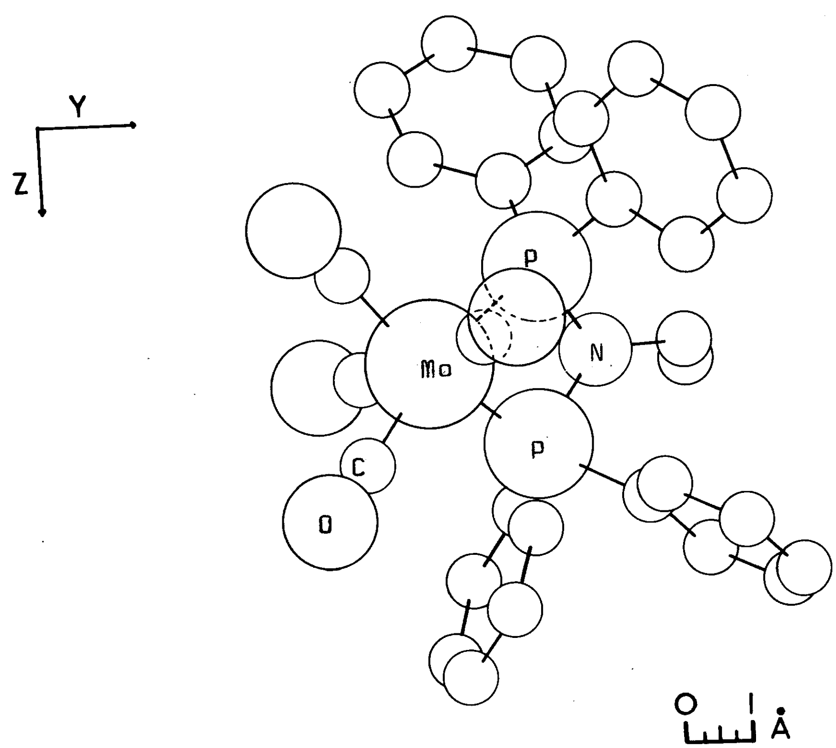


Fig. I. Atomic arrangements as viewed down the a-axis.

BIS-(DIPHENYL-PHOSPHINO)-ETHYLAMINE MOLYBDENUM TETRACARBONYL.

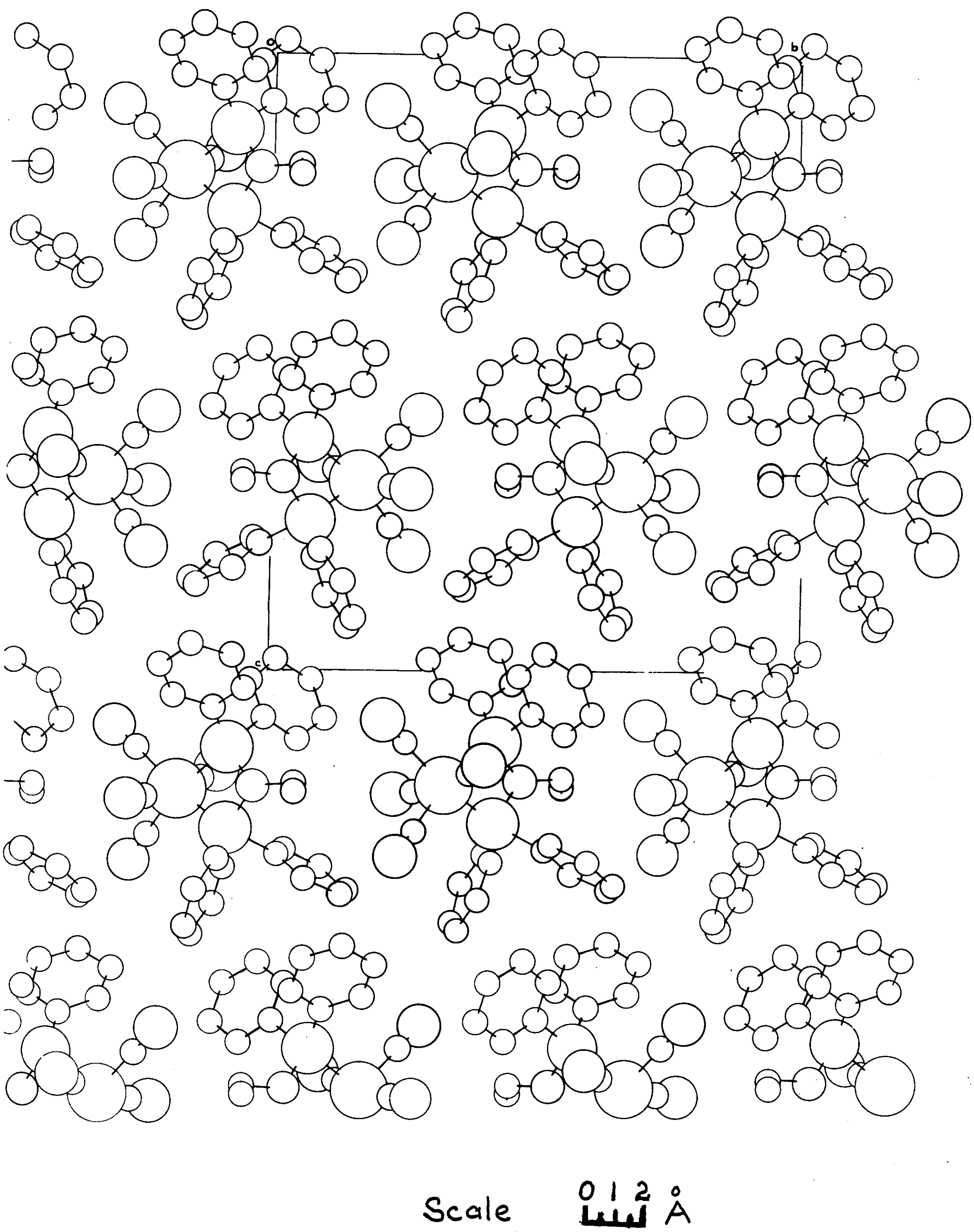


Fig. 4. Packing of the molecules in projection down the a-axis.

TABLE 28.

Inter-atomic Bond Lengths in Å, with estimated Standard Deviations.

Mo	-	P(1)	2.49(0.007)	C(10)	-	C(11)	1.35(0.04)
Mo	-	P(2)	2.52(0.007)	C(11)	-	C(12)	1.40(0.03)
Mo	-	C(3)	1.98(0.02)	C(12)	-	C(7)	1.46(0.03)
Mo	-	C(4)	2.00(0.02)	C(13)	-	C(14)	1.43(0.04)
Mo	-	C(5)	1.97(0.02)	C(14)	-	C(15)	1.41(0.03)
Mo	-	C(6)	2.00(0.02)	C(15)	-	C(16)	1.42(0.04)
P(1)	-	N	1.69(0.02)	C(16)	-	C(17)	1.42(0.04)
P(1)	-	C(8)	1.80(0.02)	C(17)	-	C(18)	1.39(0.03)
P(1)	-	C(13)	1.81(0.02)	C(18)	-	C(13)	1.42(0.03)
P(2)	-	C(19)	1.81(0.02)	C(19)	-	C(20)	1.44(0.03)
P(2)	-	C(25)	1.81(0.02)	C(20)	-	C(21)	1.36(0.04)
P(2)	-	N	1.73(0.02)	C(21)	-	C(22)	1.41(0.04)
O(1)	-	C(3)	1.17(0.03)	C(22)	-	C(23)	1.33(0.04)
O(2)	-	C(4)	1.11(0.03)	C(23)	-	C(24)	1.43(0.04)
O(3)	-	C(5)	1.18(0.03)	C(24)	-	C(19)	1.45(0.03)
O(4)	-	C(6)	1.16(0.03)	C(25)	-	C(26)	1.42(0.03)
C(1)	-	C(2)	1.57(0.03)	C(26)	-	C(27)	1.43(0.04)
C(1)	-	N	1.62(0.04)	C(27)	-	C(28)	1.22(0.04)
C(7)	-	C(8)	1.37(0.03)	C(28)	-	C(29)	1.51(0.04)
C(8)	-	C(9)	1.44(0.03)	C(29)	-	C(30)	1.49(0.04)
C(9)	-	C(10)	1.46(0.03)	C(30)	-	C(25)	1.40(0.03)

TABLE 29.

INTERBOND ANGLES (^{o})

P(1) - Mo	- P(2)	65		C(19) - P(2)	- N	107	
P(2) - Mo	- C(3)	163		N - P(2)	- C(25)	111	
C(3) - Mo	- C(4)	96		P(1) - N	- P(2)	104	
C(4) - Mo	- C(5)	91		P(1) - N	- C(1)	124	
C(5) - Mo	- C(6)	173		P(2) - N	- C(1)	125	
C(6) - Mo	- P(2)	91		Mo - C(3)	- O(1)	177	
P(1) - Mo	- C(3)	99		Mo - C(4)	- O(2)	179	
P(2) - Mo	- C(4)	100		Mo - C(5)	- O(3)	175	
C(3) - Mo	- C(5)	90		Mo - C(6)	- O(4)	175	
C(4) - Mo	- C(6)	89		Mo - P(1)	- C(5)	164	
C(5) - Mo	- P(1)	91		Mo - P(2)	- C(6)	86	
C(6) - Mo	- P(2)	100		C(3) - Mo	- C(4)	84	
Mo - P(1)	- N	96		C(12) - C(7)	- C(8)	122	
Mo - P(1)	- C(8)	111		C(7) - C(8)	- C(9)	120	
Mo - P(1)	- C(13)	126		C(8) - C(9)	- C(10)	117	
C(8) - P(1)	- C(13)	101		C(9) - C(10)	- C(11)	121	
C(8) - P(1)	- N	107		C(10) - C(11)	- C(12)	123	
C(13) - P(1)	- N	107		C(11) - C(12)	- C(7)	116	
Mo - P(2)	- N	94		(18) - C(13)	- C(14)	117	
Mo - P(2)	- C(19)	129		C(13) - C(14)	- C(15)	125	
Mo - P(2)	- C(25)	117		C(14) - C(15)	- C(16)	114	
C(19) - P(2)	- C(25)	99		C(15) - C(16)	- C(17)	124	

- Cont'd

C(16) - C(17) - C(18)	119	C(23) - C(24) - C(19)	119
C(17) - C(18) - C(13)	121	C(30) - C(25) - C(26)	122
C(24) - C(19) - C(20)	118	C(25) - C(26) - C(27)	119
C(19) - C(20) - C(21)	119	C(26) - C(27) - C(28)	121
C(20) - C(21) - C(22)	123	C(27) - C(28) - C(29)	124
C(21) - C(22) - C(23)	120	C(28) - C(29) - C(30)	115
C(22) - C(23) - C(24)	121	C(29) - C(30) - C(25)	117

<u>Some selected Bond angles with their e.s.d.</u>

P(1) - Mo - P(2) 64.8(0.18)

P(1) - N - P(2) 103.8(1.00)

BIS-(DIPHENYL-PHOSPHINO)-ETHYLAMINE MOLYBDENUM TETRACARBONYL.

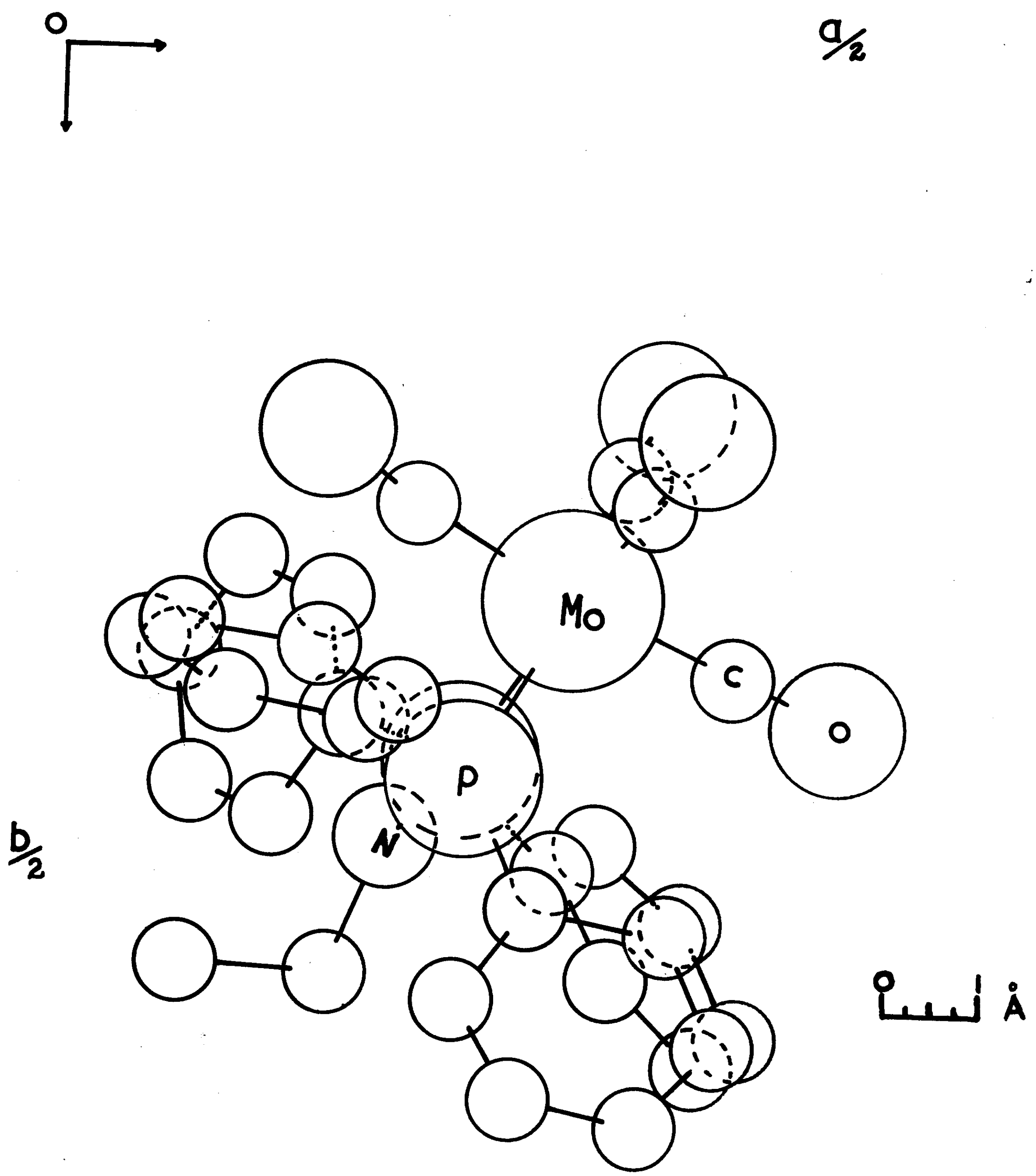


Fig. II. Atomic arrangement as viewed down the c-axis.

(Part II). Other bond lengths and angles shown in Tables 27 and 28 are normal and call for no comment except for N–C(1·62 ± 0·04 Å), which must be in error.

A four membered ring is created by P(1), N, O(2) and Mo, like the P–N–P–Pd it is approximately planar (Table 31). The regularity of the four-membered ring formed by the P–N–P ligand in complex formation with the transition metals can be seen by comparing the two rings formed by the P–N–P ligand with palladium and molybdenum atoms (Figs. III and IV). Mean values of bond lengths are used in the diagrams.

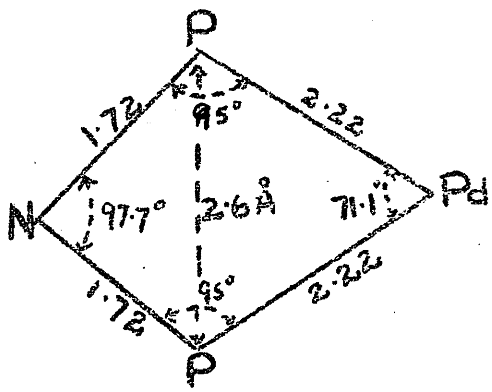


Fig III

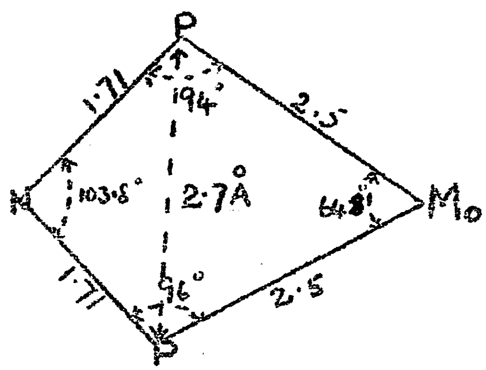


Fig IV

Examinations of the above diagrams (Figs. III and IV) shows that apart from the P–N distance which is virtually same in the two complexes, the valency angle at each of the four phosphorus atoms is approximately 95°. Even the P–P distances are about the same, despite the fact that the P–N–P ligand is attached to different entities in the two complexes.

The equation of the mean plane calculated through P(1), P(2), C(4) and C(5) is $0{\cdot}844x + 0{\cdot}530y - 0{\cdot}084z - 7{\cdot}222 = 0$, where x, y, z are co-ordinates expressed in Angstroms units. The deviations of the atoms from this plane are quite small (Table 32).

TABLE 30.

INTRA-MOLECULAR NON-BONDED DISTANCES.

Mo	... O(2)	3.09	O(1)	... C(4)	3.52	O(4)	... C(14)	3.78
Mo	... O(4)	3.13	O(1)	... C(11)	3.56	O(4)	... C(25)	3.78
Mo	... N	3.15	O(1)	... C(8)	3.72	O(4)	... C(24)	3.91
Mo	... O(1)	3.17	O(1)	... C(5)	3.74	N	... C(8)	2.80
Mo	... O(3)	3.18	O(2)	... C(1)	3.41	N	... C(13)	2.82
Mo	... C(8)	3.70	O(2)	... C(3)	3.48	N	... C(19)	2.84
Mo	... C(25)	3.71	O(2)	... C(2)	3.65	N	... C(25)	2.92
Mo	... C(13)	3.83	O(2)	... C(6)	3.66	N	... C(7)	3.17
Mo	... C(19)	3.91	O(2)	... C(5)	3.86	N	... C(30)	3.25
P(1)	... P(2)	2.69	O(3)	... C(16)	3.42	N	... C(18)	3.45
P(1)	... C(9)	2.75	O(3)	... C(15)	3.68	N	... C(6)	3.52
P(1)	... C(14)	2.78	O(3)	... C(3)	3.73	N	... C(14)	3.93
P(1)	... C(18)	2.86	O(3)	... C(6)	3.75	C(1)	... C(7)	3.29
P(1)	... C(6)	3.20	O(3)	... C(2)	3.83	C(1)	... C(20)	3.44
P(1)	... C(3)	3.22	O(3)	... C(21)	3.83	C(1)	... C(4)	3.59
P(1)	... C(4)	3.42	O(3)	... C(20)	3.85	C(2)	... C(4)	3.91
P(1)	... C(19)	3.95	O(3)	... C(4)	3.87	C(3)	... C(4)	2.65
P(2)	... C(26)	2.73	O(4)	... C(22)	3.39	C(3)	... C(5)	2.80
P(2)	... C(30)	2.81	O(4)	... C(30)	3.46	C(3)	... C(8)	3.40
P(2)	... C(6)	3.10	O(4)	... C(12)	3.50	C(3)	... C(6)	3.97

- Cont'd -

TABLE 30 - Cont'd -

INTRA-MOLECULAR NON-BONDED DISTANCES.

P(2)	...	C(5)	3.47	O(4)	...	C(7)	3.51	C(3)	...	C(9)	3.98
P(2)	...	C(3)	3.49	O(4)	...	C(23)	3.55	C(4)	...	C(6)	2.79
P(2)	...	C(8)	3.82	O(4)	...	C(4)	3.64	C(4)	...	C(5)	2.96
P(2)	...	O(4)	3.95	O(4)	...	C(21)	3.65	C(4)	...	C(14)	3.77
C(6)	...	C(25)	3.38	O(4)	...	C(5)	3.73	C(5)	...	C(6)	2.83
C(6)	...	C(30)	3.46	C(12)	...	C(14)	3.93	C(20)	...	C(9)	3.95
C(6)	...	C(14)	3.57	C(15)	...	C(18)	2.88	C(21)	...	C(24)	2.77
C(6)	...	C(13)	3.79	C(15)	...	C(12)	3.71	C(21)	...	C(9)	3.67
C(7)	...	C(24)	3.71	C(15)	...	C(11)	3.74	C(22)	...	C(28)	3.70
C(8)	...	C(13)	2.79	C(15)	...	C(21)	3.99	C(22)	...	C(29)	3.79
C(8)	...	C(18)	3.24	C(16)	...	C(13)	2.80	C(22)	...	C(9)	3.91
C(8)	...	C(14)	3.90	C(16)	...	C(20)	3.96	C(22)	...	C(27)	3.92
C(9)	...	C(13)	3.07	C(23)	...	C(23)	3.81	C(17)	...	C(14)	2.79
C(9)	...	C(18)	3.39	C(17)	...	C(20)	3.97	C(25)	...	C(28)	2.77
C(9)	...	C(14)	3.86	C(19)	...	C(25)	2.75	C(26)	...	C(29)	2.83
C(10)	...	C(7)	2.79	C(19)	...	C(26)	3.08	C(27)	...	C(30)	2.86
C(10)	...	C(26)	3.90	C(19)	...	C(30)	3.96	C(27)	...	O(2)	3.37
C(12)	...	C(23)	3.74	C(20)	...	C(23)	2.82	C(28)	...	O(2)	3.47

TABLE 31.

INTER-MOLECULAR DISTANCES < 4Å

P(1)	...	C(2)v	3.96	C(1)	...	C(30)vi	3.97
P(2)	...	C(2)v	3.77	C(2)	...	C(2)ii	3.55
P(2)	...	C(7)v	3.95	C(2)	...	C(30)vi	3.57
O(1)	...	O(3)ii	3.54	C(2)	...	C(18)vi	3.89
O(1)	...	C(5)ii	3.62	C(2)	...	C(25)vi	3.91
O(1)	...	C(23)iv	3.69	C(3)	...	C(24)v	3.64
O(1)	...	C(7)v	3.74	C(3)	...	C(7)v	3.68
O(1)	...	C(3)ii	3.79	C(3)	...	C(5)ii	3.99
O(1)	...	O(1)ii	3.81	C(3)	...	C(3)ii	3.99
O(1)	...	C(24)v	3.86	C(7)	...	C(19)vi	3.94
O(2)	...	C(28)i	3.47	C(9)	...	C(21)i	3.67
O(2)	...	C(16)ii	3.67	C(9)	...	C(22)i	3.91
O(3)	...	C(3)ii	3.77	C(9)	...	C(20)i	3.95
O(3)	...	O(3)ii	3.90	C(10)	...	C(11)iv	3.63
N	...	C(20)v	3.56	C(10)	...	C(10)iii	3.70
N	...	C(24)v	3.77	C(10)	...	C(23)v	3.92
C(1)	...	C(18)vi	3.57	C(10)	...	C(24)v	3.99
C(1)	...	C(13)vi	3.58	C(11)	...	C(15)i	3.74
C(1)	...	C(25)vi	3.80	C(12)	...	C(15)i	3.71

The subscripts refer to the following positions:

i	$\frac{1}{2}-x$, $\frac{1}{2}-y$, $-\frac{1}{2}+z$	iv	$1\frac{1}{2}+x$, $1\frac{1}{2}+y$, $1\frac{1}{2}-z$
ii	$1-x$, y, $\frac{1}{2}-z$	v	$1\frac{1}{2}-x$, $1\frac{1}{2}+y$, z
iii	$1-x$, $1-y$, $1-z$	vi	$1\frac{1}{2}-x$, $\frac{1}{2}+y$, z

TABLE 32.

EQUATIONS OF MEAN PLANES AND DISTANCES (Å) OF ATOMS FROM THESE PLANES.

(a) Plane through C(5), C(4), Mo, P(1), P(2), N,

$$0.8253x + 0.5581y - 0.0862z - 7.2590 = 0.$$

C(5)	0.027	C(1)	0.162
C(4)	-0.091	C(3)	2.002
Mo	0.033	C(6)	-1.935
P(1)	0.155		
P(2)	0.020		
N	-0.143		

(b) Plane through P(1), P(2), N, C(1),

$$0.8384x + 0.5438y - 0.0356z - 7.4242 = 0.$$

P(1)	0.060	Mo	0.049
P(2)	0.059	C(2)	-1.269
N	-0.195		
C(1)	0.076		

(c) Plane through P(1), C(4), C(5), P(2),

$$0.8442x + 0.5295y - 0.0840z - 7.2215 = 0.$$

P(1)	0.067	C(3)	1.996
C(4)	-0.061	C(6)	-1.951
C(5)	0.060		
P(2)	-0.066		

Dihedral angle between plane (a) and plane (b) is 177°

" " " " (b) " " (c) " 177.1°

The x, y, z in the plane equations refer to the coordinates in Å expressed in terms of **a**, **b**, **c**.

Equidistant from the plane are C(3) and C(6) to form a distorted octahedral arrangement as suggested by the values of the valency angles at the molybdenum.

The average value of Mo-C is 1.99 ± 0.01Å while the mean C-O bond length is 1.15 ± 0.015Å. This value of 1.99Å for Mo-C is a bit shorter than the value of 2.06 ± 0.02Å obtained by Najarian (1957) for the Mo-C bond length in molybdenum hexacarbonyl. This difference is probably significant in view of the dependence of Mo-C bond length on bond order (Cotton et al, 1965).

The bond order in the Mo-C of PNPMo tetracarbonyl can be estimated by adopting the method suggested by Cotton et al (1965). Evaluation of this is vital for a thorough understanding of the donor-acceptor property of the P-N-P ligand and probably may lead to additional evidence in support of the delocalisation of the nitrogen lone pair.

The structure of cis-(Diethylene triamine) molybdenum tricarbonyl has recently been published (Cotton et al, 1965). The comparison of the Mo-C bond lengths obtained by Cotton with those recorded in the present work shows some differences and helps towards the determination of the bond-order of Mo-C in PNPMo-tetracarbonyl.

Cotton et al.		Present work.	
Mo - C(1)	1.93 ± 0.02Å	Mo - C(3)	2.00 ± 0.02Å
Mo - C(2)	1.95 ± 0.02Å	Mo - C(4)	1.98 ± 0.02Å
Mo - C(3)	1.94 ± 0.02Å	Mo - C(5)	2.00 ± 0.02Å
		Mo - C(6)	1.98 ± 0.02Å
Mean Mo - C = 1.94Å.		Mean Mo - C = 1.99Å.	

These two values of Mo-C though close differ appreciably in their values of bond-orders (Fig. V). The values of 2.06 ± 0.02Å (Najarin, 1957) and 2.08 ± 0.04Å (Brockway, 1938) for Mo-C in molybdenum hexacarbonyl are on the other hand much longer than either Cotton's value or that obtained in the present work.

From all available data, Cotton et al (1965) obtained the graph shown below (Fig. V) for determining the Mo-C bond-order from a known value of Mo-C bond-length. The value of Mo-C bond length (1.99Å) in the present work is plotted on Cotton's graph and its position is indicated by A. Position B corresponds to the Mo-C bond length and bond-order in the molybdenum hexacarbonyl.

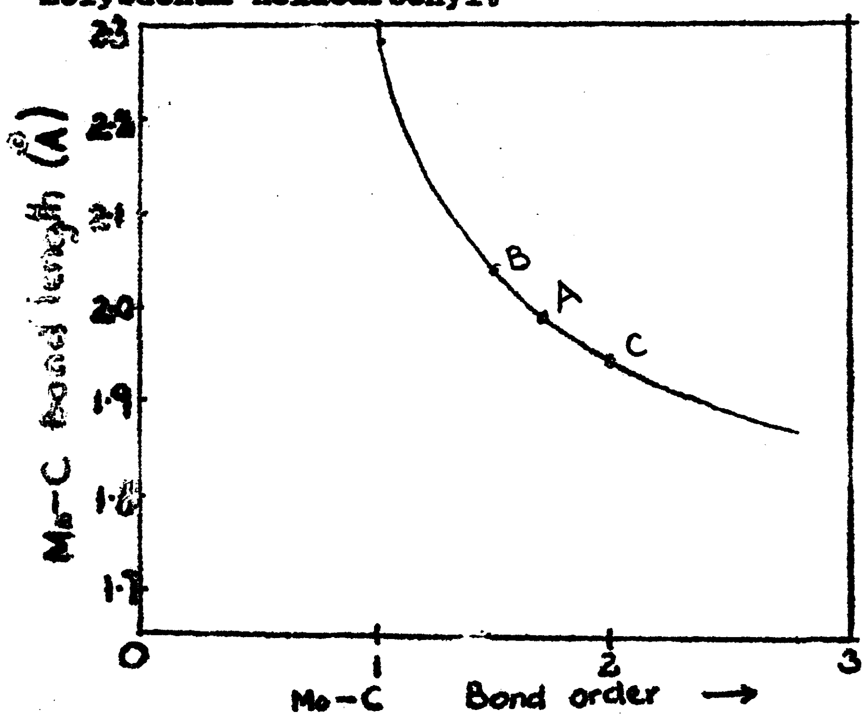


Fig V

Bond-orders 1.5 and 2.0 have been assigned to Mo-C in molybdenum hexacarbonyl (B) and cis-Mo(diene) tricarbonyl marked (C). The basis of assignment has been discussed by Cotton (1964). From the position of A on the graph the bond-order in Mo-C of PNP-Mo-tetracarbonyl is about 1.75Å. This is consistent with the theory that there should be more of double bond character in Mo-C of PNP-Mo-tetracarbonyl than in the Mo-C of the molybdenum hexacarbonyl since P-N-P ligand is a poorer donor than carbon monoxide.

The shortening observed in Mo-C would cause the lengthening of the C-O bond, although C-O bond lengths in complexes are not reliable enough for determining differences between bond-orders in the range 2 to 3, there is evidence to support the above statement of C-O lengthening from the spectra study. Payne et al (1965) obtained the values of 1980cm^{-1} for the C-O stretching frequency in the hexacarbonyl and 1873cm^{-1} in the PNP-Mo-tetracarbonyl.

The above value of bond-order (1.75) for Mo-C suggests therefore that there is more of dπ-pπ bonding in the Mo-C of the complex than of the molybdenum hexacarbonyl. This will also mean that the central metal atom dissipates more of its charge into the p -orbital of the C-atom rather than into the d -orbital of phosphorus. The situation leaves the Mo-P as formed from almost σ-bond. Also if there is partial double bond formation in P-N due to delocalisation of electrons as previously discussed, this will enhance the single bond character of Mo-P. In fact, the value of 2.50 ± 0.005Å obtained for Mo-P in this P-N-P complex is not significantly different from the expected value for a Mo-P single bond (2.46Å) (Rundqvist, 1965). This result supports the established fact that C-O is a better π-bonder than phosphorus compounds and gives a conclusive evidence on the delocalisation of electrons in P-N-P ligand.

TABLE 33.

Summary of some P-C(alkyl) and P-C(aryl) bond-lengths.

Compound	P-Calkyl	P-Caryl	References.
$[Pt_2(SCN)_2Cl_2(PC_3H_7)_2]$	1.88	-	Rowe et al., 1960
$[(C_6H_5)(C_2H_5)_2P]ReCl_3$	1.86±0.05	1.77±0.08	Cotton et al., 1964
$[(Ph_2P)_2NEt]PdCl_2$	-	1.81±0.01	Present work.
$P(CH_3)_3$	1.84±.003	-	Lide et al., 1958
$P(CH_3)_3$	1.85±.003	-	Bartell et al., 1960
$P(Ph)_3$	-	1.83±.003	Daly, J.J., 1964
$[Ph_2PNEtP.Ph_2Et]^+I^-$	1.81±0.05	1.81±0.02	Present work.
$[ReOCl_3(PEt_2Ph)_2]$	1.86	1.78	Ehrlich et al., 1963
$[Ph_2P.NEt.PPh_2]Mo(CO)_4$	-	1.81±0.01	Present work.

(Bond-length values are mean where there are several of similar type).

PART IV

X-RAY STRUCTURE ANALYSIS OF LEAD THIOCYANATE

4.1. INTRODUCTION

The complexing ability of the thiocyanate ion has led to its use in qualitative and quantitative analyses, (Vogel, 1962) The thiocyanate ion exhibits linkage isomerism, bonding to the metal ion either through its sulphur or nitrogen atom. When bonded through sulphur, the compounds formed are called thiocyanate. If, however, the bond is through nitrogen, the name isothiocyanate is appropriate. For simplicity this class of compounds will be referred to as thiocyanates (without regard to whether the metal ion is S-bonded or N-bonded) throughout this text.

Very little has been done in the study of transition metal thiocyanates by X-Ray methods, but information is available from other physical methods for some thiocyanate complexes. By studying the C-N and C-S stretching frequencies attempts have been made (Lewis et al, 1961) to classify the isomers of the transition metal thiocyanates. In their discussions, it can be inferred that the elements of the first transition series are bonded through N in the formation of thiocyanate complexes whereas the elements of the second and third series are bonded through sulphur. Lieber et al, (1959), used measured C-N frequencies to decide between thiocyanato - and isothiocyanato - bonding. Fujita et al, (1956), Mitchell et al, (1960) have all examined this criterion in extensive details and have made some broad correlations. Difficulty arises, however, in that the C-N frequency is affected by a number of variables apart from the donor atom, and in particular overlap occurs between the two classes.

From the measurements of the C–S (755 cm^{-1}) and the C–N (2114 cm^{-1}) stretching frequencies of lead thiocyanate, Torrance (1965) found that there was not enough evidence from the above values to predict the type of linkage involved in lead thiocyanate. Previous workers have proved that Mn, Ni, Co and Cu form isothiocyanates (that is N–bonded). This is established in the crystal structure analysis of $[Co(NCS)_4]^{2-}$, Takencki, 1957, of $[Ni(NH_3)_4(NCS)_2]$, Zudanov et al, 1950. N. Gilli (1961) has shown that thiocyanate groups serve two functions in the structure of $Cd(SCN)_4^{2-}$, that is bonding through sulphur and nitrogen to form a structure such as SCN – M – SCN. The situation in lead thiocyanate is not certain.

4.2. EXPERIMENTAL

A sample of the compound – lead thiocyanate – prepared by Dr. Bacon of the Queen's University, Belfast was kindly made available to us by Miss Ida Woodward also of Queen's University. Crystals for the X–Ray work were obtained by cutting to suitable sizes. A crystal of an average width 0·015 cm was used for collecting intensity data. The value of μR = 5·2 was used to correct for absorptions, R – the radius – being taken as half the average width. The ratios of the unit translations as predicted by Groth, (1908) are 0·631 : 1 : 1·623. Groth cell as related to that used in this work is shown in Fig. 1. The unit cell transformation matrix is given by 100/010/$\bar{1}$02.

LEAD THIOCYANATE

UNIT CELL TRANSFORMATION.

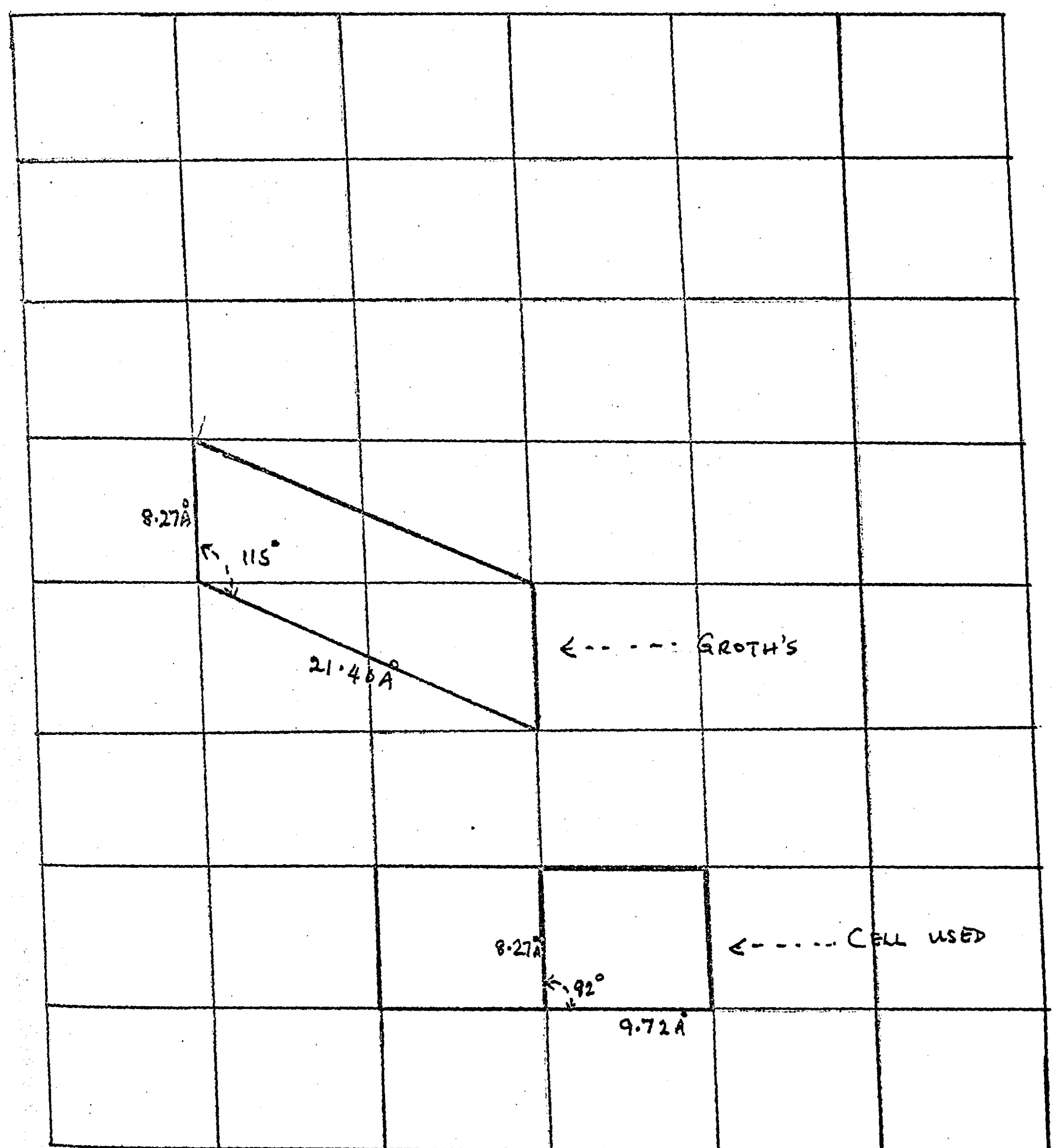


Fig. 1

4.3. INTENSITY DATA

Rotation, oscillation and Weissenberg photographs were taken using Cu-Kα radiation ($\lambda = 1{\cdot}542$ Å). The intensity data were measured visually from Weissenberg photographs for the h0l, h1l, h2l and h3l sets obtained by the multiple film technique (Robertson, 1943). The film factor used to correlate the intensities on successive films of a series in non-equitorial layers was calculated from

$R = 1{\cdot}29 \exp(0{\cdot}94 \sec \alpha)$ where α = the angle which the incident beam makes with the normal to the film, (Rossman, 1956). The intensities were corrected by the usual factors. The various zones were placed on the same relative scale by comparison of the observed and calculated structure amplitudes.

4.4. CRYSTAL DATA

Crystals of lead thiocyanate with M = 323·4 are monoclinic, $\underline{a} = 9{\cdot}72 \pm 0{\cdot}03$, $\underline{b} = 6{\cdot}57 \pm 0{\cdot}02$, $\underline{c} = 8{\cdot}27 \pm 0{\cdot}03$ Å; $\beta = 92{\cdot}0 \pm 0{\cdot}5°$. Volume of the unit cell, V = 527·8 Å^3. $\rho_{cal} = 4{\cdot}07$ g/cm^3, Z = 4. F(000) = 560. $\mu = 680$ cm^{-1} for X-Rays, ($\lambda = 1{\cdot}542$). $\sum f_H^2 = 6724$, $\sum f_L^2 = 682$.

Absent spectra : (hkl) when h+k is odd
(h0l) " l is odd
(0k0) " k is odd.

Space Group: C2/c - C_{2h}^6 or Cc - C_s^4. The centred space group C2/c was chosen without prior application of any statistical tests. The choice appears to have been justified by the successful solution of the structure. This requires the

Pb - atom to be in a special position either at a centre of symmetry or on a two-fold axis.

4.5. HEAVY ATOM POSITION

The position of Pb - atom was determined from a 3-D. Patterson synthesis. The atom (Pb) was found to occupy a special position 0, y, $\frac{1}{4}$. Attempt to solve other vectors obtained in the map only resulted in the probable position of sulphur. The co-ordinates thus found were for

Pb	x = 0·000 ,	y = 0·115 ,	z = 0·250.
S	x = 0·329 ,	y = -0·115 ,	z = 0·172.

Since the position of sulphur was not certain, only the co-ordinates of lead were used in the first structure - factor calculation. R-factor was 30·0%, (Table 34). Using the signs appropriate to the rest of the atoms and delta ($|Fo| - |Fc|$) as coefficients, a three-dimensional difference Fourier synthesis was computed along the z-axis. Pseudo--symmetry and anisotropic effects around Pb rendered the map obtained difficult to interpret. In the subsequent structure--factor calculation lead was assigned anisotropic temperature factor. R dropped to 27·2%, and in a second difference map, the thiocyanate group was obvious. The positions of sulphur, carbon and nitrogen (Figs. 2,3, and 4) are marked B, C, and D on Figs. 2, 3, 4. While the whole structure revealed by means of superimposed contours is shown in Fig. 5. Thus co-ordinates were assigned to sulphur, carbon and nitrogen. A set of structure-factors calculated with all atoms gave an R-value of 22·3%.

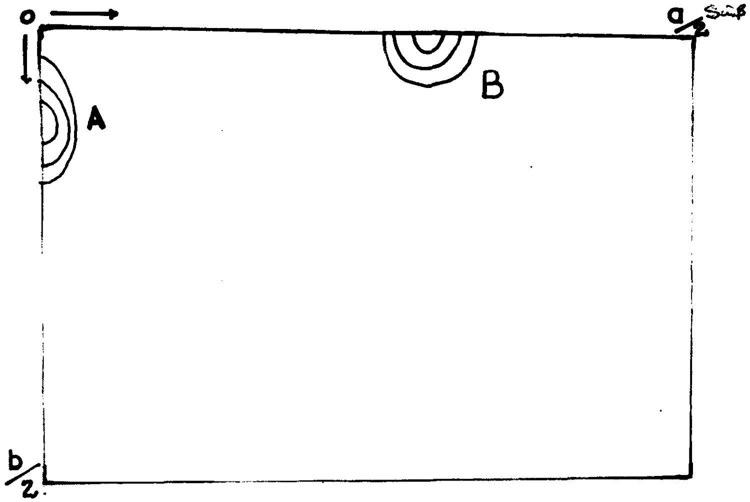


Fig 1a Section at z=0·17. 0 1 Å

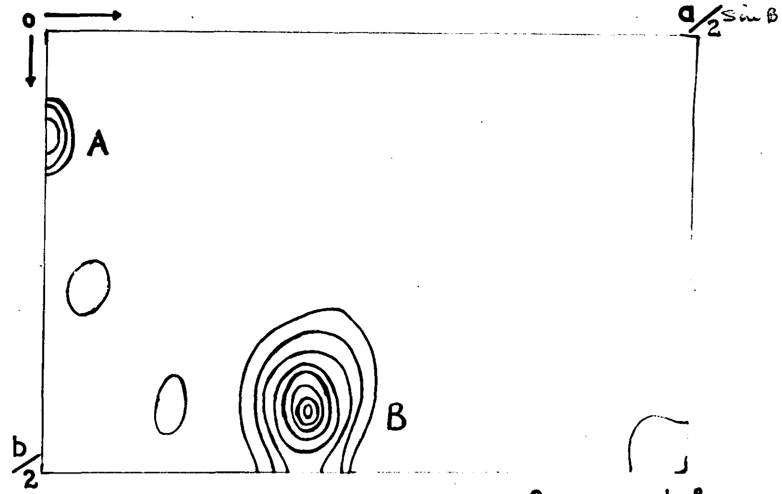


Fig 2. Section z=0·33. 0 1 Å

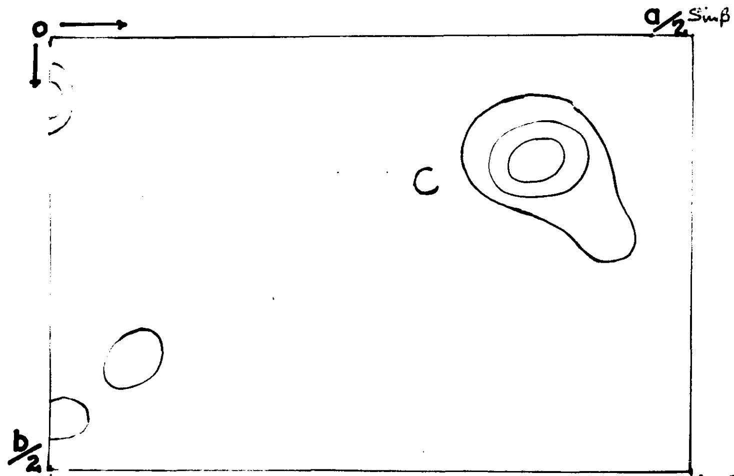


Fig 3. Section z=0·10 0 1 Å

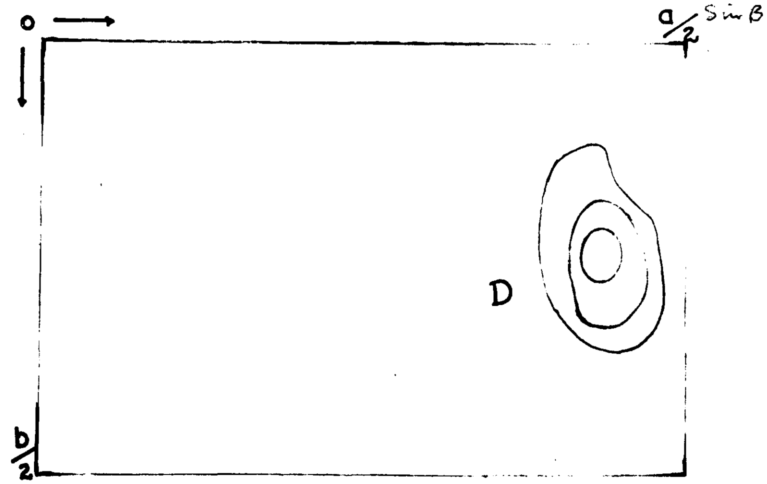


Fig 4. Section at z=0·07. 0 1 Å

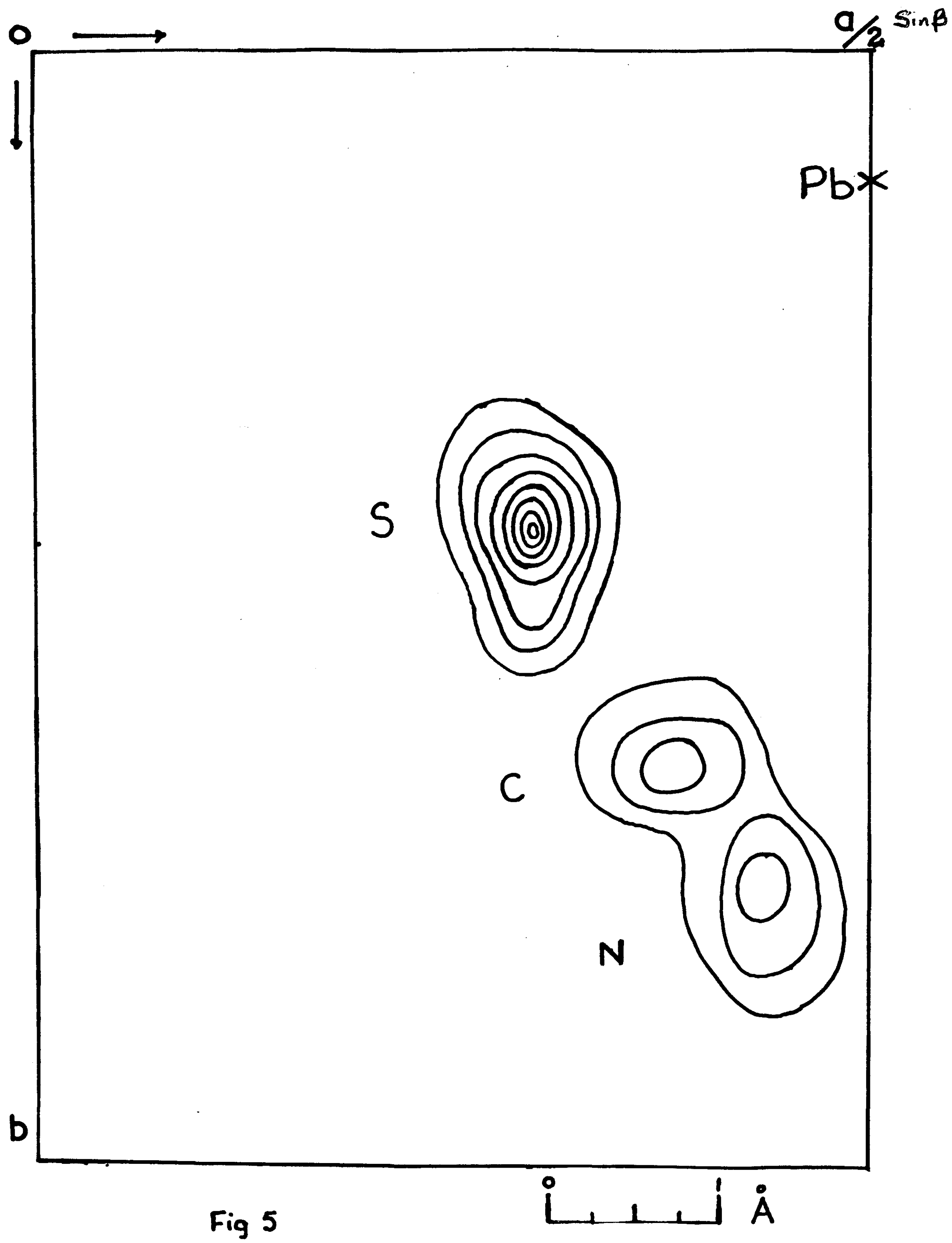


Fig 5

4.6. STRUCTURE REFINEMENT

The refinement of this structure was by the full-matrix least-squares method using the programme devised by Cruickshank and Smith. The details of the programme have been described elsewhere. After six cycles of refinement with isotropic temperature factors for all atoms apart from lead the R-factor was 15.3%. This fell to 14.6% when four reflexions believed to have been affected by extinction were removed. All atoms were now assigned anisotropic temperature factors and the refinement continued. Since the carbon and nitrogen atoms were difficult to refine at this stage, they were kept constant while the refinement of lead and sulphur continued. Convergence was attained after nine cycles and the final R-factor is 13.76%, (Table 34).

4.7. RESULTS

The final fractional co-ordinates and the corresponding standard deviations are listed in Table 35 while the final anisotropic temperature factors occupy Table 36. The orthogonal coordinates are in Table 37. Table 38 contains the inter-atomic bond lengths. The inter-bond angles are compiled in Table 39 and the final $|Fo|$ and Fc in Table 40. The packing diagram of the structure viewed down the unique axis (b) is shown in Fig. 7.

LEAD THIOCYANATE.

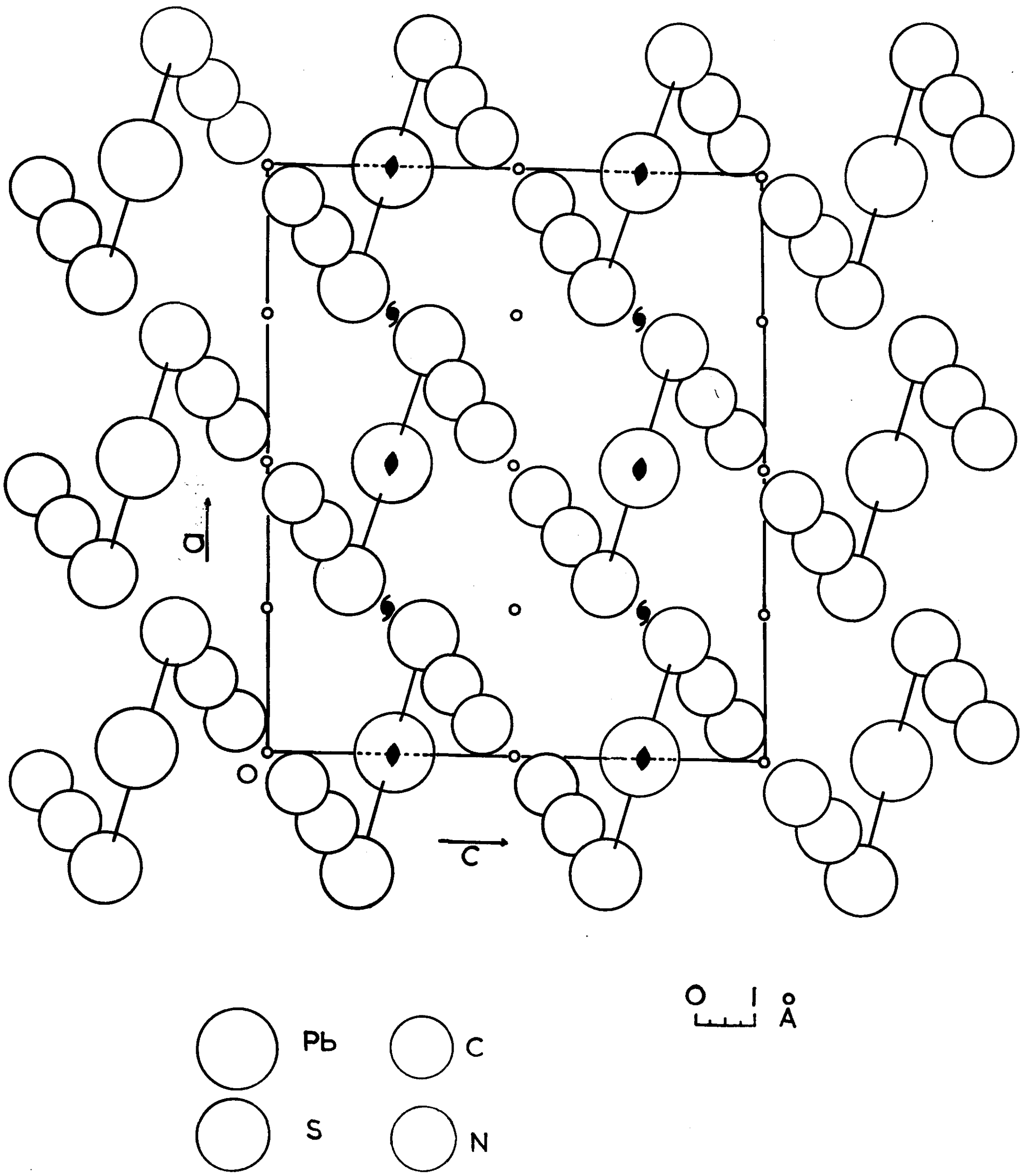


Fig. 7. Packing of the molecules viewed down the unique axis (b).

TABLE 34.

COURSE OF ANALYSIS.

3-D Patterson synthesis.

Found Pb.

1st. Structure-factor calculations, $B_{Pb} = 1.75Å^2$

$R = 30.0\%$

1st. 3-D Difference Fourier synthesis.

Spurious peaks rendered map useless.

2nd. Structure-factor calculations, (anisotropic temp. factor).

$R = 27.2\%$

2nd. 3-D Difference Fourier synthesis.

Found All light atoms.

3rd. Structure-factor calculations, $B = 3.5Å^2$ for light atoms.

$R = 22.3\%$

1st. Cycle of S.F.L.S. Refinement, only Pb is anisotropic.

$R = 20.2\%$

2nd. Cycle of S.F.L.S. Refinement,

$R = 18.6\%$

3rd. Cycle of S.F.L.S. Refinement,

$R = 17.5\%$

4th. Cycle of S.F.L.S. Refinement,

$R = 16.5\%$

5th. Cycle of S.F.L.S. Refinement,

$R = 15.8\%$

- Cont'd -

TABLE 34 -Cont'd-

COURSE OF ANALYSIS.

6th. Cycle of S.F.L.S. Refinement,

R = 15.3%

Removal of 4reflections due to extinction, (all atoms anisotropic)

R = 14.6%

7th. Cycle of S.F.L.S. Refinement, (C and N kept constant).

R = 14.0%

8th. Cycle of S.F.L.S. Refinement,

R = 13.89%

9th. Cycle of S.F.L.S. Refinement,

R = 13.63

Final scaling of data,

R = 13.76%

4.5. DISCUSSION.

The X-Ray study of $Pb(CNS)_2$ has established bonding of Pb to both S and N of different SCN-ions. Every Pb makes (close) contacts with two S and four N atoms- all of different thiocyanate residues. Each S atom makes one (close) contact with Pb while one other S atom makes a rather large contact of 3.14Å and each N atom makes two (close) contacts with different Pb atom. This arrangement gives rise to a six-fold coordination of Pb with all thiocyanate groups equidistant, Fig. 6.

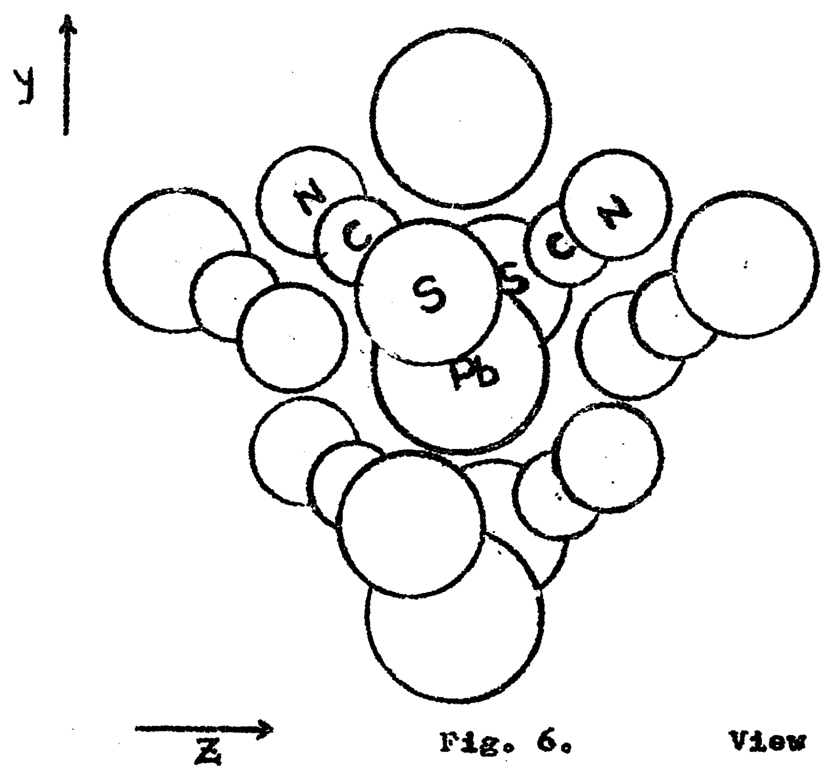


Fig. 6. View in X-direction.

The thiocyanate group is linear within the limit of the accuracy of the data. This structure agrees with the bent M-S-C bond postulated by Lewis (1964) for sulphur bonded

TABLE 35.

LEAD THIOCYANATE.

FRACTIONAL ATOMIC COORDINATES.

ATOMS	(x/a)	(y/b)	(z/c)
Pb	0.5000	-0.3867	0.2500
S	0.2957	-0.0454	0.1726
N	0.4429	0.2839	0.0586
C	0.3810	0.1351	0.1133

STANDARD DEVIATIONS.

Pb	0.0000	0.0006	0.0000
S	0.0013	0.0041	0.0020
N	0.0070	0.0149	0.0078
C	0.0085	0.0137	0.0099

TABLE 36.

FINAL ANISOTROPIC THERMAL PARAMETERS (Uij).

ATOMS	(U11)	(U22)	(U33)	(2U23)	(2U31)	(2U12)
Pb	0.014	0.006	0.018	0.000	-0.001	0.000
S	0.041	0.150	0.094	0.049	0.005	0.002
N	0.033	0.270	0.066	0.022	-0.021	0.054
C	0.064	0.126	0.073	-0.041	-0.009	-0.116

TABLE 37.

ORTHOGONAL COORDINATES.

ATOMS	(x)	(y)	(z)
Pb	4.857	-2.540	1.898
S	2.871	-0.299	1.327
N	4.303	1.865	0.334
C	3.701	0.888	0.807

TABLE 38.

INTER-ATOMIC BOND LENGTHS (in Å).

Pb	-	S	3.05	Pb	-	N	2.73
Pb	-	S	3.14	Pb	-	N	2.72
C	-	N	1.24	C	-	S	1.54

TABLE 39.

INTERBOND ANGLES (°).

N(v) - Pb - N(vi)	151	N(ii) - Pb - S(i)	110
N(v) - Pb - N(ii)	72	N(ii) - Pb - S(iii)	145
N(v) - Pb - N(iv)	134	N(ii) - Pb - N(vi)	72
N(v) - Pb - S(i)	77	N(ii) - Pb - S(vii)	77
N(v) - Pb - S(iii)	82	S(i) - Pb - S(iii)	85
N(v) - Pb - S(vii)	119	S(i) - Pb - S(viii)	72
N(v) - Pb - S(vii)	71	S(i) - Pb - S(vii)	143
N(ii) - Pb - N(iv)	75	S(viii) - Pb - S(vii)	141

The subscripts refer to the following positions:

(i)	x, y, z	(v)	$1-x, -y, -z$
(ii)	$x, -1+y, z$	(vi)	$x, -y, \frac{1}{2}+z$
(iii)	$1-x, y, \frac{1}{2}-z$	(vii)	$\frac{1}{2}+x, -\frac{1}{2}+y, z$
(iv)	$1-x, -1+y, \frac{1}{2}-z$	(viii)	$\frac{1}{2}-x, -\frac{1}{2}-y, \frac{1}{2}-z$

TABLE 40.

H	K	L	|Fo|	Fc
0	0	-10	44.5	-52.3
0	0	-8	65.3	61.0
0	0	-4	112.1	86.2
0	0	-2	188.5	-165.6
2	0	-10	42.9	-49.4
2	0	-8	89.9	69.4
2	0	-6	127.1	-116.1
2	0	-4	107.3	138.0
2	0	-2	178.5	-161.9
2	0	0	100.1	98.8
2	0	2	1.9	7.1
2	0	4	106.7	125.0
2	0	6	93.4	-112.5
2	0	8	87.2	73.1
2	0	10	41.0	-52.3
4	0	-10	39.6	-50.2
4	0	-6	71.5	-74.4
4	0	-4	74.8	59.0
4	0	-2	116.7	-108.8
4	0	0	152.8	143.5
4	0	2	156.8	-162.1
4	0	4	147.9	158.7
4	0	6	60.6	-71.0
4	0	8	51.1	54.0
6	0	-8	47.2	51.3
6	0	-6	56.4	-79.8
6	0	-4	83.5	111.3
6	0	-2	128.4	-150.5
6	0	2	112.9	-77.4
6	0	4	65.5	70.6
6	0	6	56.8	-56.1
6	0	8	68.0	64.4
8	0	-8	58.7	57.0
8	0	-6	62.4	-68.8
8	0	-4	92.2	59.3
8	0	0	87.7	59.2
8	0	2	99.2	-98.8
8	0	4	88.1	91.3
8	0	6	71.9	-67.1
10	0	-6	34.0	-41.4
10	0	-4	71.2	59.9
10	0	-2	105.4	-89.1
10	0	0	98.0	87.1
10	0	2	80.6	-78.3
10	0	4	51.7	49.6
10	0	6	21.5	-45.6
12	0	-2	41.1	-49.5
12	0	0	29.0	38.6
12	0	2	31.7	-48.6
1	1	-9	47.4	37.2
1	1	-8	77.2	57.0
1	1	-7	62.4	-47.6
1	1	-6	92.1	-73.3
1	1	-5	88.3	65.9
1	1	-4	87.6	59.7
1	1	-3	103.0	-132.4
1	1	-1	73.3	65.7
1	1	0	81.5	77.3
1	1	1	116.5	-93.3
1	1	2	132.3	-165.2
1	1	3	84.0	100.3
1	1	4	121.7	139.9
1	1	5	51.0	-44.8
1	1	6	74.7	-77.1
1	1	7	55.4	55.6
1	1	8	42.2	46.8
1	1	9	42.8	-41.1
1	1	10	31.8	-36.6
3	1	-9	44.0	39.0
3	1	-8	46.4	41.2
3	1	-7	60.4	-54.0
3	1	-6	57.1	-59.6
3	1	-5	58.8	67.9
3	1	-4	78.1	91.7
3	1	-3	84.6	-73.4
3	1	-2	122.6	-149.2
3	1	-1	39.5	33.8
3	1	0	164.4	178.9
3	1	1	121.2	-121.3
3	1	2	103.1	-95.8
3	1	3	90.2	85.7
3	1	4	52.5	45.6
3	1	5	54.0	-57.3
3	1	6	50.8	-45.3
3	1	7	55.2	58.1
3	1	8	49.4	49.7
3	1	9	32.1	-34.8
3	1	10	30.4	-39.5
5	1	-9	39.7	36.3
5	1	-8	59.0	53.1
5	1	-7	36.1	-39.8
5	1	-6	55.5	-75.4
5	1	-5	41.7	50.5
5	1	-4	61.2	72.0
5	1	-3	61.8	-70.2
5	1	-2	57.8	-56.5
5	1	-1	94.3	84.9
5	1	0	45.0	44.2
5	1	1	119.7	-107.2
5	1	2	66.3	-54.3
5	1	3	49.1	47.2
5	1	4	68.8	84.6
5	1	5	41.0	-51.9
5	1	6	59.7	-75.6
5	1	7	40.4	48.6
5	1	8	55.0	50.9
5	1	9	25.7	-30.9
7	1	-8	42.3	38.2
7	1	-7	34.1	-37.0
7	1	-6	25.5	-36.8
7	1	-5	43.7	58.0
7	1	-4	38.3	43.7
7	1	-3	50.0	-61.6
7	1	-2	81.8	-83.1
7	1	-1	58.0	54.0
7	1	0	116.4	104.5
7	1	1	68.6	-55.9
7	1	2	95.5	-91.8
7	1	3	55.5	44.5
7	1	4	64.7	67.4
7	1	5	55.6	-60.2
7	1	6	43.2	-42.6
7	1	7	37.5	40.8
7	1	8	26.7	35.0
9	1	-7	26.1	-32.0
9	1	-6	49.6	-49.1
9	1	-5	42.1	42.2
9	1	-4	76.3	68.5
9	1	-3	36.7	-37.3
9	1	-2	71.4	-67.7
9	1	-1	55.8	51.0
9	1	0	48.9	40.3
9	1	1	62.9	-59.2
9	1	2	43.8	-36.0
9	1	3	55.9	48.2
9	1	4	51.3	45.0
9	1	5	43.8	-44.9
9	1	6	46.3	-43.3
11	1	-5	31.4	35.6
11	1	-4	26.3	31.7
11	1	-3	44.5	-36.6
11	1	-2	34.1	-32.5
11	1	-1	51.6	46.9
11	1	0	51.8	45.3
11	1	1	37.0	-37.3
11	1	2	64.8	-59.8
11	1	3	32.9	32.5
11	1	4	39.2	49.6
0	2	-10	6.2	-6.5
0	2	-9	57.2	57.9
0	2	-8	9.8	6.8
0	2	-7	95.9	-87.3
0	2	-6	12.0	6.2
0	2	-5	106.2	106.0
0	2	-4	6.1	7.3
0	2	-3	119.9	-116.1
0	2	-2	75.9	-67.1
0	2	-1	98.5	118.0
2	2	-10	3.3	-5.7
2	2	-9	76.1	60.2
2	2	-8	23.4	13.9
2	2	-7	84.2	-71.4
2	2	-6	30.0	-23.2
2	2	-5	76.0	73.6
2	2	-4	42.2	44.1
2	2	-3	112.4	-115.9
2	2	-2	31.1	-14.5
2	2	-1	143.3	158.9
2	2	0	32.5	-41.1
2	2	1	129.2	-154.4
2	2	2	13.2	5.9
2	2	3	113.5	124.4
2	2	4	7.0	-3.7
2	2	5	86.9	-92.2
2	2	6	28.3	-22.2
2	2	7	65.0	71.3
2	2	8	22.2	18.4
2	2	9	50.1	-53.1
2	2	10	7.6	-7.0
4	2	-9	59.5	51.1
4	2	-8	21.2	10.7
4	2	-7	68.7	-65.1
4	2	-5	78.7	99.7
4	2	-4	6.7	-4.6
4	2	-3	114.9	-137.9
4	2	-2	7.1	6.9
4	2	-1	95.8	106.6
4	2	0	49.3	36.9
4	2	1	113.6	-88.3
4	2	2	56.0	-57.7
4	2	3	83.2	96.3
4	2	4	20.2	23.0
4	2	5	69.8	-89.3
4	2	6	19.2	-17.0
4	2	7	64.9	73.3
4	2	8	5.5	3.8
4	2	9	54.5	-53.5
6	2	-9	49.7	48.9
6	2	-8	3.4	4.4
6	2	-7	57.0	-64.9
6	2	-6	10.9	-10.9
6	2	-5	71.1	79.8
6	2	-4	32.3	35.7
6	2	-3	65.0	-74.9
6	2	-2	32.1	-32.8
6	2	-1	93.9	75.8
6	2	0	38.1	22.7
6	2	1	102.1	-117.2
6	2	3	105.3	109.6
6	2	4	6.3	-7.2
6	2	5	65.3	-78.1
6	2	6	11.6	-9.8
6	2	7	58.3	60.1
6	2	8	4.8	6.6
8	2	-8	13.4	9.1
8	2	-7	51.2	-50.9
8	2	-6	15.8	-12.9
8	2	-5	53.3	65.3
8	2	-4	6.2	5.2
8	2	-3	75.0	-79.7
8	2	-2	17.0	14.3
8	2	-1	112.4	96.2
8	2	0	10.0	2.5
8	2	1	102.0	-92.9
8	2	2	18.0	-14.4
8	2	3	62.6	62.0
8	2	4	28.5	22.7
8	2	5	58.2	-58.2
8	2	6	21.2	-15.6
8	2	7	54.8	55.7
10	2	-6	2.8	-4.8
10	2	-5	57.2	57.2
10	2	-4	14.0	6.7
10	2	-3	56.9	-59.2
10	2	-2	27.5	-17.9
10	2	-1	62.4	61.3
10	2	0	37.5	29.3
10	2	1	63.8	-60.6
10	2	2	14.7	-10.7
10	2	3	69.5	59.5
10	2	4	6.4	4.8
10	2	5	52.1	-61.7
12	2	-1	50.4	57.5
12	2	0	4.1	1.0
12	2	1	40.5	-56.1
1	3	-9	45.7	43.1
1	3	-8	34.7	-29.6
1	3	-7	65.6	-56.1
1	3	-6	65.6	49.4
1	3	-5	108.9	87.8
1	3	-4	86.0	-75.1
1	3	-3	97.2	-114.1
1	3	-2	66.1	78.9
1	3	-1	130.1	127.3
1	3	0	57.5	-74.3
1	3	1	77.4	-96.3
1	3	2	61.5	55.7
1	3	3	58.8	75.4
1	3	4	46.7	-42.3
1	3	5	72.1	-72.8
1	3	6	34.5	35.3
1	3	7	64.7	60.2
1	3	8	37.9	-33.7
1	3	9	59.8	-49.8
3	3	-9	50.3	45.6
3	3	-8	42.7	-36.1
3	3	-7	87.9	-67.4
3	3	-6	54.5	49.2
3	3	-5	59.4	81.4
3	3	-4	37.1	-40.0
3	3	-3	66.6	-68.2
3	3	-2	39.9	32.3
3	3	-1	66.5	74.4
3	3	0	65.6	-56.2
3	3	1	76.9	-91.5
3	3	2	56.1	59.4
3	3	3	92.0	106.2
3	3	4	51.9	-59.3
3	3	5	68.1	-84.9
3	3	6	54.3	49.8
3	3	7	66.3	58.7
3	3	8	40.9	-36.1
3	3	9	40.1	-45.3
5	3	-9	29.8	40.9
5	3	-8	27.8	-28.1
5	3	-7	53.8	-51.1
5	3	-6	30.3	33.4
5	3	-5	38.5	56.6
5	3	-4	35.2	-41.2
5	3	-3	72.2	-78.1
5	3	-2	60.4	72.2
5	3	-1	119.4	114.1
5	3	0	105.7	-79.7
5	3	1	120.5	-102.2
5	3	2	60.2	53.1
5	3	3	64.3	75.6
5	3	4	36.7	-44.9
5	3	5	48.2	-55.1
5	3	6	32.6	35.0
5	3	7	53.1	51.4
5	3	8	33.1	-27.4
7	3	-8	30.3	-28.5
7	3	-7	57.5	-50.4
7	3	-6	34.9	37.8
7	3	-5	56.9	63.6
7	3	-4	34.7	-45.8
7	3	-3	68.9	-76.2
7	3	-2	55.3	47.4
7	3	-1	65.5	68.0
7	3	0	39.7	-28.7
7	3	1	56.0	-52.5
7	3	2	38.7	30.6
7	3	3	74.8	63.0
7	3	4	49.2	-43.8
7	3	5	68.0	-63.4
7	3	6	36.4	35.1
7	3	7	52.9	52.9
9	3	-6	21.2	25.3
9	3	-5	30.9	43.3
9	3	-4	31.1	-29.0
9	3	-3	54.3	-52.7
9	3	-2	43.1	34.3
9	3	-1	65.1	58.4
9	3	0	46.3	-39.5
9	3	1	55.4	-67.1
9	3	2	61.3	49.9
9	3	3	60.6	66.7
9	3	4	43.8	-40.1
9	3	5	44.0	-48.7
9	3	6	19.7	25.1
11	3	-3	53.3	-52.2
11	3	-2	32.2	33.8
11	3	-1	49.5	48.5
11	3	0	34.1	-31.8
11	3	1	45.4	-47.5

END 2M 12S

ligand. The C-N and C-S bond lengths of 1.24 and 1.54Å (respectively) with high standard deviations are much different from the values expected for C-N triple bond and C-S single bond. However, they do not differ very much from the values registered in some other thiocyanates. In his study of I.R. spectra of K-thiocyanate Jones (1958) obtained values of 1.17 and 1.61Å for C-N and C-S. In some Reineche salts in which thiocyanates bond through sulphur values of 1.37 and 1.64 have been recorded, Lewis et al.,(1964).

The loss of triple bond character in C-N and the gain of double bond character in C-S are supported by the measured frequencies of C-N and C-S in different compounds. In organic nitriles, the C-N stretching frequency is usually 2,250cm^{-1} whilst the C-S stretch in mercaptains are in the region 600-700cm^{-1}, this shifts to a region 700-800cm^{-1} in thiocyanate complexes, (Nyholm et al., 1964). The shortening or lengthening of bonds in this ionic compound may be explained in terms of a resonance balance between $\langle\bar{N}=C=\bar{S}\rangle$ and $|N\equiv C-\bar{\underline{S}}|$.

P A R T V

CHEMICAL SYNTHESES

OF SOME AMINOPHOSPHINE COMPLEXES

Several samples of bis-(diphenyl-phosphino)-ethylamine palladium (II) complex were prepared in different media by varying the mole ratios of metal halide and ligand. Chemical analysis show that these are all 1:1 complexes. From the crystal structure analysis of the palladium complex (Part I), it was obvious that the ligand (PNPEt) is bidentate; further attempts were made to test this aspect by preparing the aminophosphine complexes of some other transition metals. The ligands used are bis-(diphenyl-phosphino)-alkylamine of the formula- $Ph_2.P.NR.P.Ph_2$ (R = H, Me, Et, nPr or iPr). With NiX_2 ($X = I^-$, Br^-, CNS^- or NO_3^-), apart from the 1:1 complex, it was possible to prepare the 1:2 and 2:1 complexes. Since the latter ratios do not conform to the ratio of metal to ligand in the palladium complex, the exact nature of the 1:2 and 2:1 is not known. An attempt to prepare the mercury(II) halide complexes leads to the isolation of the 1:1, 1:2 and 2:3 adducts. The arrangements of atoms in the 1:2 and 2:3 are uncertain.

The disulphides and the diselenides of bis-(diphenyl-phosphino)-methylamine were prepared by reaction of the ligand with an excess of sulphur or selenium (precipitated) in boiling benzene. In each case white needle-like crystals separated on cooling. Addition of ethyl iodide to the ligand (PNPEt) in ether resulted in a 1:1 adduct. The quaternisation has been proved by X-Ray work (Part II) to occur at one P-atom only.

Equidistant from the plane are C(3) and C(6) to form a distorted octahedral arrangement as suggested by the values of the valency angles at the molybdenum.

The average value of Mo-C is 1.99 ± 0.01Å while the mean C-O bond length is 1.15 ± 0.015Å. This value of 1.99Å for Mo-C is a bit shorter than the value of 2.06 ± 0.02Å obtained by Najarian (1957) for the Mo-C bond length in molybdenum hexacarbonyl. This difference is probably significant in view of the dependence of Mo-C bond length on bond order (Cotton et al. 1965).

The bond order in the Mo-C of PNPMo tetracarbonyl can be estimated by adopting the method suggested by Cotton et al (1965). Evaluation of this is vital for a thorough understanding of the donor-acceptor property of the P-N-P ligand and probably may lead to additional evidence in support of the delocalisation of the nitrogen lone pair.

The structure of cis-(Diethylene triamine) molybdenum tricarbonyl has recently been published (Cotton et al. 1965). The comparison of the Mo-C bond lengths obtained by Cotton with those recorded in the present work shows some differences and helps towards the determination of the bond-order of Mo-C in PNPMo-tetracarbonyl.

Cotton et al.		Present work.	
Mo - C(1)	1.93 ± 0.02Å	Mo - C(3)	2.00 ± 0.02Å
Mo - C(2)	1.95 ± 0.02Å	Mo - C(4)	1.98 ± 0.02Å
Mo - C(3)	1.94 ± 0.02Å	Mo - C(5)	2.00 ± 0.02Å
		Mo - C(6)	1.98 ± 0.02Å
Mean Mo - C = 1.94Å.		Mean Mo - C = 1.99Å.	

These two values of Mo-C though close differ appreciably in their values of bond-orders (Fig. V). The values of 2.06 ± 0.02Å (Najarin, 1957) and 2.08 ± 0.04Å (Brockway, 1938) for Mo-C in molybdenum hexacarbonyl are on the other hand much longer than either Cotton's value or that obtained in the present work.

From all available data, Cotton et al (1965) obtained the graph shown below (Fig. V) for determining the Mo-C bond-order from a known value of Mo-C bond-length. The value of Mo-C bond length (1.99Å) in the present work is plotted on Cotton's graph and its position is indicated by A. Position B corresponds to the Mo-C bond length and bond-order in the molybdenum hexacarbonyl.

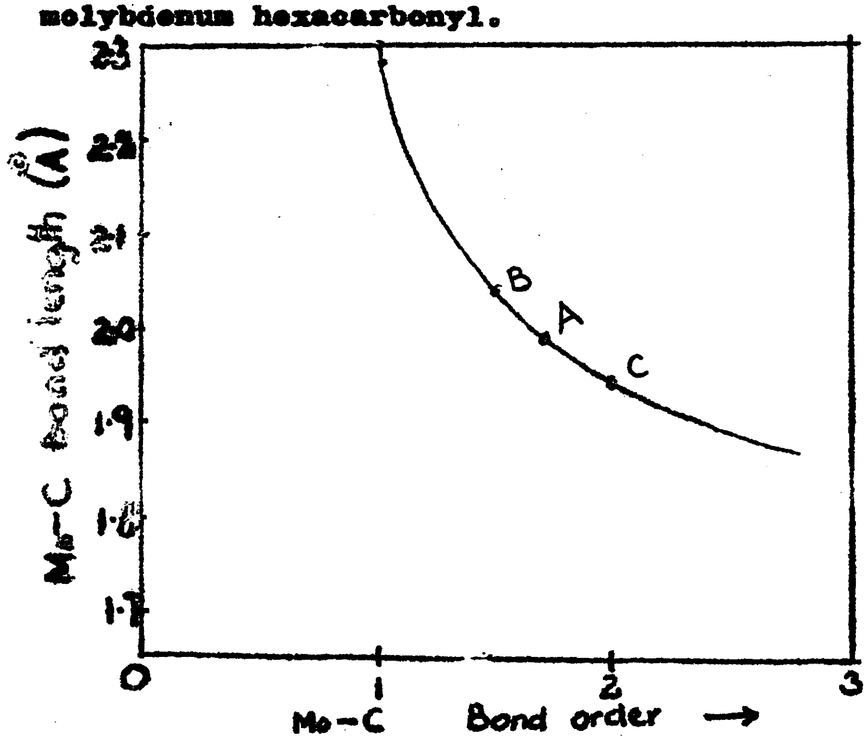


Fig V

Bond-orders 1.5 and 2.0 have been assigned to Mo-C in molybdenum hexacarbonyl (B) and cis-Mo(diene) tricarbonyl marked (C). The basis of assignment has been discussed by Cotton (1964). From the position of A on the graph the

bond-order in Mo-C of PNP-Mo-tetracarbonyl is about 1.75Å.
This is consistent with the theory that there should be more of double bond character in Mo-C of PNP-Mo-tetracarbonyl than in the Mo-C of the molybdenum hexacarbonyl since P-N-P ligand is a poorer donor than carbon monoxide.

The shortening observed in Mo-C would cause the lengthening of the C-O bond, although C-O bond lengths in complexes are not reliable enough for determining differences between bond-orders in the range 2 to 3, there is evidence to support the above statement of C-O lengthening from the spectra study. Payne et al (1965) obtained the values of $1980cm^{-1}$ for the C-O stretching frequency in the hexacarbonyl and $1873cm^{-1}$ in the PNP-Mo-tetracarbonyl.

The above value of bond-order (1.75) for Mo-C suggests therefore that there is more of $d\pi$-$p\pi$ bonding in the Mo-C of the complex than of the molybdenum hexacarbonyl. This will also mean that the central metal atom dissipates more of its charge into the p -orbital of the C-atom rather than into the d -orbital of phosphorus. The situation leaves the Mo-P as formed from almost σ-bond. Also if there is partial double bond formation in P-N due to delocalisation of electrons as previously discussed, this will enhance the single bond character of Mo-P. In fact, the value of 2.50 ± 0.005Å obtained for Mo-P in this P-N-P complex is not significantly different from the expected value for a Mo-P single bond (2.46Å) (Rundqvist, 1965). This result supports the established fact that C-O is a better π-bonder than phosphorus compounds and gives a conclusive evidence on the delocalisation of electrons in P-N-P ligand.

TABLE 33.

Summary of some P-C(alkyl) and P-C(aryl) bond-lengths.

Compound	P-Calkyl	P-Caryl	References.
$[Pt_2(SCN)_2Cl_2(PC_3H_7)_2]$	1.88	-	Rowe et al., 1960
$[(C_6H_5)(C_2H_5)_2P]ReCl_3$	1.86±0.05	1.77±0.08	Cotton et al., 1964
$[(Ph_2P)_2NEt]PdCl_2$	-	1.81±0.01	Present work.
$P(CH_3)_3$	1.84±.003	-	Lide et al., 1958
$P(CH_3)_3$	1.85±.003	-	Bartell et al., 1960
$P(Ph)_3$	-	1.83±.003	Daly, J.J., 1964
$[Ph_2PNEtP.Ph_2Et]^+I^-$	1.81±0.05	1.81±0.02	Present work.
$[ReOCl_3(PEt_2Ph)_2]$	1.86	1.78	Ehrlich et al., 1963
$[Ph_2P.NEt.PPh_2]Mo(CO)_4$	-	1.81±0.01	Present work.

(Bond-length values are mean where there are several of similar type).

PART IV

X-RAY STRUCTURE ANALYSIS OF

LEAD THIOCYANATE

4.1. INTRODUCTION

The complexing ability of the thiocyanate ion has led to its use in qualitative and quantitative analyses, (Vogel, 1962 The thiocyanate ion exhibits linkage isomerism, bonding to the metal ion either through its sulphur or nitrogen atom. When bonded through sulphur, the compounds formed are called thiocyanato. If, however, the bond is through nitrogen, the name isothiocyanate is appropriate. For simplicity this class of compounds will be referred to as thiocyanates (without regard to whether the metal ion is S-bonded or N-bonded) throughout this text.

Very little has been done in the study of transition metal thiocyanates by X-Ray methods, but information is available from other physical methods for some thiocyanate complexes. By studying the C-N and C-S stretching frequencies attempts have been made (Lewis et al, 1961) to classify the isomers of the transition metal thiocyanates. In their discussions, it can be inferred that the elements of the first transition series are bonded through N in the formation of thiocyanate complexes whereas the elements of the second and third series are bonded through sulphur. Lieber et al, (1959), used measured C-N frequencies to decide between thiocyanato - and isothiocyanato - bonding. Fujita et al, (1956), Mitchell et al, (1960) have all examined this criterion in extensive details and have made some broad correlations. Difficulty arises, however, in that the C-N frequency is affected by a number of variables apart from the donor atom, and in particular overlap occurs between the two classes.

From the measurements of the C-S (755 cm^{-1}) and the C-N (2114 cm^{-1}) stretching frequencies of lead thiocyanate, Torrance (1965) found that there was not enough evidence from the above values to predict the type of linkage involved in lead thiocyanate. Previous workers have proved that Mn, Ni, Co and Cu form isothiocyanates (that is N-bonded). This is established in the crystal structure analysis of $[Co(NCS)_4]^{2-}$, Takencki, 1957, of $[Ni(NH_3)_4(NCS)_2]$, Zudanov et al, 1950. N. Gilli (1961) has shown that thiocyanate groups serve two functions in the structure of $Cd(SCN)_4^{2-}$, that is bonding through sulphur and nitrogen to form a structure such as SCN - M - SCN. The situation in lead thiocyanate is not certain.

4.2. EXPERIMENTAL

A sample of the compound - lead thiocyanate - prepared by Dr. Bacon of the Queen's University, Belfast was kindly made available to us by Miss Ida Woodward also of Queen's University. Crystals for the X-Ray work were obtained by cutting to suitable sizes. A crystal of an average width 0·015 cm was used for collecting intensity data. The value of μR = 5·2 was used to correct for absorptions, R - the radius - being taken as half the average width. The ratios of the unit translations as predicted by Groth, (1908) are 0·631 : 1 : 1·623. Groth cell as related to that used in this work is shown in Fig. 1. The unit cell transformation matrix is given by $100/010/\bar{1}02$.

LEAD THIOCYANATE

UNIT CELL TRANSFORMATION.

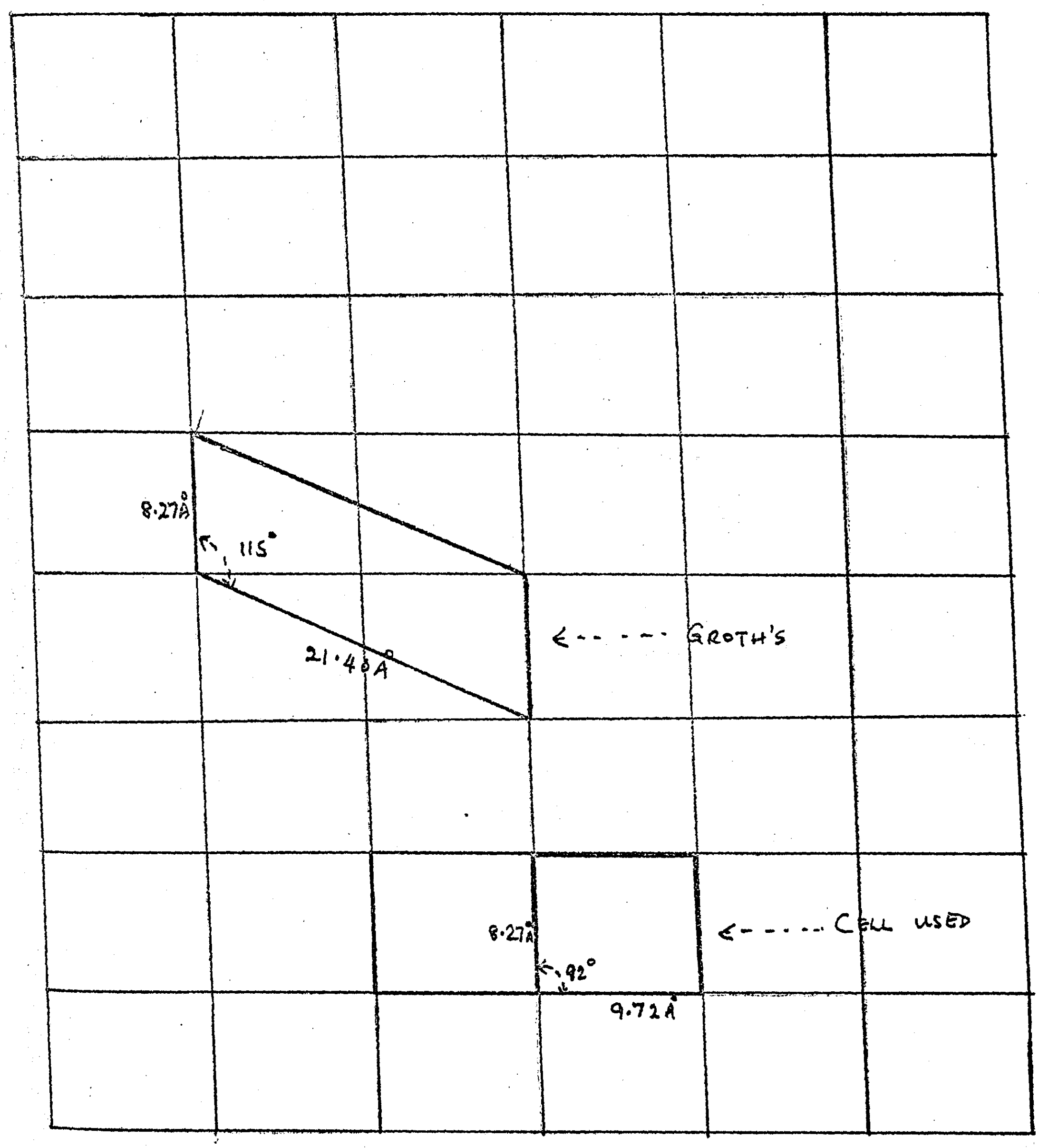


Fig. 1

4.3. INTENSITY DATA

Rotation, oscillation and Weissenberg photographs were taken using Cu-Kα radiation ($\lambda = 1{\cdot}542$ Å). The intensity data were measured visually from Weissenberg photographs for the h0l, h1l, h2l and h3l nets obtained by the multiple film technique (Robertson, 1943). The film factor used to correlate the intensities on successive films of a series in non-equitorial layers was calculated from

$R = 1{\cdot}29 \exp(0{\cdot}94 \sec \alpha)$ where α = the angle which the incident beam makes with the normal to the film, (Rossmann, 1956

The intensities were corrected by the usual factors.

The various zones were placed on the same relative scale by comparison of the observed and calculated structure amplitudes.

4.4. CRYSTAL DATA

Crystals of lead thiocyanate with M = 323·4 are monoclinic

$\underline{a} = 9{\cdot}72 \pm 0{\cdot}03$, $\underline{b} = 6{\cdot}57 \pm 0{\cdot}02$, $\underline{c} = 8{\cdot}27 \pm 0{\cdot}03$ Å;

$\beta = 92{\cdot}0 \pm 0{\cdot}5°$. Volume of the unit cell, $V = 527{\cdot}8$ Å^3.

$\rho_{cal} = 4{\cdot}07$ g/cm^3, Z = 4. F(000) = 560. $\mu = 680$ cm^{-1} for X-Rays, ($\lambda = 1{\cdot}542$). $\sum f_H^2 = 6724$, $\sum f_L^2 = 682$.

Absent spectra : (hkl) when h+k is odd

(h0l) " l is odd

(0k0) " k is odd.

Space Group: C2/c - C_{2h}^6 or Cc - C_s^4. The centred space group C2/c was chosen without prior application of any statistical tests. The choice appears to have been justified by the successful solution of the structure. This requires the

Pb - atom to be in a special position either at a centre of symmetry or on a two-fold axis.

4.5. HEAVY ATOM POSITION

The position of Pb - atom was determined from a 3-D. Patterson synthesis. The atom (Pb) was found to occupy a special position 0, y, ¼. Attempt to solve other vectors obtained in the map only resulted in the probable position of sulphur. The co-ordinates thus found were for

Pb	x = 0·000 ,	y = 0·115 ,	z = 0·250.
S	x = 0·329 ,	y = -0·115 ,	z = 0·172.

Since the position of sulphur was not certain, only the co-ordinates of lead were used in the first structure - factor calculation. R-factor was 30·0%, (Table 34). Using the signs appropriate to the rest of the atoms and delta ($|Fo| - |Fc|$) as coefficients, a three-dimensional difference Fourier synthesis was computed along the z-axis. Pseudo--symmetry and anisotropic effects around Pb rendered the map obtained difficult to interpret. In the subsequent structure--factor calculation lead was assigned anisotropic temperature factor. R dropped to 27·2%, and in a second difference map, the thiocyanate group was obvious. The positions of sulphur, carbon and nitrogen (Figs. 2, 3, and 4) are marked B, C, and D on Figs. 2, 3, 4. While the whole structure revealed by means of superimposed contours is shown in Fig. 5. Thus co-ordinates were assigned to sulphur, carbon and nitrogen. A set of structure-factors calculated with all atoms gave an R-value of 22·3%.

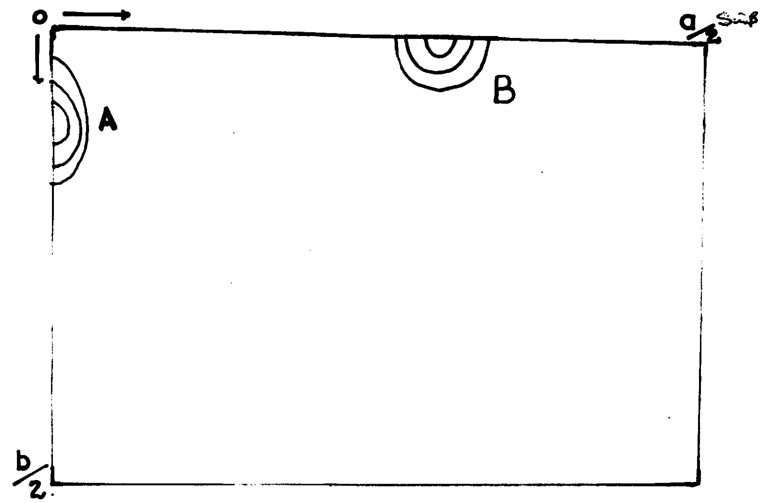


Fig 1a Section at z=0·17. 0 Å

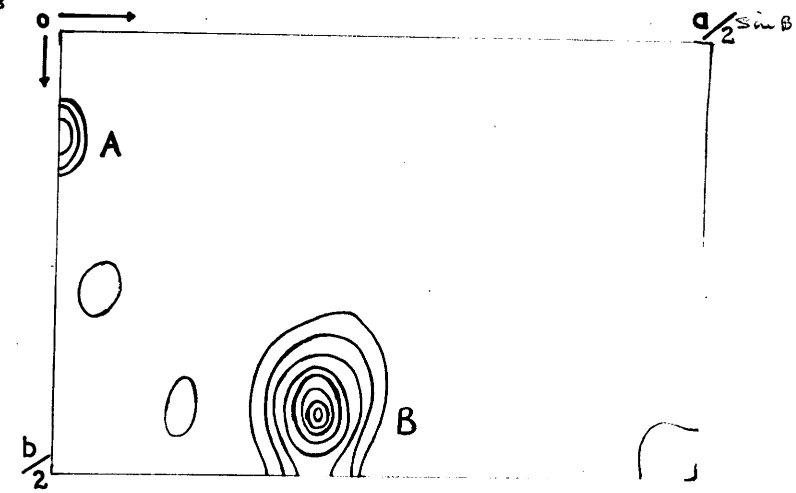


Fig 2. Section z=0·33. 0 Å

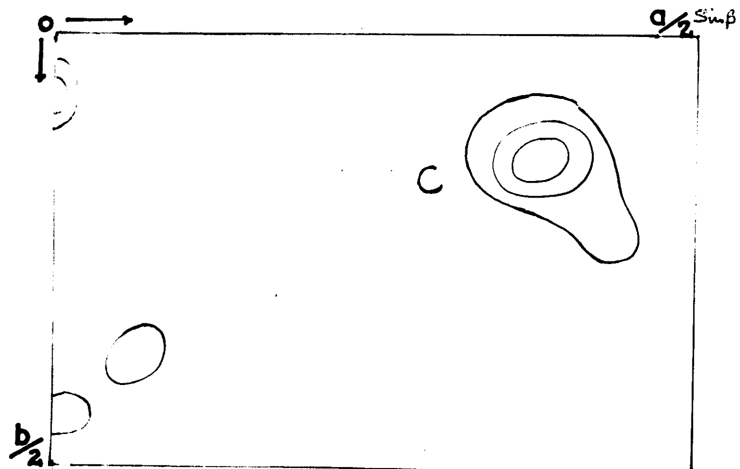


Fig 3. Section z = 0·10 0 Å

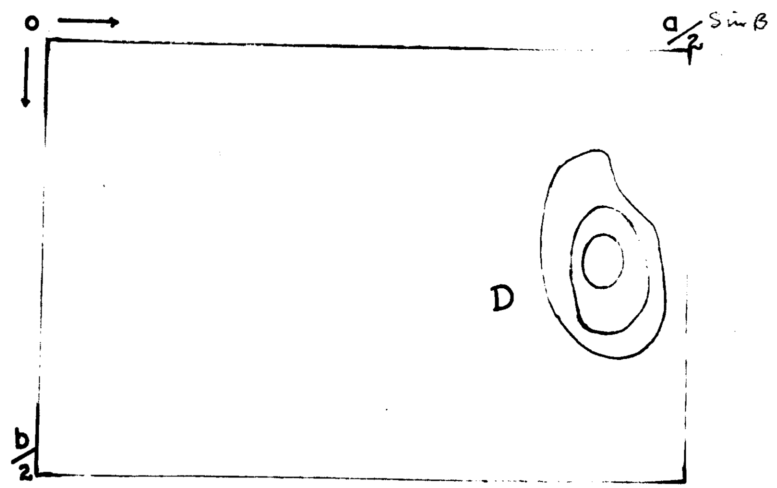


Fig 4. Section at z = 0·07. 0 Å

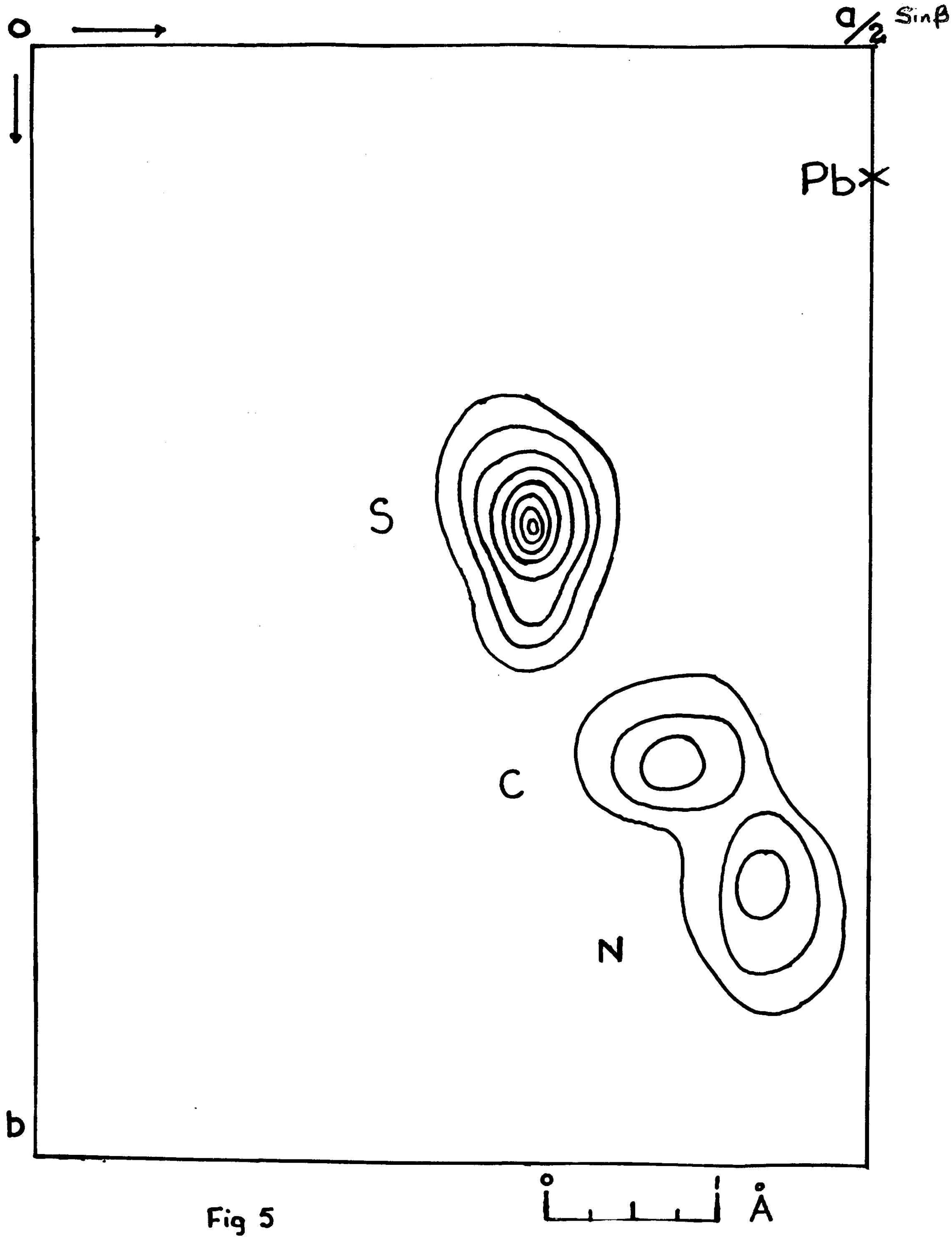


Fig 5

4.6. STRUCTURE REFINEMENT

The refinement of this structure was by the full-matrix least-squares method using the programme devised by Cruickshank and Smith. The details of the programme have been described elsewhere. After six cycles of refinement with isotropic temperature factors for all atoms apart from lead the R-factor was 15.3%. This fell to 14.6% when four reflexions believed to have been affected by extinction were removed. All atoms were now assigned anisotropic temperature factors and the refinement continued. Since the carbon and nitrogen atoms were difficult to refine at this stage, they were kept constant while the refinement of lead and sulphur continued. Convergence was attained after nine cycles and the final R-factor is 13.76%, (Table 34).

4.7. RESULTS

The final fractional co-ordinates and the corresponding standard deviations are listed in Table 35 while the final anisotropic temperature factors occupy Table 36. The orthogonal coordinates are in Table 37. Table 38 contains the inter-atomic bond lengths. The inter-bond angles are compiled in Table 39 and the final $|Fo|$ and Fc in Table 40. The packing diagram of the structure viewed down the unique axis (b) is shown in Fig. 7.

LEAD THIOCYANATE.

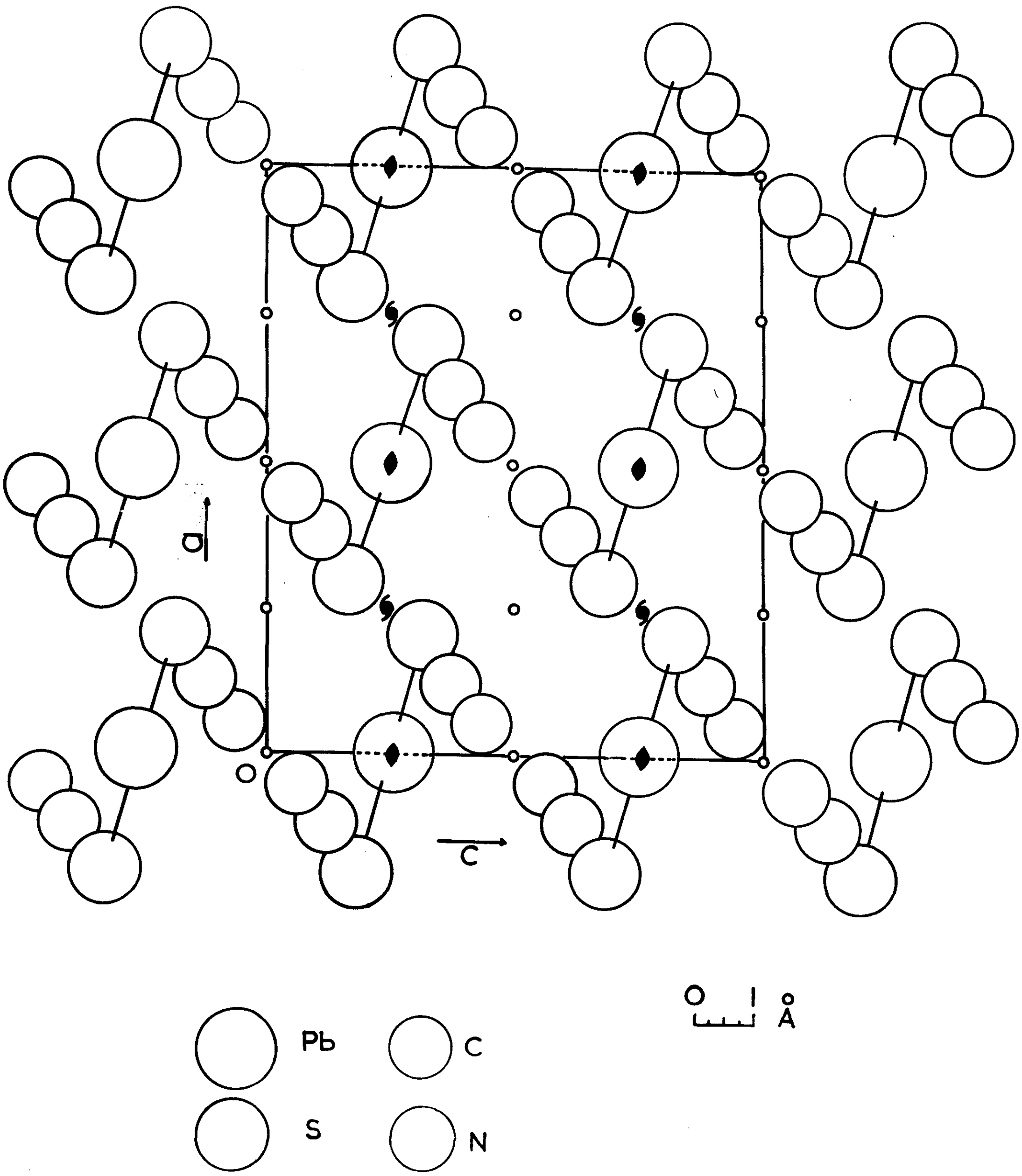


Fig. 7. Packing of the molecules viewed down the unique axis (b).

TABLE 34.

COURSE OF ANALYSIS.

3-D Patterson synthesis.

Found Pb.

1st. Structure-factor calculations, $B_{Pb} = 1.75Å^2$

R = 30.0%

1st. 3-D Difference Fourier synthesis.

Spurious peaks rendered map useless.

2nd. Structure-factor calculations, (anisotropic temp. factor).

R = 27.2%

2nd. 3-D Difference Fourier synthesis.

Found All light atoms.

3rd. Structure-factor calculations, $B = 3.5Å^2$ for light atoms.

R = 22.3%

1st. Cycle of S.F.L.S. Refinement, only Pb is anisotropic.

R = 20.2%

2nd. Cycle of S.F.L.S. Refinement,

R = 18.6%

3rd. Cycle of S.F.L.S. Refinement,

R = 17.5%

4th. Cycle of S.F.L.S. Refinement,

R = 16.5%

5th. Cycle of S.F.L.S. Refinement,

R = 15.8%

- Cont'd -

TABLE 34 -Cont'd-

COURSE OF ANALYSIS.

6th. Cycle of S.F.L.S. Refinement,

R = 15.3%

Removal of 4reflections due to extinction, (all atoms anisotropiC)

R = 14.6%

7th. Cycle of S.F.L.S. Refinement, (C and N kept constant).

R = 14.0%

8th. Cycle of S.F.L.S. Refinement,

R = 13.89%

9th. Cycle of S.F.L.S. Refinement,

R = 13.63

Final scaling of data,

R = 13.76%

4.5. DISCUSSION.

The X-Ray study of $Pb(CNS)_2$ has established bonding of Pb to both S and N of different SCN-ions. Every Pb makes (close) contacts with two S and four N atoms- all of different thiocyanate residues. Each S atom makes one (close) contact with Pb while one other S atom makes a rather large contact of 3.14Å and each N atom makes two (close) contacts with different Pb atom. This arrangement gives rise to a six-fold coordination of Pb with all thiocyanate groups equidistant, Fig. 6.

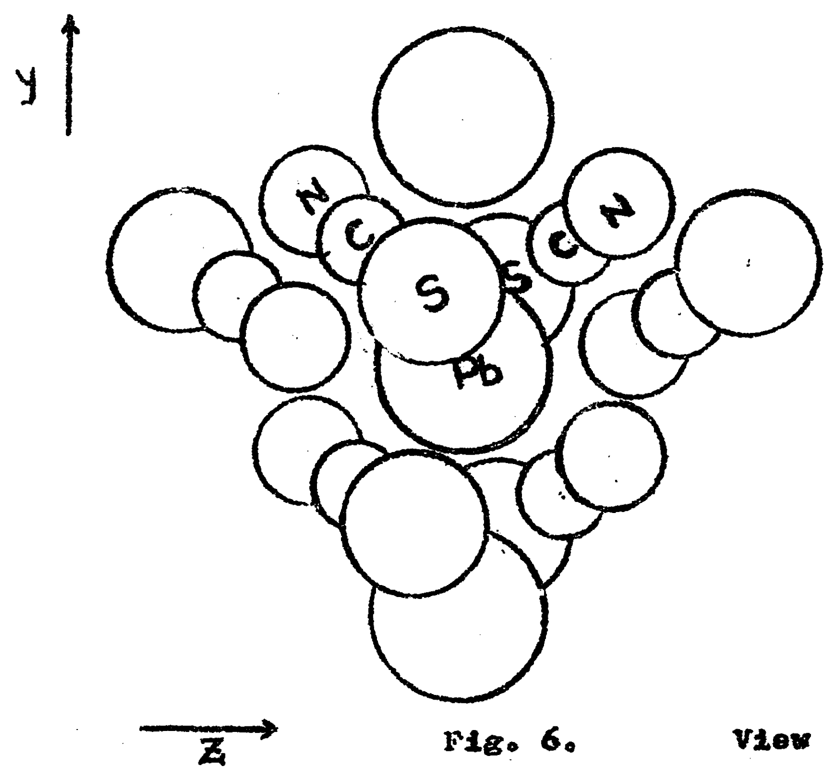


Fig. 6. View in X-direction.

The thiocyanate group is linear within the limit of the accuracy of the data. This structure agrees with the bent M-S-C bond postulated by Lewis (1964) for sulphur bonded

TABLE 35.

LEAD THIOCYANATE.

FRACTIONAL ATOMIC COORDINATES.

ATOMS	(x/a)	(y/b)	(z/c)
Pb	0.5000	-0.3867	0.2500
S	0.2957	-0.0454	0.1726
N	0.4429	0.2839	0.0586
C	0.3810	0.1351	0.1133

STANDARD DEVIATIONS.

Pb	0.0000	0.0006	0.0000
S	0.0013	0.0041	0.0020
N	0.0070	0.0149	0.0078
C	0.0085	0.0137	0.0099

TABLE 36.

FINAL ANISOTROPIC THERMAL PARAMETERS (Uij).

ATOMS	(UII)	(U22)	(U33)	(2U23)	(2U31)	(2U12)
Pb	0.014	0.006	0.018	0.000	-0.001	0.000
S	0.041	0.150	0.094	0.049	0.005	0.002
N	0.033	0.270	0.066	0.022	-0.021	0.054
C	0.064	0.126	0.073	-0.041	-0.009	-0.116

TABLE 37.

ORTHOGONAL COORDINATES.

ATOMS	(x)	(y)	(z)
Pb	4.857	-2.540	1.898
S	2.871	-0.299	1.327
N	4.303	1.865	0.334
C	3.701	0.888	0.807

TABLE 38.

INTER-ATOMIC BOND LENGTHS (in Å).

Pb - S	3.05	Pb - N	2.73
Pb - S	3.14	Pb - N	2.72
C - N	1.24	C - S	1.54

TABLE 39.

INTERBOND ANGLES (°).

N(v) – Pb – N(vi)	151	N(ii) – Pb – S(i)	110
N(v) – Pb – N(ii)	72	N(ii) – Pb – S(iii)	145
N(v) – Pb – N(iv)	134	N(ii) – Pb – S(vii)	72
N(v) – Pb – S(i)	77	N(ii) – Pb – S(vii)	77
N(v) – Pb – S(iii)	82	S(i) – Pb – S(iii)	85
N(v) – Pb – S(viii)	119	S(i) – Pb – S(viii)	72
N(v) – Pb – S(vii)	71	S(i) – Pb – S(vii)	143
N(ii) – Pb – N(iv)	75	S(viii) – Pb – S(vii)	141

The subscripts refer to the following positions:

(i)	x, y, z	(v)	$1-x, -y, -z$
(ii)	$x, -1+y, z$	(vi)	$x, -y, \frac{1}{2}+z$
(iii)	$1-x, y, \frac{1}{2}-z$	(vii)	$\frac{1}{2}+x, -\frac{1}{2}+y, z$
(iv)	$1-x, -1+y, \frac{1}{2}-z$	(viii)	$\frac{1}{2}-x, -\frac{1}{2}-y, \frac{1}{2}-z$

TABLE 40.

H	K	L	|Fo|	Fc
0	0	-10	44.5	-52.3
0	0	-8	65.3	61.0
0	0	-4	112.1	86.2
0	0	-2	188.5	-165.6
2	0	-10	42.9	-49.4
2	0	-8	89.9	69.4
2	0	-6	127.1	-116.1
2	0	-4	107.3	138.0
2	0	-2	178.5	-161.9
2	0	0	100.1	98.8
2	0	2	1.9	7.1
2	0	4	106.7	125.0
2	0	6	93.4	-112.5
2	0	8	87.2	73.1
2	0	10	41.0	-52.3
4	0	-10	39.6	-50.2
4	0	-6	71.5	-74.4
4	0	-4	74.8	59.0
4	0	-2	116.7	-108.8
4	0	0	152.8	143.5
4	0	2	156.8	-162.1
4	0	4	147.9	158.7
4	0	6	60.6	-71.0
4	0	8	51.1	54.0
6	0	-8	47.2	51.3
6	0	-6	56.4	-79.8
6	0	-4	83.5	111.3
6	0	-2	128.4	-150.5
6	0	2	112.9	-77.4
6	0	4	65.5	70.6
6	0	6	56.8	-56.1
6	0	8	68.0	64.4
8	0	-8	58.7	57.0
8	0	-6	62.4	-68.8
8	0	-4	92.2	59.3
8	0	0	87.7	59.2
8	0	2	99.2	-98.8
8	0	4	88.1	91.3
8	0	6	71.9	-67.1
10	0	-6	34.0	-41.4
10	0	-4	71.2	59.9
10	0	-2	105.4	-89.1
10	0	0	98.0	87.1
10	0	2	80.6	-78.3
10	0	4	51.7	49.6
10	0	6	21.5	-45.6
12	0	-2	41.1	-49.5
12	0	0	29.0	38.6
12	0	2	31.7	-48.6
1	1	-9	47.4	37.2
1	1	-8	77.2	57.0
1	1	-7	62.4	-47.6
1	1	-6	92.1	-73.3
1	1	-5	88.3	65.9
1	1	-4	87.6	59.7
1	1	-3	103.0	-132.4
1	1	-1	73.3	65.7
1	1	0	81.5	77.3
1	1	1	116.5	-93.3
1	1	2	132.3	-165.2
1	1	3	84.0	100.3
1	1	4	121.7	139.9
1	1	5	51.0	-44.8
1	1	6	74.7	-77.1
1	1	7	55.4	55.6
1	1	8	42.2	46.8
1	1	9	42.8	-41.1
1	1	10	31.8	-36.6
3	1	-9	44.0	39.0
3	1	-8	46.4	41.2
3	1	-7	60.4	-54.0
3	1	-6	57.1	-59.6
3	1	-5	58.8	67.9
3	1	-4	78.1	91.7
3	1	-3	84.6	-73.4
3	1	-2	122.6	-149.2
3	1	-1	39.5	33.8
3	1	0	164.4	178.9
3	1	1	121.2	-121.3
3	1	2	103.1	-95.8
3	1	3	90.2	85.7
3	1	4	52.5	45.6
3	1	5	54.0	-57.3
3	1	6	50.8	-45.3
3	1	7	55.2	58.1
3	1	8	49.4	49.7
3	1	9	32.1	-34.8
3	1	10	30.4	-39.5
5	1	-9	39.7	36.3
5	1	-8	59.0	53.1
5	1	-7	36.1	-39.8
5	1	-6	55.5	-75.4
5	1	-5	41.7	50.5
5	1	-4	61.2	72.0
5	1	-3	61.8	-70.2
5	1	-2	57.8	-56.5
5	1	-1	94.3	84.9
5	1	0	45.0	44.2
5	1	1	119.7	-107.2
5	1	2	66.3	-54.3
5	1	3	49.1	47.2
5	1	4	68.8	84.6
5	1	5	41.0	-51.9
5	1	6	59.7	-75.6
5	1	7	40.4	48.6
5	1	8	55.0	50.9
5	1	9	25.7	-30.9
7	1	-8	42.3	38.2
7	1	-7	34.1	-37.0
7	1	-6	25.5	-36.8
7	1	-5	43.7	58.0
7	1	-4	38.3	43.7
7	1	-3	50.0	-61.6
7	1	-2	81.8	-83.1
7	1	-1	58.0	54.0
7	1	0	116.4	104.5
7	1	1	68.6	-55.9
7	1	2	95.5	-91.8
7	1	3	55.5	44.5
7	1	4	64.7	67.4
7	1	5	55.6	-60.2
7	1	6	43.2	-42.6
7	1	7	37.5	40.8
7	1	8	26.7	35.0
9	1	-7	26.1	-32.0
9	1	-6	49.6	-49.1
9	1	-5	42.1	42.2
9	1	-4	76.3	68.5
9	1	-3	36.7	-37.3
9	1	-2	71.4	-67.7
9	1	-1	55.8	51.0
9	1	0	48.9	40.3
9	1	1	62.9	-59.2
9	1	2	43.8	-36.0
9	1	3	55.9	48.2
9	1	4	51.3	45.0
9	1	5	43.8	-44.9
9	1	6	46.3	-43.3
11	1	-5	31.4	35.6
11	1	-4	26.3	31.7
11	1	-3	44.5	-36.6
11	1	-2	34.1	-32.5
11	1	-1	51.6	46.9
11	1	0	51.8	45.3
11	1	1	37.0	-37.3
11	1	2	64.8	-59.8
11	1	3	32.9	32.5
11	1	4	39.2	49.6
0	2	-10	6.2	-6.5
0	2	-9	57.2	57.9
0	2	-8	9.8	6.8
0	2	-7	95.9	-87.3
0	2	-6	12.0	6.2
0	2	-5	106.2	106.0
0	2	-4	6.1	7.3
0	2	-3	119.9	-116.1
0	2	-2	75.9	-67.1
0	2	-1	98.5	118.0
2	2	-10	3.3	-5.7
2	2	-9	76.1	60.2
2	2	-8	23.4	13.9
2	2	-7	84.2	-71.4
2	2	-6	30.0	-23.2
2	2	-5	76.0	73.6
2	2	-4	42.2	44.1
2	2	-3	112.4	-115.9
2	2	-2	31.1	-14.5
2	2	-1	143.3	158.9
2	2	0	32.5	-41.1
2	2	1	129.2	-154.4
2	2	2	13.2	5.9
2	2	3	113.5	124.4
2	2	4	7.0	-3.7
2	2	5	86.9	-92.2
2	2	6	28.3	-22.2
2	2	7	65.0	71.3
2	2	8	22.2	18.4
2	2	9	50.1	-53.1
2	2	10	7.6	-7.0
4	2	-9	59.5	51.1
4	2	-8	21.2	10.7
4	2	-7	68.7	-65.1
4	2	-5	78.7	99.7
4	2	-4	6.7	-4.6
4	2	-3	114.9	-137.9
4	2	-2	7.1	6.9
4	2	-1	95.8	106.6
4	2	0	49.3	36.9
4	2	1	113.6	-88.3
4	2	2	56.0	-57.7
4	2	3	83.2	96.3
4	2	4	20.2	23.0
4	2	5	69.8	-89.3
4	2	6	19.2	-17.0
4	2	7	64.9	73.3
4	2	8	5.5	3.8
4	2	9	54.5	-53.5
6	2	-9	49.7	48.9
6	2	-8	3.4	4.4
6	2	-7	57.0	-64.9
6	2	-6	10.9	-10.9
6	2	-5	71.1	79.8
6	2	-4	32.3	35.7
6	2	-3	65.0	-74.9
6	2	-2	32.1	-32.8
6	2	-1	93.9	75.8
6	2	0	38.1	22.7
6	2	1	102.1	-117.2
6	2	3	105.3	109.6
6	2	4	6.3	-7.2
6	2	5	65.3	-78.1
6	2	6	11.6	-9.8
6	2	7	58.3	60.1
6	2	8	4.8	6.6
8	2	-8	13.4	9.1
8	2	-7	51.2	-50.9
8	2	-6	15.8	-12.9
8	2	-5	53.3	65.3
8	2	-4	6.2	5.2
8	2	-3	75.0	-79.7
8	2	-2	17.0	14.3
8	2	-1	112.4	96.2
8	2	0	10.0	2.5
8	2	1	102.0	-92.9
8	2	2	18.0	-14.4
8	2	3	62.6	62.0
8	2	4	28.5	22.7
8	2	5	58.2	-58.2
8	2	6	21.2	-15.6
8	2	7	54.8	55.7
10	2	-6	2.8	-4.8
10	2	-5	57.2	57.2
10	2	-4	14.0	6.7
10	2	-3	56.9	-59.2
10	2	-2	27.5	-17.9
10	2	-1	62.4	61.3
10	2	0	37.5	29.3
10	2	1	63.8	-60.6
10	2	2	14.7	-10.7
10	2	3	69.5	59.5
10	2	4	6.4	4.8
10	2	5	52.1	-61.7
12	2	-1	50.4	57.5
12	2	0	4.1	1.0
12	2	1	40.5	-56.1
1	3	-9	45.7	43.1
1	3	-8	34.7	-29.6
1	3	-7	65.6	-56.1
1	3	-6	65.6	49.4
1	3	-5	108.9	87.8
1	3	-4	86.0	-75.1
1	3	-3	97.2	-114.1
1	3	-2	66.1	78.9
1	3	-1	130.1	127.3
1	3	0	57.5	-74.3
1	3	1	77.4	-96.3
1	3	2	61.5	55.7
1	3	3	58.8	75.4
1	3	4	46.7	-42.3
1	3	5	72.1	-72.8
1	3	6	34.5	35.3
1	3	7	64.7	60.2
1	3	8	37.9	-33.7
1	3	9	59.8	-49.8
3	3	-9	50.3	45.6
3	3	-8	42.7	-36.1
3	3	-7	87.9	-67.4
3	3	-6	54.5	49.2
3	3	-5	59.4	81.4
3	3	-4	37.1	-40.0
3	3	-3	66.6	-68.2
3	3	-2	39.9	32.3
3	3	-1	66.5	74.4
3	3	0	65.6	-56.2
3	3	1	76.9	-91.5
3	3	2	56.1	59.4
3	3	3	92.0	106.2
3	3	4	51.9	-59.3
3	3	5	68.1	-84.9
3	3	6	54.3	49.8
3	3	7	66.3	58.7
3	3	8	40.9	-36.1
3	3	9	40.1	-45.3
5	3	-9	29.8	40.9
5	3	-8	27.8	-28.1
5	3	-7	53.8	-51.1
5	3	-6	30.3	33.4
5	3	-5	38.5	56.6
5	3	-4	35.2	-41.2
5	3	-3	72.2	-78.1
5	3	-2	60.4	72.2
5	3	-1	119.4	114.1
5	3	0	105.7	-79.7
5	3	1	120.5	-102.2
5	3	2	60.2	53.1
5	3	3	64.3	75.6
5	3	4	36.7	-44.9
5	3	5	48.2	-55.1
5	3	6	32.6	35.0
5	3	7	53.1	51.4
5	3	8	33.1	-27.4
7	3	-8	30.3	-28.5
7	3	-7	57.5	-50.4
7	3	-6	34.9	37.8
7	3	-5	56.9	63.6
7	3	-4	34.7	-45.8
7	3	-3	68.9	-76.2
7	3	-2	55.3	47.4
7	3	-1	65.5	68.0
7	3	0	39.7	-28.7
7	3	1	56.0	-52.5
7	3	2	38.7	30.6
7	3	3	74.8	63.0
7	3	4	49.2	-43.8
7	3	5	68.0	-63.4
7	3	6	36.4	35.1
7	3	7	52.9	52.9
9	3	-6	21.2	25.3
9	3	-5	30.9	43.3
9	3	-4	31.1	-29.0
9	3	-3	54.3	-52.7
9	3	-2	43.1	34.3
9	3	-1	65.1	58.4
9	3	0	46.3	-39.5
9	3	1	55.4	-67.1
9	3	2	61.3	49.9
9	3	3	60.6	66.7
9	3	4	43.8	-40.1
9	3	5	44.0	-48.7
9	3	6	19.7	25.1
11	3	-3	53.3	-52.2
11	3	-2	32.2	33.8
11	3	-1	49.5	48.5
11	3	0	34.1	-31.8
11	3	1	45.4	-47.5

END 2M 12S

ligand. The C-N and C-S bond lengths of 1.24 and 1.54Å (respectively) with high standard deviations are much different from the values expected for C-N triple bond and C-S single bond. However, they do not differ very much from the values registered in some other thiocyanates. In his study of I.R. spectra of K-thiocyanate Jones (1958) obtained values of 1.17 and 1.61Å for C-N and C-S. In some Reinecke salts in which thiocyanates bond through sulphur values of 1.37 and 1.64 have been recorded, Lewis et al, (1964).

The loss of triple bond character in C-N and the gain of double bond character in C-S are supported by the measured frequencies of C-N and C-S in different compounds. In organic nitriles, the C-N stretching frequency is usually 2,250cm^{-1} whilst the C-S stretch in mercaptains are in the region 600-700cm^{-1}, this shifts to a region 700-800cm^{-1} in thiocyanate complexes, (Nyholm et al., 1964). The shortening or lengthening of bonds in this ionic compound may be explained in terms of a resonance balance between $\langle\bar{N}=C=S\rangle$ and $|N\equiv C-\bar{\underline{S}}|$

PART V

CHEMICAL SYNTHESES

OF SOME AMINOPHOSPHINE COMPLEXES

Several samples of bis-(diphenyl-phosphino)-ethylamine palladium (II) complex were prepared in different media by varying the mole ratios of metal halide and ligand. Chemical analysis show that these are all 1:1 complexes. From the crystal structure analysis of the palladium complex (Part I), it was obvious that the ligand (PNPEt) is bidentate; further attempts were made to test this aspect by preparing the aminophosphine complexes of some other transition metals. The ligands used are bis-(diphenyl-phosphino)-alkylamine of the formula- $Ph_2.P.NR.P.Ph_2$ (R = H, Me, Et, nPr or iPr). With NiX_2 ($X = I^-$, Br^-, CNS^- or NO_3^-), apart from the 1:1 complex, it was possible to prepare the 1:2 and 2:1 complexes. Since the latter ratios do not conform to the ratio of metal to ligand in the palladium complex, the exact nature of the 1:2 and 2:1 is not known. An attempt to prepare the mercury(II) halide complexes leads to the isolation of the 1:1, 1:2 and 2:3 adducts. The arrangements of atoms in the 1:2 and 2:3 are uncertain.

The disulphides and the diselenides of bis-(diphenyl-phosphino)-methylamine were prepared by reaction of the ligand with an excess of sulphur or selenium (precipitated) in boiling benzene. In each case white needle-like crystals separated on cooling. Addition of ethyl iodide to the ligand (PNPEt) in ether resulted in a 1:1 adduct. The quaternisation has been proved by X-Ray work (Part II) to occur at one P-atom only.

EXPERIMENTS AND RESULTS.

Dichlorobis(diphenylphosphino)ethylaminepalladium(II).-
Bis(diphenylphosphino)ethylamine (8.268 g., 0.0200 mole) in warm acetone (120 ml.) and water (3 ml.) was added dropwise to potassium tetrachloropalladate(II) (3.265 g., 0.010 mole) in water (100 ml.) and acetone (4 ml.), and on standing gave a yellow crystalline solid (6.081 g., 67%), m.p. 276-278° (from alcohol) Found: C,53.1; H,4.3; Cl,10.8; N,2.7; P,10.2%; M (from unit-cell and density measurements), 590. $C_{26}H_{25}Cl_2NP_2Pd$ requires C,52.8; H,4.3; Cl,12.0; N,2.4; P,10.5%; M,591 .

Bis(diphenylphosphino)ethylamine ethyliodide.-
Bis(diphenylphosphino)ethylamine (0.974 g., 2.36 mmole) with (0.58 ml., 5.65 mmoles) of ethyl iodide gave white needle-like crystals (0.533 g.; 40%) (Found: I,23.2. $C_{28}H_{30}INP_2$ requires I,22.2%).

Bis(diphenylphosphino)methylamine (1.509 g., 3.79 mmoles) was refluxed with sulphur (0.253 g., 7.91 mmoles) in sodium-dried benzene (25 ml.). After removal of the excess of sulphur, the solution was evaporated, to give bis(diphenylphosphinothioyl)methylamine, which formed long white needles(from absolute alcohol), m.p. 168-170° (Found: C,64.8; H,5.0; N,3.0; P,13.1. $C_{25}H_{23}NP_2S_2$ requires C,64.8; H,5.0; N,3.0; P,13.4%). The diselenide was prepared by refluxing with an excess of selenium (precipitated) in benzene. The filtrate gave white needle-like crystals $Ph_2P.NMe.PPh_2$ Se_2 (96.7%), m.p. 192±1°C. (Found: C,53.8;

H, 4.2; P, 11.3% requires C, 53.9; H, 4.2; P, 11.1%).

The aminophosphine complexes of nickel (II) and mercury (II) were prepared by the addition of the ligand dissolved in hot acetone to the corresponding metal salt in hot ethanol. The results of their chemical analyses are listed in Table 41. The word 'requires' is abbreviated 'R' and 'found' is abbreviated 'F'; other symbols in the table refer to the following compounds :-

$R^{I} = Ph_2PNPHPh_2$

$R^{II} = Ph_2PNPMePh_2$

$R^{III} = Ph_2PNPEtPh_2$

$R^{IV} = Ph_2PNPnPrPh_2$

$R^{V} = Ph_2PNPiPrPh_2$.

TABLE 41.

RESULTS OF CHEMICAL ANALYSES (Cont'd).

SPECIMEN No.		COMPLEXES	R %C	F %C	R %H	F %H	R %N	F %N	M.Pt. (°C)
MOKS.	1	$R^{III}PdCl_2$	52.8	53.1	4.30	4.30	2.40	2.70	277±1
"	2	$R^{IV}(HgBr_2)_2$	28.2	28.4	2.35	2.60	1.20	1.23	178±2
"	3	$R^{IV}(HgCl_2)_2$	33.4	32.9	2.79	3.02	2.00	1.80	174±1
"	4	$R^{II}(Se)_2$	53.9	53.8	4.20	4.20	2.52	2.50	192±1
"	5	$R^{II}(NiI_2)_2$	29.5	26.2	2.28	3.63	1.35	1.33	234±2
"	6	$R^{IV}(NiI_2)_2$	30.8	29.9	2.57	3.96	1.30	1.40	194±2
"	7	$R^{V}NiI_2$	43.8	43.7	3.66	3.51	1.89	1.78	200±1
"	8	$R^{IV}NiBr_2$	50.2	45.0	4.18	4.22	2.17	2.32	295±1
"	9	$R^{V}NiBr_2$	50.2	50.0	4.18	4.32	2.17	0.59	300±2
"	10	$R^{II}NiBr_2$	48.6	48.4	3.72	3.79	2.27	2.00	308±2
"	11	$R^{I}NiI_2$	41.3	42.9	3.00	3.50	2.01	1.80	168±1
"	12	$R^{I}NiBr_2$	47.7	47.9	3.48	3.66	2.32	2.20	250±1
"	13	$(R^{II})_2Ni(NO_3)_2$	57.5	58.2	4.41	4.48	5.70	6.26	185±3
"	14	$(R^{IV})_2Ni(NO_3)_2$	57.2	59.7	4.92	5.21	5.50	6.27	174±1
"	15	$(R^{V})_2Ni(NO_3)_2$	57.2	57.4	4.92	5.28	5.50	6.46	178±2
"	16	$R^{I}HgBr_2$	38.6	38.8	2.82	3.00	1.90	1.76	157±1
"	17	$R^{II}HgBr_2$	39.5	39.4	3.03	2.98	1.84	2.00	202±2
"	18	$R^{III}HgBr_2$	40.3	40.2	3.23	3.20	1.81	2.06	187±1
"	19	$(R^{IV})_2(HgBr_2)_3$	33.5	32.7	2.80	2.96	1.40	1.70	163±1
"	20	$R^{V}HgBr_2$	41.1	41.1	3.43	3.55	1.78	1.86	173±2
"	21	$R^{I}HgI_2$	34.3	34.1	2.50	2.67	1.67	1.80	150±2
"	22	$(R^{II})_2HgI_2$	47.8	47.6	3.70	4.04	1.83	1.79	165±1
"	23	$(R^{III})_2HgI_2$	49.1	47.8	3.90	4.00	2.00	1.80	182±2

R E F E R E N C E S.

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A P P E N D I X

1.1. INTRODUCTION

An impact was made on the physical aspect of crystal studies in 1912, when Max von Laue made his announcement of the X-Ray diffraction by crystals. This discovery quickly gave rise to two important fields. The X-Ray spectroscopy which is associated with the names of W.H. Bragg, Moseley and de Broglie; and, the X-Ray crystal structure analysis which is mostly linked to the names of Bragg and his son Lawrence. Soon X-Ray diffraction became a powerful tool for investigating the structure of matter on an atomic scale and explaining the details of the stereochemistry involved in various molecules and crystals.

In November 1912, W.L. Bragg published the first paper on crystal structure analysis in which he gave the entire interpretation of Laue's diagram of zinc blend. Soon after, he obtained the complete structure of NaCl, KCl and few others. By this determination a scale for the measurement of atomic distances in crystals and also of X-Ray wave lengths was obtained for the first time. The first great triumphs of the new science of X-Ray crystal structure analysis were mostly in the field of inorganic chemistry. W.H. and W.L. Bragg in their study of calcite and found the carbonate ion to be planar and the three oxygen atoms to be equivalently related to the carbon atom. This wiped out the old theory that one of the oxygen atoms was attached to the carbon atom by a double bond.

With the advancement in this X-Ray technique, W.L. Bragg's School solved some of the problems involved in silicate structures.

The heavy computation often involved in this work of structure analysis made the early work very slow and tedious. Many structures solved at first were in two dimensions but the availability of the recent high speed digital electronic computers has made possible the investigation in three dimensions of structures which might not have yielded to the efforts of one individual in a lifetime of old style computation.

Among organic compounds, progress was at first slow but the pace accelerated as soon as the structures of the normal paraffin chain, of the benzene ring and naphthalene nucleus were well established (since these form the skeleton of many organic structures). Subsequently, structures of such complex substances as phthalocyanines, steroids, carbohydrates, penicillin and vitamin B 12 were determined.

1.2. X-RAY DIFFRACTION ACCORDING TO LAUE

A crystal can be defined as a substance in which the internal atomic or molecular arrangement is regular and periodic in three dimensions over distances which are large compared with the unit of periodicity.

If the atoms in a crystal are replaced by points each array of points thus formed represents a lattice of the crystal. In order to provide the lattice with the means of scattering radiation, it is assumed that an electron is situated at each lattice point so that each point becomes a source of scattered spherical wavelets under the stimulation by an incident monochromatic X-Ray radiation.

The mode of propagation (Fig. 1) is represented by its wave vector $\underline{V}$ and its direction is that of the normal to the planes of equal phase or wave front.

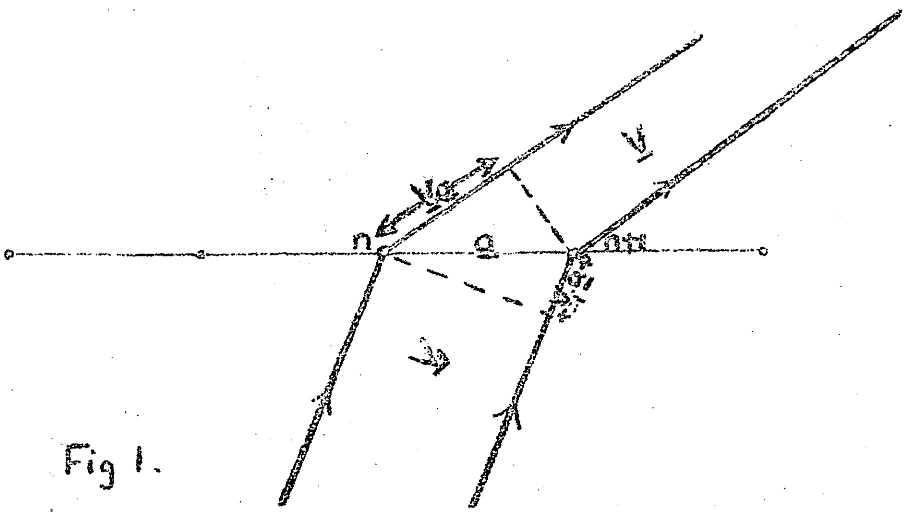

Fig 1.

If the three vectors by which a crystal is described are represented by $\underline{a}$, $\underline{b}$ and $\underline{c}$, then any lattice point can be described by the co-ordinate vector $\underline{r} = u\underline{a} + v\underline{b} + w\underline{c}$ where u, v and w are integers and are called the co-ordinate numbers.

In fig. 1, if an atom is indexed n, the next one is n + 1, and the vector between them is the translation $\underline{a}$, then for full co-operation of all wavelets from these atoms, a condition is sought such that wavelets from atoms n and n + 1 arrive at the point of observation without any difference in phase. The path difference between wavelets of n + 1 and n is $\underline{va} - \underline{v}_1\underline{a}$ when measured in wave lengths.

For best reinforcement, this must be an integral number of wave lengths say h. Thus a diffracted maximum occurs if v is such that

$$(\mathbf{v} - \mathbf{v}_1).\mathbf{a} = h. \qquad (1.1)$$

Similarly for the translations b and c, one has

$$(\mathbf{v} - \mathbf{v}_1).\mathbf{b} = k \qquad (1.2)$$

and $$(\mathbf{v} - \mathbf{v}_1).\mathbf{c} = l\ ; \qquad (1.3)$$

if $$(\mathbf{v} - \mathbf{v}_1) = \mathbf{S}. \qquad (1.4)$$

$$\therefore \quad (\mathbf{v} - \mathbf{v}_1)\ \mathbf{a} = \mathbf{S}.\mathbf{a}, \qquad (1.5)$$

$$(\mathbf{v} - \mathbf{v}_1)\ \mathbf{b} = \mathbf{S}.\mathbf{b}, \qquad (1.6)$$

and $$(\mathbf{v} - \mathbf{v}_1)\ \mathbf{c} = \mathbf{S}.\mathbf{c}, \qquad (1.7).$$

So that

$$\left.\begin{aligned} \mathbf{S}.\mathbf{a} &= h \quad (1.8), \\ \mathbf{S}.\mathbf{b} &= k \quad (1.9), \\ \text{and} \quad \mathbf{S}.\mathbf{c} &= l \quad (1.10). \end{aligned}\right\} \text{These are known as Laue equations.}$$

1.3. X-RAY REFLECTION - W.L. BRAGG

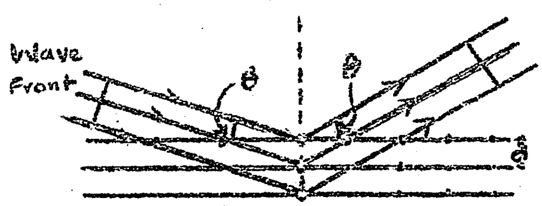

Fig 2.

If one considers a set of N+1 equidistant atomic planes of spacing d, and a monochromatic X-Ray beam falling on it at a glancing angle θ, Fig. 2, and also assumes that each atom reflects a very small fraction of the incident amplitude, small enough for the weakening effect of this reflection on the incident amplitude to be neglected throughout the crystal, then full reinforcement is obtained should all the reflected waves arrive in the same phase.

The Laue equations are unsuitable for direct application to diffraction problems. W.L. Bragg (1) (1913) showed their significance by relating the integers h, k, l to the Millerian indices of the lattice planes. The relationship between Bragg's Law and the Laue equations is shown below:

Since $\underline{a}/h.\underline{S} = 1,$ (1.8)

$\underline{b}/k.\underline{S} = 1,$ (1.9)

and $\underline{c}/l.\underline{S} = 1;$ (1.10)

therefore, by subtracting equation (1.9) from (1.8)

$(\underline{a}/h - \underline{b}/k).\underline{S} = 0$; (1.11) i.e. the vector $\underline{S}$ is perpendicular to $(\underline{a}/h - \underline{b}/k)$; the latter can be shown to be the plane of Miller indices. Similarly $\underline{S}$ is perpendicular to $(\underline{a}/h - \underline{c}/l)$. Thus in Fig. 3 (i) $\underline{S}$ is perpendicular to the plane defined by the intercepts $\underline{a}/h$, $\underline{b}/k$, $\underline{c}/l$; i.e. plane with Miller indices hkl.

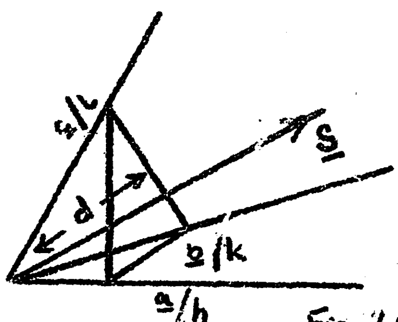

Fig. 3(i)

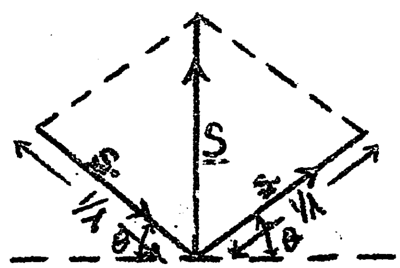

Fig. 3(ii).

Since by definition the vector $\underline{S}$ bisects the incident and the diffracted beams, Fig. 3(ii), and it is perpendicular to the lattice hkl, a close analogy with reflection is easily drawn. The spacings d(hkl) of the planes is the perpendicular distance from the plane hkl to the origin (Fig. 3(i) and it is equal to the projection of $\underline{a}/h$, $\underline{b}/k$

and $\underline{c}/l$ on the vector $\underline{S}$, i.e.

$$d_{hkl} = \underline{a}/h \cdot \underline{S}/|S| \quad (1.12).$$

But from the Laue equations, $\underline{a}/h \cdot \mathbf{S} = 1$; (1.8)

and $|S| = 2 \sin \theta/\lambda$ (1.13), (Fig. 3(ii), where θ is the glancing angle on plane hkl. Therefore $2d \sin \theta = \lambda$. (1.14) This is known as the Bragg's Law and indicates that a reflection from a lattice plane can only take place when the angle of incidence of the X-Ray beam satisfies the condition of the equation.

1.4. THE ATOMIC SCATTERING FACTOR

It is often said that the actual scattering units in crystals are the electrons and not atoms so that the atomic linear dimensions may be neglected in comparison with both the space lattice dimensions and the wave lengths of X-Rays. Also since these electrons are assumed to be loosely bound in atoms any change of phase on scattering is the same for all of them; thus the amplitude scattered in the forward direction could be written as Z times that due to a single electron where Z is the atomic number of the atom. Atoms in crystals, however, have the diameter of the electron cloud of the same order as the interatomic distances; hence they cannot be regarded as points. Thus there always exists interference between rays scattered from different parts of the atom and therefore the intensity of the resultant emergent beam is reduced i.e. less than Z times that due to a single electron. In general, the phase differences depend upon the angle of scattering, the wave length of the radiation and the volume throughout which the electrons are distributed. Thus the scattering factor, f, will approach Z for small angles of scattering and will fall off with increasing angle at a rate that for a given wave length is determined by the distribution of electrons in the atom.

Atomic scattering factors have been deduced for many atoms from the intensities of reflections measured for crystals whose structures have been established (James (2) and Brindley, 1931). But it is also possible to calculate the values from the electronic structures (Hartree, 1928) of the atoms. Other workers who have done enormous work in this branch include (Thomas (3), Fermi (4) McWeeny (5), Tomile and Starn (6), Berghuis et al (7). So far the calculated values have agreed quite reasonable with the experimental.

1.5. TEMPERATURE FACTOR

In practice the theoretical atomic scattering factors available in the literatures make no allowance for the atomic thermal vibration. For such calculations atoms are assumed to be at rest but even at absolute zero atoms have a finite amplitude of oscillation. The frequency of this oscillation is so much smaller than that of the X-Rays that to a train of X-Ray waves the atoms would appear stationary but displaced from their true positions in the lattice.
The general result is to spread the electron distribution and so decrease the intensities of the spectra. If the X-Rays are incident at an angle θ and the mean thermal

displacement of an atom normal to the plane of reflection is represented by $\bar{\mu}$, then the path difference compared to that of an atom at rest is $2\bar{\mu}\sin\theta$ and the phase change is $2\pi/_{\lambda}$. $2\bar{\mu}\sin\theta = 4\pi\mu\sin\theta/\lambda$. If f_o is the scattering factor of the undisplaced atom, then the effect of thermal vibration is given as

$f = f_o \sum^{\mu_j} e^{4\pi i\,\mu_j(\sin\theta/\lambda)}$ (1.15a), when summed over the displacements μ_j. If the above is an isotropic displacement for a centrosymmetric case, the sine terms of the above expression disappear and its cosine component can be written as

$$f = f_o \cos\{4\pi\bar{\mu}(\sin\theta/\lambda)\} \quad (1.15b).$$

But $\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!}$ (1.16),

while $\exp(-\frac{1}{2}x^2) = 1 - \frac{x^2}{2} + \frac{x^4}{4.2!}$ (1.17).

Thus to a good approximation

$$\cos x = \exp(-\tfrac{1}{2}x^2) \quad (1.18),$$

$f = f_o e^{-8\pi^2\bar{\mu}^2(\sin^2\theta/\lambda^2)}$, (1.19), where $\bar{\mu}^2$ is the mean square displacement of the atom at right angles to the reflecting plane.

But $B = 8\pi^2\bar{\mu}^2$ (B is the Debye (8) temp. factor.

$$\therefore f = f_o e^{-B\sin^2\theta/\lambda^2} \quad (1.20)$$

The overall value of B can be determined by Wilson's method (9).

In many organic crystals, the molecules behave as rigid bodies. Since these are linked by relatively weak van der Waals attraction, they perform oscillations which are large compared with the movements of atoms which have strong covalent bonds within the molecule. For such cases, anisotropic temperature factor may be required. This problem has been discussed by Cruickshank (1956) (10a, b).

If the motion is anisotropic, then the thermal displacements require an assumption of an ellipsoidal distribution rather than spherical. In this case, the mean displacement is represented by a vector function or a tensor instead of a single vector normal to the reflecting plane. Thus in an anisotropic harmonic potential field the vibrations of atoms can be described (10a, b) by a symmetrical tensor U^r with six independent components.

Each atom in the structure requires one such tensor U^r. The mean square displacement or amplitude of vibration in a direction of a unit vector $\underline{l}$ with components (l_1, l_2, l_3) can be written as

$$\overline{u^2} = \sum_{i=1}^{3} \sum_{j=1}^{3} U_{ij}\, l_i\, l_j \qquad (1.21)$$

$$= U_{11}l^2{}_1 + U_{22}l^2{}_2 + U_{33}l^2{}_3 + 2U_{12}l_1l_2 + 2U_{13}l_1l_3 + 2U_{23}l_2l_3$$

Since $U_{23} = U_{32}$, etc. (1.22)

U and l are here defined w.r.t. the reciprocal axes $\underline{a}^*$, $\underline{b}^*$, $\underline{c}^*$, so that the component of $\underline{U}$ in the (1,0,0) direction parallel to a* is

$$\overline{u^2} = U_{11}$$

In this anisotropic case the transform of the smearing function is

$$q(\underline{s}) = \exp[-2\pi^2(\Sigma\ \Sigma\ U_{ij}\ s_i\ s_j)] \qquad (1.23) \qquad (1.23)$$

where $\underline{s} = (s_1, s_2, s_3)$ is the reciprocal vector. If the units of U_{ij} are $\mathring{A}^2$, the units of s_i are $\mathring{A}^{-1}$. At a reciprocal lattice point $\underline{s} = (ha^*, kb^*, lc^*)$ and we may write

$$q(hkl) = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2}$$

$$+ 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)] \qquad (1.24)$$

This is the form used for anisotropic vibrations in the Glasgow SFLS programme.

1.6. STRUCTURE FACTOR EXPRESSION

A crystal with N atoms per unit cell can be imagined to consist of N interpenetrating lattices with all lattice points occupied by atoms. Individually, each of these lattices will obey Laue and Bragg conditions but in general the intensities of the various planes will depend on the atomic arrangements within the unit cell.

The position of the j^{th} atom, situated at the point x_j, y_j, z_j where x_j, y_j and z_j are fractions of the unit cell vectors can be represented by

$$\underline{r}_j = x_j\underline{a} + y_j\underline{b} + z_j\underline{c} \qquad (1.25).$$

The path difference between the waves scattered by the atom in j^{th} position and an atom at the origin can be written as $\lambda\underline{r}_j\ \underline{S}$ and the corresponding phase difference as $2\pi\underline{r}_j\ S$. So that for all the atoms in the j^{th} unit cell, the wave scattered has an expression $f_j\exp(\frac{2\pi i}{\lambda}.\lambda r_j.S) = f_je^{2\pi i}r_j.S$ (1.26)

An expression for all the atoms in the unit cell is given by

$F = \sum_{j=1}^{N} f_j \exp 2\pi i\, \underline{r}_j . \underline{S}$, (1.27) where f_j is the atomic scattering factor of the j^{th} atom.

$$\therefore F = \sum_{j=1}^{N} f_j e^{2\pi i(x_j \underline{a}\underline{S} + y_j \underline{b}\underline{S} + z_j \underline{c}\underline{S})}. \quad (1.28)$$

since $r_j = x_j\underline{a} + y_j\underline{b} + z_j\underline{c}$. (1.25)

This quantity F is called the structure factor. It is a complex resultant which can be represented by an amplitude $|F|$ and a phase constant α. The structure amplitude $|F|$ can be obtained from measured intensities but the phase is not an observable quantity (hence the phase problem). The amplitude and phase of the wave scattered by the reflection (hkl) are given by the equation

$F_{(hkl)} = |F_{(hkl)}| e^{i\alpha(hkl)}$ (1.29). The complex $F_{(hkl)}$ can be separated into the real and imaginary parts

$F_{(hkl)} = A_{(hkl)} + iB_{(hkl)}$ (1.30), so that

$$A_{(hkl)} = \sum_{j=1}^{N} f_j \cos 2\pi(hx_j + ky_j + lz_j) \quad (1.31)$$ and

$$B_{(hkl)} = \sum_{j=1}^{N} f_j \sin 2\pi(hx_j + ky_j + lz_j). \quad (1.32)$$

B = 0, for a centrosymmetric system (provided origin is at centre of symmetry).

$$|F_{(hkl)}| = \sqrt{(A^2 + B^2)} \quad (1.33)$$

and $$\alpha_{(hkl)} = \tan^{-1} B/A \quad (1.34)$$

The structure factor can also be expressed in terms of the electron density, $\rho(xyz)$. At a point x, y, z, the amount of scattering matter in the volume element dxdydz is ρ(dxdydz); so that, the structure factor expression for the total scattering in unit cell volume V is given as

$$F_{(hkl)} = V\int_0^1\int_0^1\int_0^1 \rho(xyz)\,\exp[2\pi i(hx+ky+lz)]\,dxdydz \qquad (1.35).$$

1.7. FOURIER SERIES AS APPLIED TO CRYSTALS

It is an established fact that a periodic function can be represented by an appropriate sum of the cosine and sine terms known as the Fourier Series. Since a crystal involves such a periodic function in three dimensions, its electron density can be easily represented by a Fourier Series. In general, a Fourier Series can be written as a function T(φ) which is the sum of an infinite number of weighted exponentials of positive and negative values of a phase angle φ, expressed as

$$T(\varphi) = \sum_{n=-\infty}^{+\infty} A_n \exp(in\varphi) \qquad (1.36),$$

$$\text{or} \quad T(\varphi) = \sum_{-\infty}^{+\infty} A_n \exp(-in\varphi) \qquad (1.37).$$

The latter form has been found useful in the crystal studies. This function can be extended to accommodate several variables such as the case with the electron density, ρ(xyz), which is a function of the three axial co-ordinates. Since every point in space has to be covered, there should be a triply infinite number of Fourier coefficients A_n.

The periodicity of the crystal lattice however limits the number of terms to those whose direction and wave length correspond to a particular crystal plane.

A Fourier series which represents the electron density as a function of x, y, z, i.e. the fractions of the three co-ordinates axes of the unit cell, has a term for every crystal plane hkl.

Thus an electron density at the point (xyz) may be represented by a Fourier series in the form

$$\rho(x,y,z) = \sum_{-\infty}^{+\infty}\sum\sum A(pqr)\, e^{-2\pi i(px+qy+rz)} \qquad (1.38),$$

where p, q, r are integers and $A(p,q,r)$ the Fourier coefficient which must first be known before the value of $\rho(xyz)$ is obtained at any point in the crystal.

Since the expression for the structure factor is given by $F_{(hkl)} = V\int_0^1\int_0^1\int_0^1 \rho(xyz)\exp 2\pi i(hx+ky+lz)\, dxdydz$ (1.39),

therefore by substituting the $\rho(xyz)$ value from equation (1.38), the $F_{(hkl)}$ expression becomes

$$F_{(hkl)} = \int_0^1\int_0^1\int_0^1 \sum_{-\infty}^{+\infty}\sum\sum VA \exp 2\pi i[(h-p)x+(k-q)y+(l-r)z]\, dxdydz \qquad (1.40).$$

Because of the periodic nature of the exponential functions, on integration, every term is zero over a single complete period except in the case when $h = p$, $k = q$ and $l = r$.

Thus $F_{(hkl)} = \int_0^1\int_0^1\int_0^1 VA_{(pqr)}\, dx\, dy\, dz$, (1.41),

$$= VA_{(pqr)} \qquad (1.42)$$

So that $A_{(pqr)} = F_{(hkl)}/V \qquad (1.43)$

When this value [equation (1.43)] of the Fourier coefficient is substituted in equation (1.38), the expression for the electron density becomes

$$\rho(xyz) = \frac{1}{V} \sum_{-\infty}^{+\infty}\sum\sum F_{(hkl)}\, e^{-2\pi i(hx+ky+lz)}. \qquad (1.44)$$

but the above Fourier series expression for the electron density can be written in such a way that the resultant $F_{(hkl)}$ is split into its components $-|F_{(hkl)}|$, the amplitude and $\alpha_{(hkl)}$, the phase angle.

Thus the appropriate equation in the most general case (no centre of symmetry) is

$$\rho(xyz) = \sum_{-\infty}^{+\infty}\sum\sum \frac{|F_{(hkl)}|}{V} \cos 2\pi[hx+ky+lz-\alpha_{hkl}]. \qquad (1.45)$$

The phase angle $\alpha_{(hkl)}$ can be regarded as measuring the displacement of the peak of the wave from the origin. In the centrosymmetrical case however the displacement is restricted to 0 or π in radians provided the origin is taken as a centre of symmetry. These two possible values of the displacement can be taken care of by making the signs of the coefficients either positive or negative, and so for *

* This should read:- .... and so for such a centrosymmetrical structure the Fourier series can be written as

$$\rho(xyz) = \sum_{-\infty}^{+\infty}\sum\sum \frac{|F(hkl)|}{V} \cos 2\pi(hx+ky+lz) \quad \ldots\ldots\ldots 1.46.$$

1.8. **THE PATTERSON FUNCTION - F^2 series.**

In 1934, a new approach to the solution of phase problem was developed by A.L.Patterson. In this technique, the calculation does not involve the phase, instead the known structure factor amplitude is used to generate all possible interatomic vector peaks available the structure. This however often results in the overlap of many vectors but immediate success of this method lies in the fact that t interatomic vector peaks due to relatively heavy atoms are very prominent and these often lead to the atomic coordinates of the heav atoms whose phases are used as a prelude to the actual phases due to all the atoms. Thus the structure is solved. The Patterson Function can be written as

$$P(U,V,W) = V\int_0^1\int_0^1\int_0^1 \rho(xyz)\rho(x+u,y+v,z+w)dxdydz \quad \ldots\ldots\ldots\ldots\ldots 1.4$$

In general, for a system of N atoms, N(N-1)/2 non-origin vector peaks will appear on a Patterson map.

The probability that every vecto peak that appears on ....

continued on page 15.

the map will be resolved is very small. Peaks which are due to a group of atoms of nearly the same scattering powers tend to overlap and this often renders the map too difficult to interpret except where there is a relatively heavy atom. If, however, one of the unit cell axes is fairly short, say of the order 3-5 Å, the molecules occupying such cells tend to be flat and projection down such an axis often leads to the correct structure.

The expression (1.47) on integration could be written as

$$P(u,v,w) = \frac{1}{V^2} \sum_h \sum_k \sum_l {}_{-\infty}^{+\infty} \left| F_{(hkl)} \right|^2 \exp 2\pi i(hu+kv+lw) \qquad (1.48)$$

For the purpose of computation, the $F^2_{(hkl)}$ forms the coefficient of the Fourier series given by the Patterson expression.

The sharpening of the F^2 can be effected by modifying the F^2 values with the values obtained from the expression $M(SL) = [\hat{f} \exp(\sin^2\theta/\lambda^2)]^{-2}$. The product of F^2 and $M(SL)$ gives the sharpened values of F^2. The sharpening of these F^2 before they are used in the Patterson expression often enhances the chances of getting those vector peaks which are due to the relatively heavy atoms while it helps to suppress diffuse ones.

In 1936, Harker pointed out that for crystals with symmetry elements, it should be possible to specify on which plane or along which line of the vector cell, the symmetry related peaks could be found. This often provides a useful means of solving the Patterson function.

When a crystal has one heavy atom per unit cell together with some light atoms, the vectors arising between the heavy atom and the light ones are very prominent and often result in a picture that reveal the positions of the light atoms. This characteristic of the Patterson maps is shown in the work of Speakman (11) on the Rubidium and Potassium hydrogen bisphenyl-acetates.

1.9. HEAVY ATOM TECHNIQUE

The heavy atom method as the name implies is based on the high atomic scattering power of the relatively heavy atom in a structure. The structure factor expression for a crystal with one atom in the unit cell may be written as

$$F_{(hkl)} = f_H \exp 2\pi i(hx_H + ky_H + lz_H) + \sum_{j=1}^{n} f_n \exp 2\pi i(hx_j + ky_j + lz_j) \qquad (1.50).$$

Where f_H is the scattering factor of the heavy atom whose co-ordinates are $x_H y_H z_H$ and n is the number of light atoms. The first knowledge of the co-ordinates $x_H y_H z_H$ is obtained from the solution of the Patterson function.

Since the Patterson map can also reveal distinctly vector peaks between the heavy atom and fairly heavy atom, it is often possible to locate as well the co-ordinates of such atoms.

The term 'heavy' is relative, where this means that $\sum f^2_H / \sum f^2_L < 1$, the heavy atom might be too light for the purpose of phasing. If $\sum f^2_H / \sum f^2_L > 1$, although nearly all the phases predicted by the heavy atom will be right, the positions of very light atoms might be difficult to locate.

because of high absorption coefficient of crystals containing such heavy atoms and because of diffraction ripples, associated with them. If however $\sum f^2_H / \sum f^2_L$ is just greater than unity, the conditions are optimum for solution of the structure.

G. Sim (1957) (12) has performed calculations on the fraction of structure factors whose phases should be determined within specified limits by a selected atom or group of atoms. Those structure factor terms whose phases can be regarded as being approximately correct are used to carry out a first Fourier synthesis which results in a map revealing some, or all, of the features of the structure. If only part of the structure is obtained after the first Fourier synthesis the position of atoms revealed are included in the next round of phasing calculations and this successive approximation is continued until the whole structure is revealed.

J.M. Robertson and Woodward in 1937 (13) demonstrated the strength of the Heavy Atom Technique in the solution of the structures of Phthalocyanine complexes of Ni and Pt. Though it is true that, in general, direct methods of structure analysis are not possible, yet in special cases they can be applied. Sometimes the structure contains one or two heavy atoms in special positions, and this atom may so much overshadow all the other atoms in the unit cell that it controls the signs of the structure factors. One such heavy atom at the origin will make all, or nearly all, the structure factors positive. A first Fourier synthesis based on these terms will reveal the positions of all atoms but if calculations of the subsequent structure factors result in signs of the terms changing, then one or two further Fourier syntheses are often sufficient. This method was used in the case of platinum phthalocyanine (Robertson et al (1957) (14), where it was clear that although there were two molecules/unit cell the two Platinum atoms had to lie at centres of symmetry and predominantly determined the signs of the Fourier terms.

1.10. METHODS OF STRUCTURE REFINEMENT

(a) DIFFERENCE FOURIER SYNTHESIS

The discussion up to this point has been mainly on the methods of determining the atomic positions in crystals in order to establish the structure and the stereochemistry of the compound under investigation. Even when the structure is revealed by these preliminary methods, the atomic parameters are seldom accurate enough to give the best possible atomic co-ordinates that can be derived from the intensity data and hence the process of refinement is necessary.

A very efficient method of refinement discussed by Booth (1948,b) (15) and Cochran (1951) (16) is based on the "Difference Fourier Synthesis". The expression for the Difference Fourier synthesis is easily obtained by subtracting the ρ_c expression from that of ρ_o.

Thus if $$\rho_o = \sum_{-\infty}^{+\infty}\sum\sum \frac{F_o}{V} e^{-i\varphi} \qquad (1.51),$$

where $$\varphi = 2\pi(hx/a + ky/b + lz/c) \qquad (1.52),$$

and $$\rho_c = \sum_{-\infty}^{+\infty}\sum\sum \frac{F_c}{V} e^{-i\varphi} \qquad (1.53).$$

Then by subtracting equation (1.53) from (1.52),

$$\rho_o - \rho_c = \sum_{-\infty}^{+\infty}\sum\sum \frac{F_o - F_c}{V} e^{-i\varphi} \qquad (1.54).$$

But (F_o) and (F_c) are both complex quantities characterised by amplitude $|F|$ and phase constant α,

Therefore if $(F_o) = |F_o| e^{i\alpha}$ (1.55),

and $(F_o) = |F_c| e^{i\alpha}$ (1.56).

When F_o and F_c values in (1.55) and (1.56) are substituted in equation (1.54) the expression becomes

$$\rho_o - \rho_c = \sum_{-\infty}^{+\infty}\sum\sum \frac{|F_o| - |F_c|}{V} e^{-i(\varphi-\alpha)} \qquad (1.57),$$

$$= \sum_{-\infty}^{+\infty}\sum\sum \pm \frac{|\Delta|_{hkl}}{V} e^{-i(\varphi-\alpha_{hkl})} \qquad (1.58)$$

Applying F odel's Law, $F_{hkl} = F_{\bar{h}\bar{k}\bar{l}}$

Thus $\rho_o - \rho_c = \sum_{-\infty}^{+\infty}\sum\sum \pm \frac{|\Delta|_{hkl}}{V} \cos\left(\frac{2\pi hx}{a} + \frac{2\pi ky}{b} + \frac{2\pi lz}{c} - \alpha_{hkl}\right)$,

(1.59)

where $\alpha = \tan^{-1} B/_A$

Thus $|\Delta|$ becomes a coefficient of the Fourier synthesis but unlike F_o synthesis, signs precede $|\Delta|$.

The sign, positive or negative, depends on whether or not $|F_o| - |F_c| < 0$. When $|F_o| - |F_c| = 0$, the expression gives zero and this is the case expected theoretically when a structure has been exactly determined. However, this does not happen in practice. The final difference map often contains some peaks and troughs due to errors in the estimation of atomic parameters and some due to imperfections in the data.

According to Booth and Cochran, if the calculated co-ordinates $(x_c y_c z_c)$ are plotted on the difference map, the directions of steepest ascent at these points give the directions of the shifts of the atoms from their positions as revealed by the electron-density map. The magnitude of the shift can be calculated from the relation

$$\varepsilon = r = \left[\frac{d(\rho_o - \rho_c)}{dr}\right] / [2_o(0)p] \quad (1.60), \text{ where } \rho_o = z(p/\pi)^{3/2}$$

ε is the magnitude of the shift;

ρ_o, ρ_c are the observed and calculated electron densities respectively, and $\rho_o(0)$ is the electron density at the atomic centre where p has an average value of 5.0.

1.10(b) <u>LEAST-SQUARES METHOD</u>

Hughes (1941) introduced the method of least-squares refinement. This like the difference Fourier synthesis overcomes the effects due to termination of series and also provides a means of diminishing the influence of inaccurate coefficients on the results.

The object of this process is to find the best set of atomic parameters that will result in minimising the quantity

$$R = \sum_{hkl} W(hkl)[|F_{o(hkl)}| - |F_{c(hkl)}|]^2 \quad (1.61),$$

where the sum is over the set of crystallographically independent observed planes and W(hkl) is a weight for each term. In the derived parameters, the value of the weight which gives the lowest standard deviation can be represented by

$W(hkl) = 1/\sigma^2_{(hkl)}$ where $\sigma_{(hkl)}$ is the standard deviation for each F_{hkl} . Calculated structure factors are obtained from the relation

$$F_c = \sum_n f_n e^{2\pi i(hx_n + ky_n + lz_n)} \qquad (1.62).$$

By using Taylor's series, the expression (1.61) can approximate to a linear equation. If the unrefined co-ordinates of the n^{th} atom are x_n, y_n, z_n; the correct position can be defined as

$$x_n + \epsilon x_n, y_n + \epsilon y_n, z_n + \epsilon z_n.$$

So that

$$F_o = f(x_n + \epsilon x_n, y_n + \epsilon y_n, z_n + \epsilon z_n); \qquad (1.63)$$

and $F_c = F(x_n y_n z_n)$. (1.64)

Then by applying Taylor's series,

$$F = F_o - F_c + \sum [(\epsilon x_n \frac{\partial F_c}{\partial x} + \epsilon y_n \frac{\partial F_c}{\partial y_n} + \epsilon z_n \frac{\partial F_c}{\partial z_n}) - F_c] \qquad (1.65),$$

Thus $$F = \sum_n (\epsilon x_n \frac{\partial F_c}{\partial x_n} + \epsilon y_n \frac{\partial F_c}{\partial y_n} + \epsilon z_n \frac{\partial F_c}{\partial z_n}) \qquad (1.66).$$

An equation of the type (1.66) can be set up for all the measured structure amplitudes and these equations usually greatly out number the unknowns. If refinement is along x, y, z, these equations can be reduced to 3N normal equations (N being the number of atoms) and the n^{th} of these can be obtained by multiplying both sides of the observational equations by $W \frac{\partial F_c}{\partial x_n}$ and, adding the left-hand sides and right-hand sides of the equations separately, W being the weighting function for the summation over all the terms within the limiting sphere. Thus

$$\sum_{t} W(\Delta F)\frac{\partial F_c}{\partial x_n} = \sum_{n} W[(\frac{\partial F_c}{\partial x_n})^2 \varepsilon x_n + (\frac{\partial F_c}{\partial x_n})(\frac{\partial F_c}{\partial y_n})\varepsilon y_n + (\frac{\partial F_c}{\partial x_n})(\frac{\partial F_c}{\partial z_n})\varepsilon z_n]$$

$$+ \sum_{m} \frac{\partial F_c}{\partial x_n}(\frac{\partial F_c}{\partial x_m}\cdot \varepsilon x_m + \frac{\partial F_c}{\partial y_m}\cdot \varepsilon y_m + \frac{\partial F_c}{\partial z_m}\cdot \varepsilon z_m). \qquad (1.67)$$

where $\sum_{m}$ denotes a sum over all the terms except the n^{th},

If the atoms are well resolved, such terms as $\sum W\frac{\partial F_c}{\partial x_n}\frac{\partial F_c}{\partial x_m}$ are likely to be small compared with $\sum_{t} W(\frac{\partial F_c}{\partial x_n})^2$.

Also if the axes are orthogonal or nearly so. $\sum_{t} W\frac{\partial F_c}{\partial x_n}\frac{\partial F_c}{\partial y_n}$ can be neglected and the normal equation (1.67) reduces to

$$\varepsilon x_n \sum_{t} W(\frac{\partial F_c}{\partial x_n})^2 = \sum_{t} W (\Delta F) \frac{\partial F_c}{\partial x_n} \qquad (1.68)$$

Hence the normal equation can now be solved by ordinary methods. Similar equations can be obtained for the temperature factors, the x_n being replaced by up to six thermal parameters ($b_{11}, b_{22}, b_{33}, b_{23}, b_{12}$) to give up to 6N normal equations. The scale factor can also be refined by the least squares method.

Alternatively equation 1.68 can be expressed in matrix form

$$\sum_{i} a_{ij} \varepsilon_i = b_j \qquad (1.69)$$

where $a_{ij} = \sum W\frac{\partial F_c}{\partial p_i}\frac{\partial F_c}{\partial p_j}$ **(1.70);**

and $b_j = \sum W\Delta\frac{\partial F_c}{\partial p_j}$ (1.71),

where p_1, p_2, p_n are the parameters occurring in the F_c.

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