THE MOLECULAR STRUCTURES OF CHLORPROMAZINE AND THIETHYLPERAZINE AND A DISCUSSION OF THE ACTION MECHANISM OF THE PHENOTHIAZINE DERIVATIVES

by

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To the memory of Professor R.W. James, F.R.S.,
who inspired in his students an enthusiasm for
the great science of Physics

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INTRODUCTION

A very important group of the derivatives of phenothiazine are termed the major tranquillizers. The introduction into clinical psychiatry by Delay and Deniker in 1952 of chlorpromazine and its analogues has revolutionized the treatment of psychotic conditions and of mental diseases in general. Although the phenothiazines have been subjected to extensive clinical tests, their chemical structural features have not so far been found to have a sufficiently constant association with pharmacological, psychological and clinical effects to develop a theory of their mode of action.

The phenothiazines are divided into three groups according to the chemical nature of the side chain attached to the nitrogen atom:- (1), dimethylamino-propyl, (2), piperidine, and (3), piperazine radical. Chlorpromazine, pyscho-tropically potent, belonging to the first group, and thiethylperazine, with relatively little tranquillizing or sedative action, belonging to the third, were chosen for complete structural analyses and are reported in Sections B and C respectively. The original intention was to determine the structure of phenothiazine for comparative purposes, but information was received during the course of the present study that its structure had been solved. Crystal data on phenothiazine and on another derivative, chlorpromazine hydrochloride, form the subject of Section A.

Chlorpromazine, one of the best known of the series, is 3-chloro-10 (3' dimethyl-amino-*n*-propyl) phenothiazine. It is the valuable drug Largactil used in general medicine (for relief of nausea and vomiting, and radiation sickness), psychiatry (to control schizophrenic or manic states), surgery and anaesthesia (to modify or prevent traumatic and haemorrhagic shock). The drug has a depressant action on the brain stem, with little or no action on the cerebral cortex or the spinal cord.
(Colloquium, Paris, 1955; Buxton Hopkin, 1955; Courvoisier,

Fournel, Ducrot, Kolsky & Koetschet, 1953; Takayanagi, 1964).

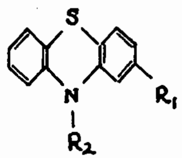
Thiethylperazine (trade name Torecan) is 2-ethylthio-10-[3-(4-methylpiperazine-1-yl) propyl] phenothiazine. It is valued mainly for its antiemetic properties and is used for the control of postoperative vomiting, vomiting associated with malignant disease, radiation therapy, etc. (Progress in Drug Research, 1963; Extra Pharmacopoeia, 1967).

The study of the series has been undertaken with the eventual hope of correlating molecular structure with psychopharmacological properties. It seems likely that in seeking the precise mechanism of action of the drugs, the problems must be "viewed through the glasses of the submolecular". (Szent-Györgyi, 1960). Section D gives a brief description of the properties of the drugs and outlines a possible relation between the molecular structure and the action mechanism.

Section A in abridged form has been published (Feil, Linck & McDowell, 1965, Nature) and condensed versions of Sections B and C have been submitted for publication to Acta Crystallographica (McDowell, Chlorpromazine, accepted Dec. 1968; McDowell, Thiethylperazine, accepted Sept. 1969). The structure of chlorpromazine is the first of the phenothiazines to have been solved.

TABLE 1

CRYSTAL DATA OF PHENOTHIAZINE AND THREE DERIVATIVES

	Phenothiazine	Chlorpromazine hydrochloride	Chlorpromazine base	Thiethylperazine
R_1	H	$C\ell$	$C\ell$	SC_2H_3
R_2	H	$(CH_2)_3N\langle^{CH_3}_{CH_3}$ $+HC\ell$	$(CH_2)_3N\langle^{CH_3}_{CH_3}$	$(CH_2)_3N\langle\;\rangle NCH_3$
Formula	$C_{12}H_9NS$	$C_{17}H_{20}N_2SC\ell_2$	$C_{17}H_{19}N_2SC\ell$	$C_{22}H_{29}N_3S_2$
Molecular weight	199.266	355.326	318.861	399.602
Density				
Flotation liquids	Water+mercury potassium iodide	Benzene+carbon tetrachloride	Water+mercury potassium iodide	Water+mercury potassium iodide
g/c.c. meas.	1.355	1.31	1.289	1.187
g/c.c. calc.	1.342	1.28	1.285	1.198
No. of mols.	4	8	8	4
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic
Space group	*Pnma*	$P2_1/c$	*Pbca*	$P2_12_12_1$
a(Å)	7.94±0.01	11.96±0.02	23.50±0.04	12.057±0.01
b(Å)	21.02±0.01	31.77±0.06	15.20±0.02	19.953±0.01
c(Å)	5.91±0.01	9.84±0.01	9.23±0.01	9.215±0.01
β	-	98.9°±1°	-	-
Volume ($Å^3$)	986.4	3,694	3,297	2,217
Solvent	Carbon tetrachloride or methyl alcohol	Benzene+ethanol under nitrogen	Low b.p. petrol ether under nitrogen	Petrol ether

See "Note on Table 1" on P. 18

SECTION A

THE CRYSTAL STRUCTURES OF PHENOTHIAZINE AND OF CHLORPROMAZINE HYDROCHLORIDE

Phenothiazine (Thiodiphenylamine)

1. Crystals

Pale yellow needle-shaped crystals were prepared by evaporating slowly from a solution of carbon tetrachloride. Methyl alcohol was also a satisfactory solvent.

2. Cell dimensions

X-ray rotation and Weissenberg photographs taken about the needle axis (c) have shown the unit cell to be orthorhombic with dimensions as given in Table 1. Wood, McCale & Williams (1941) obtained the values a = 5.91, b = 7.90, c = 21.0 Å, in good agreement with the results of the present study.

3. Space group

The conditions for non-extinction were found to be

1) $h00, h = 2n$ → [100] screw axis, component $a/2$
2) $0k0, k = 2n$ → [010] " " " $b/2$
3) $00l, l = 2n$ → [001] " " " $c/2$
4) $0kl$, $k+l = 2n$ → (100) glide plane, component $b/2 + c/2$
5) $hk0, h = 2n$ → (001) " " " $a/2$

These indicate the centrosymmetric space group $Pnma$. However, if the b and c axes are interchanged, such that $b' = c$ and $c' = b$, conditions (1)-(4) remain unaltered but condition (5) becomes $h0l', h = 2n$, and space group $Pna2_1$ (non-centrosymmetric) is indicated.

Table 2. Space group of phenothiazine

Space group	*Pnma* centrosym.	$Pna2_1$ non-centrosym.
Indices	*hkl*	*hk'l'*
Conditions for non-extinction	$hk0, h = 2n$	$h0l', h = 2n$
Intensity data	*hk*0	*h*0*l'*
Projection	001	010
Symmetry of special projection	*pgm* centrosym.	*p*1*g* non-centrosym.

In order to assign the correct space group to phenothiazine, the statistical method of Howells, Phillips & Rogers (1950) was applied. The *hk*0 intensity data was measured on the densitometer, corrected for Lp factor, divided into three $\frac{\sin^2\theta}{\lambda^2}$ zones:- (1), 0.02 → 0.10, (2), 0.10 → 0.20, and (3), 0.20 → 0.40, and the average intensity, $\langle I \rangle$, of each zone calculated. From Table 2 it can be seen that a statistical test on *hk*0 data for space group *Pnma* is equivalent to a test on *h*0*l'* data for $Pna2_1$, and that the former gives a centrosymmetric projection whereas the latter has a non-centrosymmetric projection.

For each zone N(Z) was calculated for values of Z from 0.1 to 1.0 in steps of 0.1, where

N(Z) is the fraction of reflections with intensity ≤ the fraction Z of the average intensity of the zone,

i.e. N(Z) = number of reflections with intensity ≤ $Z\langle I \rangle$ divided by the total number of reflections in the zone.

The graph of the averaged values of N(Z) plotted against Z, together with the theoretical curves for a centrosymmetrical and a non-centrosymmetrical distribution, are shown in Figure 1. From the values obtained it was assumed that the space group is *Pnma*.

4. Density

The density measured by the standard flotation method (International Tables Vol. III, 1962) was 1.355 $g.cc^{-1}$, which implied 4 molecules per unit cell, in the special positions

$x, \frac{1}{4}, z; \quad \frac{1}{2}+x, \frac{1}{4}, \frac{1}{2}-z;$

$\frac{1}{2}-x, \frac{3}{4}, \frac{1}{2}+z; \quad \bar{x}, \frac{3}{4}, \bar{z}.$

5. Intensity measurements

Although the crystals darkened on exposure to air, they appeared to be unaffected by X-rays and it was consequently possible to use one crystal only throughout the photographic process. A full set of 5-film Weissenberg integrated photographs from the zero layer up to the fourth layer (for which $\mu = 30.25^{\circ}$) was obtained. An exposure time of approximately 200 hours was required for each layer. In addition, short 5-film exposures of about 25 hours were taken of the zero and first layers in order to obtain reliable readings of the high intensities.

The intensities were measured on a Nonius microdensitometer. Before the measurements were completed, however, information was received from Drs. Briscoe and Freeman of Sydney University, Australia, that the structure of phenothiazine had been solved by them, and work on this compound was therefore suspended. Subsequent correspondence with Drs. Briscoe and Freeman revealed that they had undertaken the solution of a monoclinic form of phenothiazine and were interested in comparative results obtained by the author, who recommenced the intensity measurements. Some weeks later further information that Dr. Feil in Enschede, Holland, had solved an orthorhombic form of phenothiazine finally terminated the work.

Figure 1

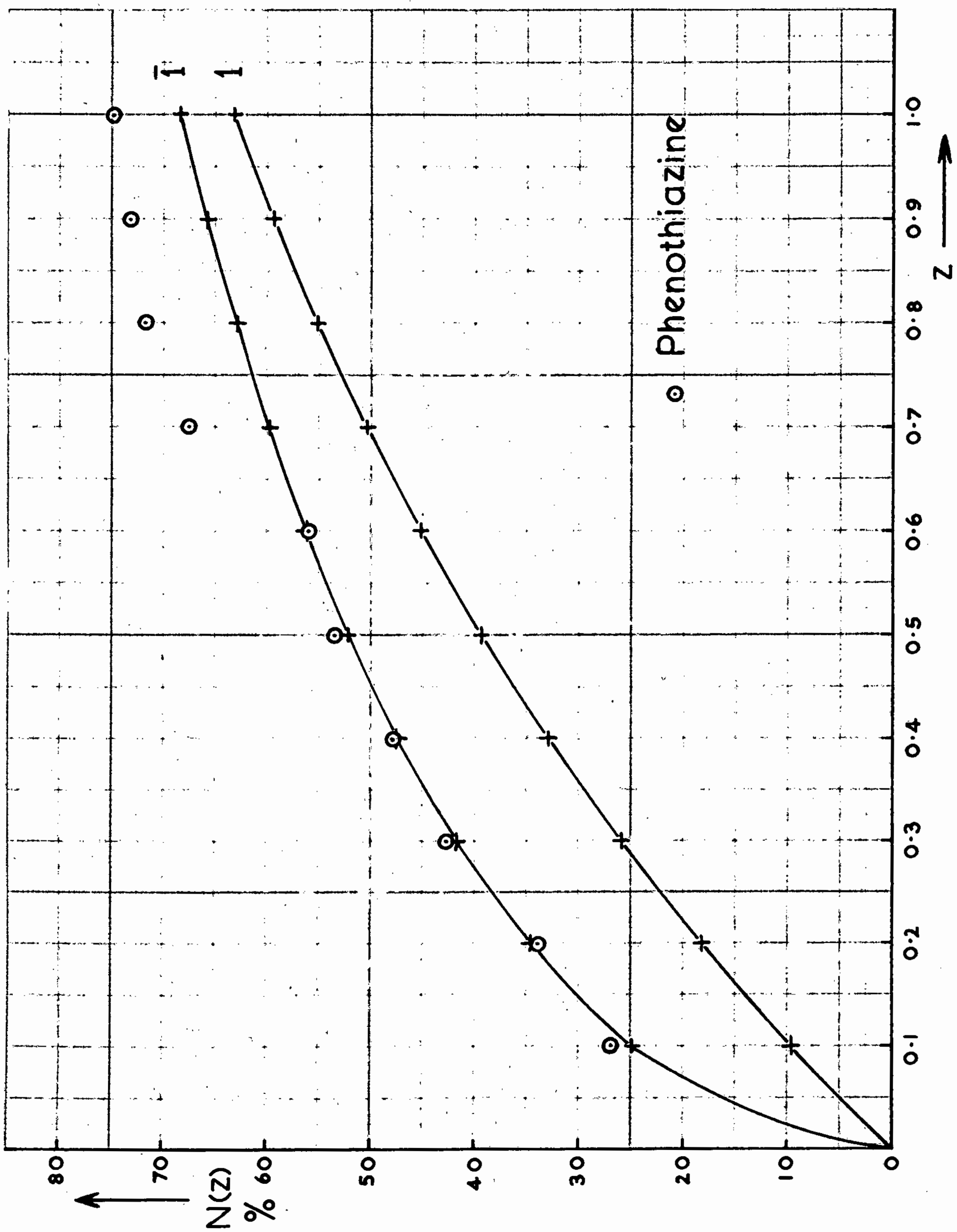
Distribution of intensities for phenothiazine compared with theoretical curves for non-centrosymmetrical (1) and centrosymmetrical ($\bar{1}$) distributions.

$$_{1}N(Z) = 1 - e^{-Z}$$

$$_{\bar{1}}N(Z) = \mathrm{erf}\,(\tfrac{1}{2}Z)^{\frac{1}{2}}$$

Z	N(Z)%		
	Non-centro	Centro	Pheno-thiazine
0	0	0	0
0.1	9.52	24.81	26.9
0.2	18.13	34.53	33.8
0.3	25.92	41.87	42.7
0.4	32.97	47.38	47.8
0.5	39.35	52.05	53.5
0.6	45.12	56.14	56.0
0.7	50.34	59.72	67.6
0.8	55.07	62.89	71.8
0.9	59.34	65.72	73.1
1.0	63.21	68.33	74.8

FIGURE 1


Phenothiazine
N(Z) %
Z
0
10
20
30
40
50
60
70
80
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
1̄
1

Chlorpromazine hydrochloride

1. Crystals

The substance was obtained in powder form from the May and Baker Laboratories, and crystals were formed by slow evaporation from a heated solution of benzene to which a few drops of ethanol had been added. The crystals were thin, transparent plates, forming in clusters which were difficult to separate. They turned brownish-yellow if exposed to light and were affected by exposure to X-rays when in air. Following a valuable suggestion made by the Société des Usines Chimiques, Rhône-Poulenc, better crystals were obtained when the evaporation was carried out under nitrogen, and the deleterious action of the X-rays in air was considerably reduced by mounting the crystals in fine capillary tubes which were also filled with nitrogen and sealed.

2. Cell dimensions

Oscillation photographs were taken of crystals mounted along the x and z axes, so that the cylindrical coordinates, $\zeta_{\perp a}$ and $\zeta_{\perp c}$ were obtainable from the relation

$$\zeta_n = \frac{y_n}{\sqrt{r^2 + y_n^2}} \qquad (1)$$

where y_n is the distance of the n'th layer line from the zero layer line,
r = radius of camera,
and a and c calculated from

$$a, c = \frac{n\lambda}{\zeta_n} \qquad (2)$$

TABLE 3

DETERMINATION OF CELL CONSTANTS OF CHLORPROMAZINE HYDROCHLORIDE

Determination of a, b, c.

	Film 1. Oscillation about x-axis	Film 2. Weissenberg about x-axis	Film 3. Oscillation about z-axis	Film 4. Weissenberg about z-axis	$\frac{1}{a^* \sin \beta}$, $\frac{1}{c^* \sin \beta}$	Average Å
$\frac{1}{a^*}$				11.84±0.02		
a	11.94±0.01				11.98±0.02	11.96±0.02
$\frac{1}{b^*} = b$		31.74±0.06		31.80±0.03		31.77±0.06
$\frac{1}{c^*}$		9.71±0.01				
c			9.85±0.01		9.83±0.01	9.84±0.01

Determination of β.

$\lambda a^* = 0.130$

$\lambda b^* = 0.0485$

	Method 3.		Method 1.		Method 2.	
	First-level Weissenberg about z-axis	Second-level Weissenberg about z-axis	Film 2 + Film 3	Film 1 + Film 4	Direct Measurement	Average
ζ	.1565	.3130				
δ	.0236	.0496				
β	98.6°	99.0°	99.6°	97.2°	98.9°	98.9°

Measurements on zero level Weissenberg photographs taken about the two axes gave values for $\frac{1}{b^*}$, $\frac{1}{c^*}$ and $\frac{1}{a^*}$, $\frac{1}{b^*}$ respectively. First and second level photographs confirmed that the space group was monoclinic with b the unique axis, hence the following relations hold:-

$$\left.\begin{aligned} a &= \frac{1}{a^*} \sin\beta \\ b &= \frac{1}{b^*} \\ c &= \frac{1}{c^*} \sin\beta \\ \beta &= 180^\circ - \beta^* \\ V &= abc \sin\beta \end{aligned}\right\} \quad (3)$$

$$\sin\beta = \sin\beta^* = \frac{1}{cc^*} = \frac{1}{aa^*} \quad (4)$$

3. <u>Determination of β</u>

β was determined by three methods:-

1. Comparison of oscillation film about z axis and Weissenberg film about x axis; comparison of oscillation film about x axis and Weissenberg film about z axis.
2. Measurement with rotating microscope of angle between crystal surfaces.
3. Method of angular lag.

The results are given in Table 3.

The last method is illustrated in Figure 2 and will be briefly described because it is quick and fairly accurate for use when a crystal can be set up about only one axis (the c-axis is used in this example). The crystal axis must be accurately oriented along the rotation axis;

an oscillation film and zero, first and preferably higher level Weissenbergs about that axis are required.

From Fig. 2A it is clear that for each layer n

$$\tan \beta^* = \frac{\zeta_n}{\delta_n} = -\tan \beta \qquad (5)$$

ζ_n is obtainable from the oscillation film using equation (1)

The level offset δ_n can be derived by measuring the angular lag ψ of the reflections of the n'th level behind those of the zero level.

Fig. 2B shows a superposition of the zero and first level Weissenbergs. The ψ'_k are measured in mms. for each spot $0k1$.

$$\psi_k \text{ in degrees} \simeq C_2\psi'_k = 2\psi'_k \qquad (6)$$

for the normal coupling constant of 2.

The ψ_k so obtained are plotted on the reciprocal lattice of the zero level, as shown in Fig. 2C. The values of δ_1 for each k are obtained by measuring the distances between the k axis of the zero level (i.e. the $0k0$ reciprocal lattice line) and the points of intersection of the angles ψ_k with the lines $hk0$. These points of intersection should lie on a straight line, as clearly they are the reciprocal lattice points $0k1$. Fig. 2C shows the results obtained for chlorpromazine hydrochloride for the first and second levels.

The method is not quite the same as that described by Buerger (X-Ray Crystallography, pp.375-383) but the mathematical equivalence can be shown by comparing the geometry of Fig. 2 with the equation for β given by Buerger, which is

Figure 2

Determination of β for a monoclinic crystal

A. Part of reciprocal lattice net for a crystal rotated about the *c*-axis, with direct axes also shown.

δ_1 = level offset for first level.

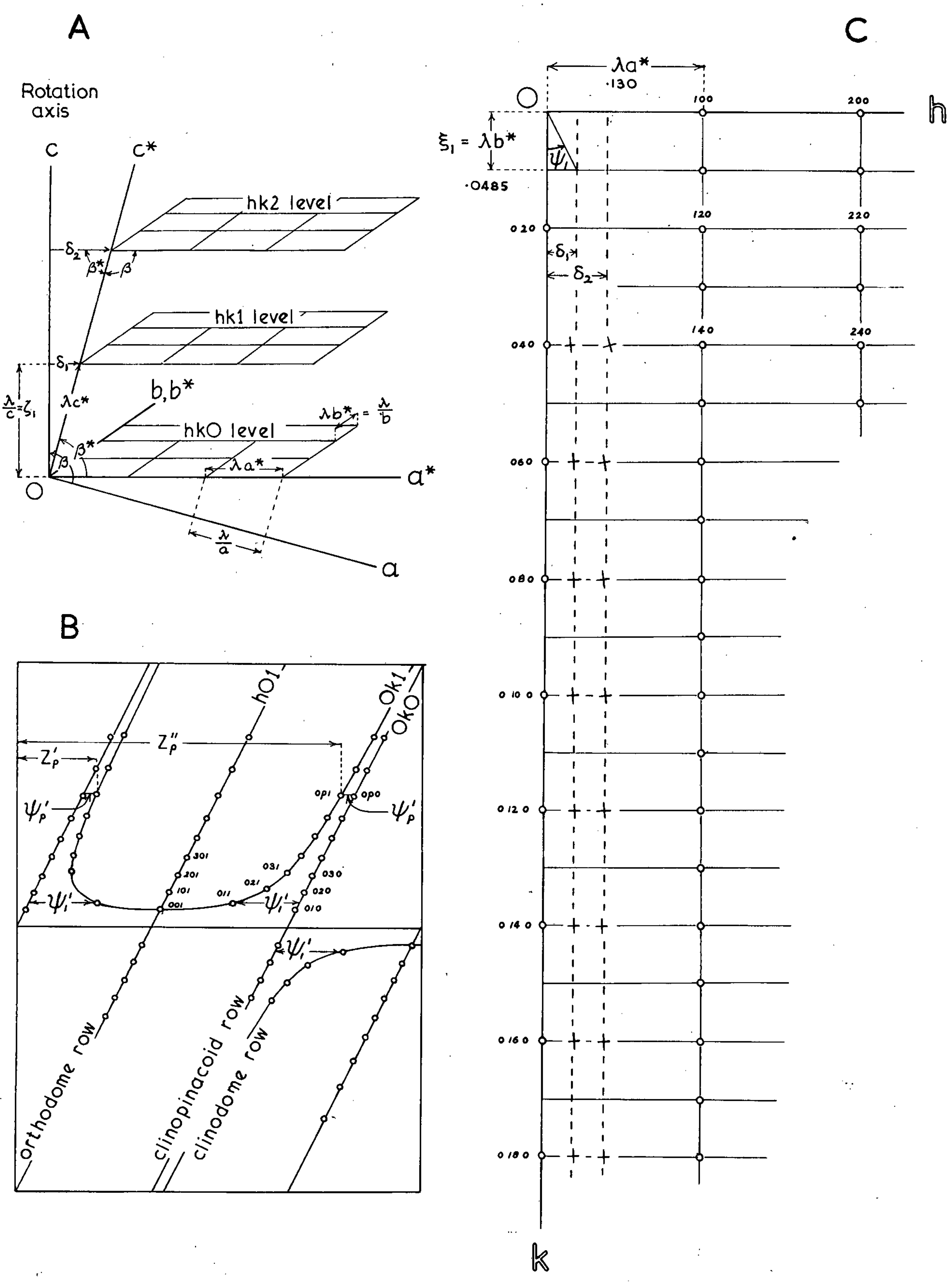
δ_2 = level offset for second level.

B. Superposition of zero and first level Weissenberg photographs of a monoclinic crystal.

ψ_k in degrees (corresponding to $2\psi'_k$ in mms.) = angular lag of axis spot $0kl$ of first level behind the zero level axis.

C. Part of zero level reciprocal lattice net of chlorpromazine hydrochloride with the ψ_k obtained from first and second level photographs marked by crosses.

FIGURE 2


A
Rotation axis
c
c*
hk2 level
hk1 level
hk0 level
b,b*
a*
a
λa*
λb*
λc*
B
hO1
Ok1
OkO
orthodome row
clinopinacoid row
clinodome row
C
λa*
·130
·0485
100
200
120
220
140
240
h
k

$$\beta = \tan^{-1} \frac{\zeta}{\xi_o \tan\{90^\circ - \frac{C_2(z''-z')}{2}\}} \qquad (7)$$

where ξ_o is the cylindrical coordinate of the spot $0p0$, and is obtained from the relation

$$\xi_o = \frac{\lambda}{d_{(010)}} \qquad (8)$$

There is an inaccuracy in Buerger's equations in that the ξ_o of eqn. (7) is not the same as the ξ_o of eqn. (8). The corrected equations should read:-

$$\beta = \tan^{-1} \frac{\zeta}{\xi_p \tan\{90^\circ - \frac{C_2(z''_p - z'_p)}{2}\}} \qquad (7')$$

where ξ_p is the cylindrical coordinate of the spot $0p0$, and

$$\xi_1 = \frac{\lambda}{d_{(010)}}, \quad \xi_p = \frac{p\lambda}{d_{(010)}} \qquad (8')$$

From Fig. 2B it is clear that

$$[(z''_p - z'_p) + 2\psi'_p] \; C_2 = 180^\circ$$

$$\therefore \; C_2(z''_p - z'_p) = 180^\circ - 2\psi_p \text{ , from (6)}$$

$$\therefore \; 90^\circ - \frac{C_2(z''_p - z'_p)}{2} = \psi_p \qquad (9)$$

Fig. 2C shows that

$$\tan\psi_1 = \frac{\delta}{\lambda b^*} = \frac{\delta}{\frac{\lambda}{d_{(010)}}} = \frac{\delta}{\xi_1}$$

and

$$\tan\psi_p = \frac{\delta}{p\lambda b^*} = \frac{\delta}{p \cdot \frac{\lambda}{d_{(010)}}} = \frac{\delta}{\xi_p} \qquad (10)$$

Combining eqns. (9) and (10) with (5) leads to (7') :-

$$\tan\beta = -\frac{\zeta}{\delta} \qquad \text{from (5)}$$

$$= -\frac{\zeta}{\xi_p \tan\psi_p} \qquad \text{from (10)}$$

$$= -\frac{\zeta}{\xi_p \tan\{90^\circ - \frac{C_2(z_p'' - z_p')}{2}\}} \qquad \text{from (9)}$$

$$= (7')$$

4. Space group

The conditions for non-extinction were found to be:-

$0k0,\ k = 2n \rightarrow [010]$ screw axis, component $\frac{b}{2}$

$h0l,\ l = 2n \rightarrow (010)$ glide plane, component $\frac{c}{2}$

The above two symmetry elements uniquely define space group $P2_1/c$.

5. Density

The density of the crystals was determined by flotation using a mixture of benzene and carbon tetrachloride.

$D_m = 1.31$ g.cc^{-1}

$D_c = 1.28$ g.cc^{-1} for 8 molecules per unit cell.

6. Powder data

X-ray powder data have been obtained for both phenothiazine and chlorpromazine hydrochloride from powder photographs and, in good agreement, from the automatic diffractometer.

7. Intensity measurements

Owing to the problems experienced in obtaining high quality crystals which, in any case, disintegrated even under nitrogen, it was decided not to proceed with intensity measurements. As a consequence, the study of chlorpromazine base was undertaken.

<u>Note on Table 1</u>: Estimation of standard deviations in cell dimensions.

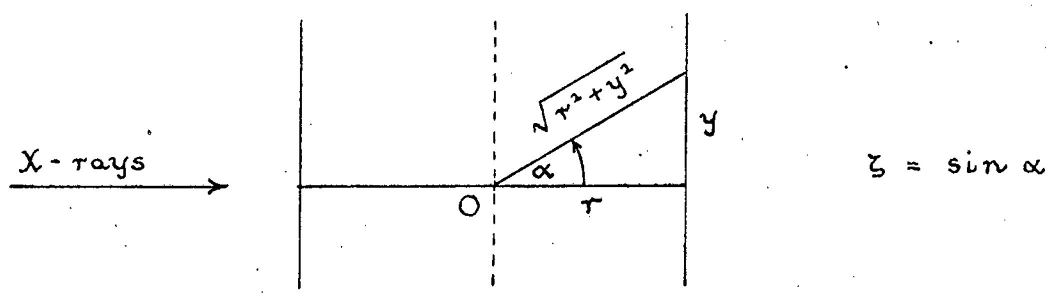
<u>Oscillation film</u>

The distances y of the layer line from the zero layer line are measured.
Using Δ for the differential,

$$\Delta y = \sqrt{\frac{\Sigma(y - \bar{y})^2}{n(n-1)}} \qquad (1)$$

where n = number of readings.

Equation (1) P. 9 is obtained from the following diagrammatic representation of X-rays reflected from a crystal at 0 inside a camera of radius r.



The angle α is calculated from

$$\tan \alpha = \frac{y}{r}$$

Differentiating,

$$\sec^2 \alpha \Delta\alpha = \frac{\Delta y}{r}$$

$$\therefore \quad \Delta\alpha = \frac{\cos^2 \alpha}{r} \Delta y \qquad (2)$$

The direct lattice constant d is calculated from

$$d = \frac{n\lambda}{\sin \alpha}$$

$$\therefore \Delta d = -\frac{n\lambda \cos \alpha}{\sin^2 \alpha} \Delta\alpha \qquad (3)$$

Eqns. (1), (2) and (3) combined give the value of the standard deviation in the direct lattice constant, d.

Weissenberg film

The film coordinates x_1 and x_2 of pairs of axis spots on each side of the centre line of a zero layer photograph are measured.

For a camera of standard radius, r = 28.648 mm.,

$$1 \text{ mm.}x \simeq 2^\circ \text{ arc} \simeq 2^\circ(2\theta) \simeq 1^\circ\theta$$

$$\text{i.e. } \theta = x = \frac{x_2 - x_1}{2}$$

$$\therefore \Delta\theta = \Delta x \qquad (4)$$

and is calculated from (1)

The reciprocal lattice constant d^* is calculated from

$$d^* = \frac{2 \sin\theta}{n\lambda}$$

$$\therefore \Delta d^* = \frac{2 \cos\theta}{n\lambda} \Delta\theta \qquad (5)$$

Equations (4),(5) and (1) combined give the value of the standard deviation in the reciprocal lattice constant d^*.

SECTION B

THE CRYSTAL AND MOLECULAR STRUCTURE OF CHLORPROMAZINE

1. Crystals

Powdered chlorpromazine was supplied by the Smith, Kline and French Laboratories (United States) and colourless needle-shaped crystals were prepared by evaporation from a solution of the powder dissolved in low boiling point petroleum spirit.

Because of the deleterious effects of light, air and X-rays and the consequent difficulties, the following procedure was finally adopted, with successful results:- (1), the crystals were grown in darkness under an atmosphere of nitrogen, (2), single crystals were sealed in nitrogen-filled Lindemann-glass capillaries, and (3), exposure to light rays was avoided as far as possible throughout the photographic process.

2. Cell dimensions

X-ray oscillation and equi-inclination Weissenberg photographs, with the use of Ni-filtered Cu$K\alpha$ radiation, taken about the y and z axes gave an orthorhombic system with cell dimensions as listed in Table 4. These are in good agreement with the values of $a = 15.20 \pm .03$, $b = 23.53 \pm .03$, and $c = 9.27 \pm .02$ Å obtained by Falkenberg & Ringertz (1967).

3. Space group

The conditions for non-extinction were found to be

$0kl$, $k = 2n \rightarrow$ (100) glide plane, component $\frac{b}{2}$

$h0l$, $l = 2n \rightarrow$ (010) " " " $\frac{c}{2}$

$hk0$, $h = 2n \rightarrow$ (001) " " " $\frac{a}{2}$

$h00$, $h = 2n \rightarrow$ [100] screw axis, component $\frac{a}{2}$

$0k0$, $k = 2n \rightarrow$ [010] " " " $\frac{b}{2}$

$00l$, $l = 2n \rightarrow$ [001] " " " $\frac{c}{2}$

The above conditions lead uniquely to the space group *Pbca*.

In Appendix A the simplest general form of the structure factor and the simplification which arises in special cases for space group *Pbca* have been calculated from the coordinates of equivalent positions, and the conditions for non-extinction have been derived from the results. The calculations for *Pnma* are also shown.

4. Density

The measured density = 1.289 $g.cc^{-1}$.

The number of molecules per unit cell,

$$N = \frac{D \times V \times Av}{M}$$

where D = density in $g.\ cc^{-1}$

V = volume of unit cell in cc.

Av = Avogadro's number.

M = gram molecular weight.

$$\therefore N = \frac{1.289 \times (3297 \times 10^{-24}) \times (6.023 \times 10^{23})}{318.861}$$

$$= 8.03$$

From this result it was concluded that there were 8 molecules in the unit cell. The calculated density for 8 molecules = 1.285 $g.cc^{-1}$.

5. Absorption

The crystal selected for intensity measurements was approximately cylindrical with length 0.11 cm. and diameter 0.03 cm.

The linear absorption coefficient, μ, was calculated from

$$\mu = D \times \sum p \left(\frac{\mu}{\rho}\right)$$

where D = density,

p = fraction of total weight of element present,

$\frac{\mu}{\rho}$ = mass absorption coefficient of element (Int. Tab. III, P.162).

From Table 5,

$$\sum p \left(\frac{\mu}{\rho}\right) = 25.91 \text{ cm}^2/\text{gm}.$$

$$\therefore \mu = 1.289 \times 25.91 = 33.4 \text{ cm}^{-1}$$

$$\text{and } \mu R = 33.4 \times 0.015 = 0.50$$

As the corresponding absorption correction factor for Cu$K\alpha$ radiation ranges from 2.29 for $\theta = 0^\circ$ to 2.05 for $\theta = 90^\circ$ (Int. Tab. II, P.295), absorption corrections were not applied.

6. Intensity measurements

Eight layer-lines ($hk0$ to $hk7$) were photographed using the standard multiple-film technique. An exposure time of about 100 hours was required for each set of 5 films.

An intensity scale was set up by selecting a reflection of suitable intensity and shielding out all others from the film. A number of accurately timed exposures of the chosen reflection were taken, each exposure being equal to some integral number of oscillations of the crystal. The

TABLE 4

CELL DIMENSIONS OF CHLORPROMAZINE

	Oscillation about y-axis	Weissenberg about y-axis	Oscillation about z-axis	Weissenberg about z-axis	Average Å	Number of values	% Error
a		23.53 ± 0.03		23.47 ± 0.03	23.50 ± 0.04	20	0.17
b	15.21 ± 0.03			15.19 ± 0.02	15.20 ± 0.02	14	0.13
c		9.22 ± 0.01	9.23 ± 0.01		9.23 ± 0.01	9	0.11

TABLE 5

CALCULATION OF LINEAR ABSORPTION COEFFICIENT OF CHLORPROMAZINE

Atom	Atomic weight	Total weight	P Fraction of total weight	$\frac{\mu}{\rho}$ for CuKα radiation	$P\left(\frac{\mu}{\rho}\right)$
Cl	35.457	35.457	0.1182	106	12.540
S	32.066	32.066	0.1069	89.1	9.530
N	14.008	28.016	0.0935	7.52	0.703
C	12.010	204.170	0.6814	4.60	3.134

TABLE 6

VALUES OF THE TEMPERATURE FACTOR OBTAINED BY WILSON'S METHOD AND LAYER-LINE SCALE FACTORS OBTAINED BY VARIOUS METHODS

Layer	Wilson's method (b)			Method (a)	K from film exposure times	K from least-squares refinement
	B	$\log_e \frac{1}{K}$	K	K from $h1l$ Weissenberg		
$hk0$	3.88	0.30	0.741	1.000	1.00	0.673
$hk1$	4.50	0.00	1.000	0.707	1.03	0.913
$hk2$	4.69	0.40	0.670	1.014	1.05	0.689
$hk3$	3.98	0.92	0.400	1.284	2.10	0.557
$hk4$	3.60	0.60	0.549	0.487	1.07	0.757
$hk5$	3.08	0.16	0.853	0.247	0.84	1.037
$hk6$	3.20	0.57	0.566	0.312	0.86	0.829
$hk7$	3.58	1.05	0.350	0.612	0.86	0.566

intensities on the scale had the relative values 1,2,3,4,6, 8,12,16,20,25,30,35,40,50,75,100,125,150 and 200, where 1 represented an exposure time of 20 seconds.

The intensities were estimated by visual comparison of the spot with the spots on the intensity scale. Each reflection was measured on each of the films upon which it appeared and the film factor between every pair of films was calculated by taking the average of all film factors obtained for individual reflections. Thus most of the individual intensity values represented an average of 3,4 or 5 readings.

On each set of films $I_{(hkl)}$, $I_{(h\bar{k}l)}$, plus either $I_{(\bar{h}kl)}$ or $I_{(\bar{h}\bar{k}l)}$ were measured; for *Pbca* these are all equal. Thus by collating their symmetry relationships about 6000 measured intensities were reduced, by averaging, to 1893 independent reflections.

7. Lorentz and polarisation factors

Corrections for the Lorentz (L) and polarisation (p) factors were applied to the measured intensities by the use of the programme "Lp and Scattering Factor". The formulae used in all programmes are included in Appendix A.

The relationship between the L and p factors and the measured intensity is expressed by

$$\left|F_{(hkl)}\right|^2 = \frac{1}{K} \cdot \frac{1}{2L_{(hkl)}P_{(hkl)}} \left|F_{(hkl)}\text{obs.}\right|^2$$

where K is the scale factor for the layer-line to be discussed in sub-section 8.

8. Preliminary temperature factor and scale factors

Scale factors for the individual layer-lines were obtained by the following two methods:-

(a), the crystal was rotated about the y-axis and a five-film Weissenberg gave 120 independent $h1l$ intensities with which to set the z-axis photograph on to the same scale, (b), Wilson's (1942) method of obtaining absolute K's for each layer-line was used.

Wilson's method is most conveniently applied in the form of Buerger's[†] equation:-

$$\log_e \frac{\overline{\sum_j {}^{o}f_j^2}}{\overline{|F_{obs}|^2}} = \log_e \left(\frac{1}{K}\right) + 2B\,\frac{\sin^2\theta}{\lambda^2}$$

where $\overline{|F_{obs}|^2}$ is the average intensity of the corresponding $\frac{\sin^2\theta}{\lambda^2}$ zone,

${}^{o}f_j$ is the scattering power of atom j at rest.

B is the temperature coefficient.

It is clear that the graph of $\log_e\left(\overline{\sum_j {}^{o}f_j^2}\Big/\overline{|F_{obs}|^2}\right)$ plotted against $\frac{\sin^2\theta}{\lambda^2}$ is a straight line of slope 2B and intercept $\log_e\left(\frac{1}{K}\right)$.

The results for chlorpromazine are illustrated in Figure 3, and listed in Table 6, from which it can be noted that Wilson's method, in comparison with method(a), gave values for K more closely consistent with the scale factors obtained by the least-squares refinement.

The values calculated for B are listed in Table 6. The average value of 3.8 was used in subsequent calculations.

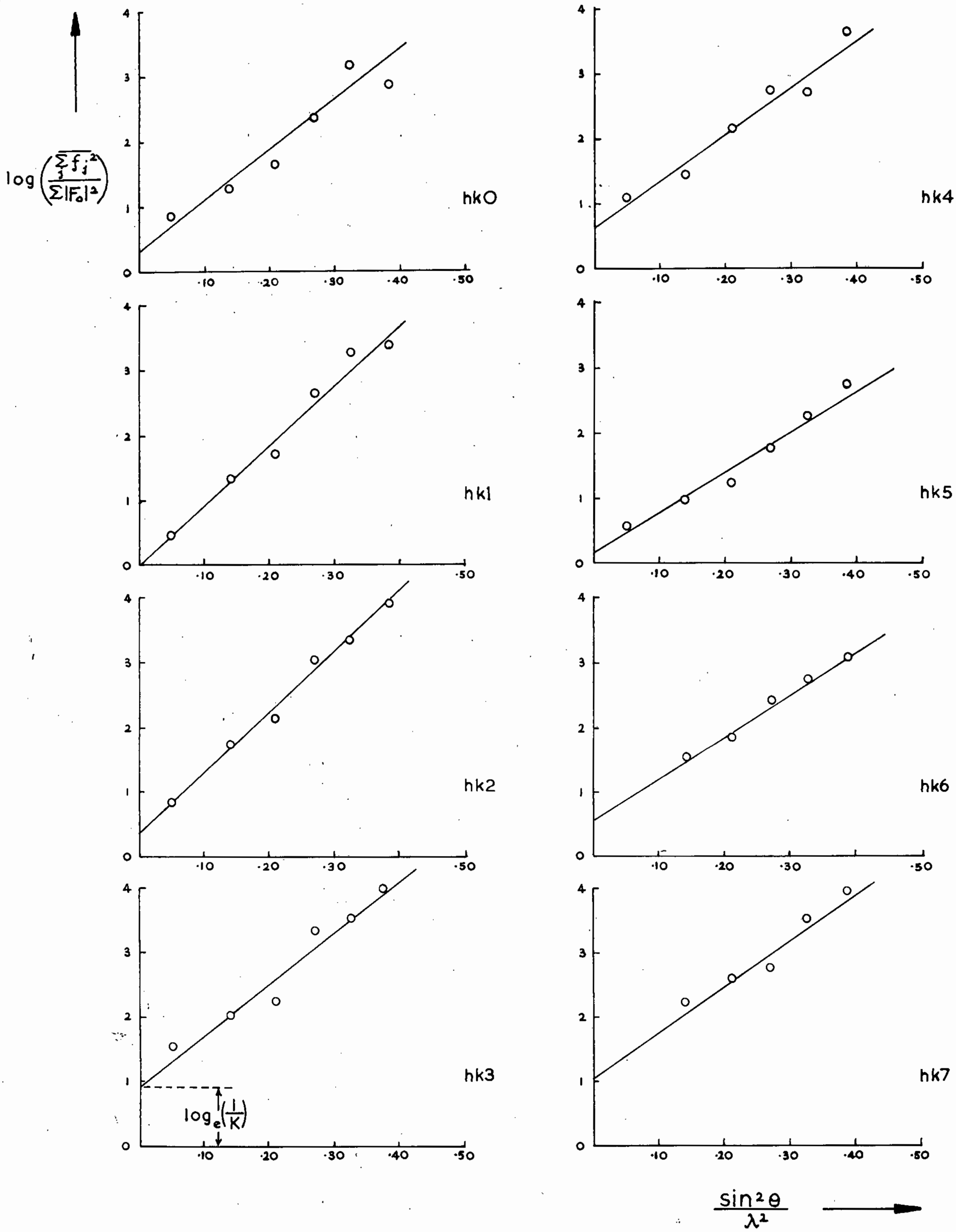
9. The Patterson function

The three-dimensional unsharpened Patterson function,

[†]Crystal-Structure Analysis, P. 235.

FIGURE 3

CHLORPROMAZINE : WILSON PLOT



$$P(x,y,z) = \frac{1}{V} \sum_h \sum_k \sum_l \left|F_{(hkl)}\right|^2 \cos 2\pi \quad (hx + ky + lz)$$

where x, y, and z are fractional coordinates, was calculated on the I.C.T. 1301 computer. Because the symmetry of the Patterson of space group *Pbca* is *Pmmm* , it was necessary to calculate $^1/_8$th only of the unit cell. The Patterson values were computed in steps of $\frac{2}{100}$ along each axis in sections perpendicular to the z-axis (Figure 4).

The study of Table 7 shows that rotation and reflection peaks could be expected not only on the $z = \frac{1}{2}$ sheet but in addition on the $x = \frac{1}{2}$ and $y = \frac{1}{2}$ sheets; therefore, the additional calculation of the Patterson sections $x = \frac{1}{2}$, perpendicular to the x-axis, and $y = \frac{1}{2}$, perpendicular to the y-axis, were specially done to facilitate the more rapid location of the satellite peaks.

Figure 4 is a photograph of the Patterson function traced on to glass sheets; the positive contours were drawn in steps of 10 units.

10. Interpretation of the Patterson.

(a) Calculated heights of Patterson peaks

The magnitudes of the peaks to be expected were calculated as follows:-†

The volume V_{ij} , of a Patterson peak due to a pair of atoms i and j is $z_i z_j$ where z_i is the number of electrons in an atom i:

The volume, V_o , of the multiple origin peak is $\sum_j z_j^2$ where the sum is taken over all the atoms in the unit cell.

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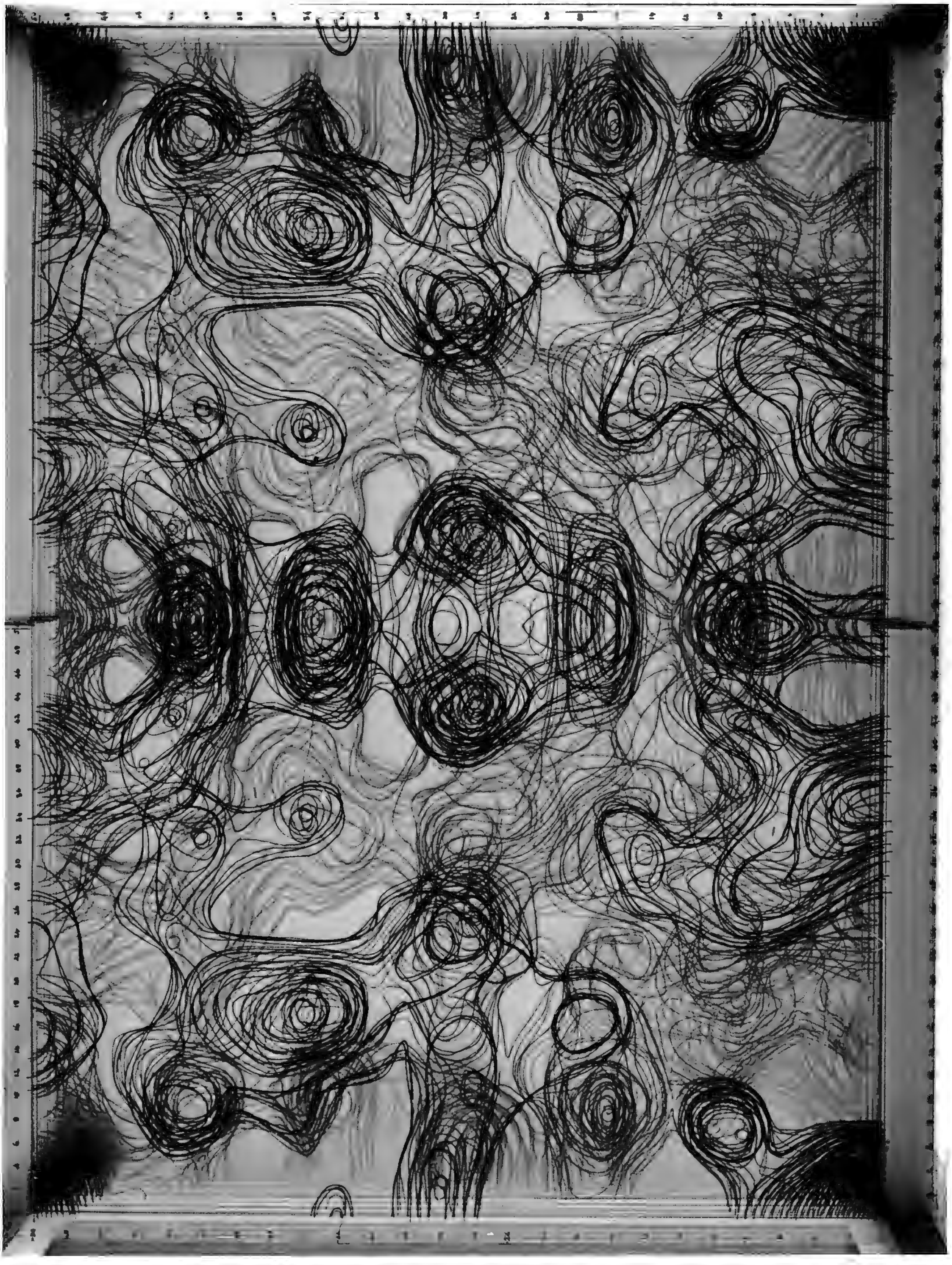
† Buerger: Vector Space, P. 127.

FIGURE 4

THE THREE-DIMENSIONAL PATTERSON FUNCTION



Logically it follows that, whatever scale is used, the volume of any peak due to atoms i and j can be expressed as a fraction of the volume of the origin peak,

$$\text{i.e.} \quad V_{ij} = \frac{z_i z_j}{\sum_j z_j^2} \cdot V_o$$

or, since the height of a peak is approximately proportional to its volume,

$$H_{ij} = \frac{z_i z_j}{\sum_j z_j^2} H_o$$

For chlorpromazine, the size of the Patterson origin was 650 units,

$$\sum_j z_j = 8\{17 \times 6^2 + 2 \times 7^2 + 1 \times 16^2 + 1 \times 17^2\}$$
$$= 10{,}040$$

For a Cℓ-Cℓ peak, $z_i z_i = 17^2 = 289$

Therefore the expected height of a Cℓ-Cℓ peak of single weight on the Patterson map, i.e. an inversion peak,

$$H_{ii} = \frac{289}{10{,}040} \times 650$$
$$\simeq 20 \text{ units,}$$

and the expected heights of the rotation and reflection satellites were 40 units and 80 units respectively.

The values for S-S and S-Cℓ peaks would be of the same order.

(b) Calculated positions of Harker† peaks

The coordinates of the Harker peaks, derived from the coordinates of equivalent positions, are shown in Table 7. The peaks which occur in the relevant 1/8th of the unit

---

†The term Harker peak denotes a peak corresponding to an interatomic vector between symmetry-equivalent atoms (after Buerger).

TABLE 7

THEORETICAL POSITIONS OF REFLECTION PEAKS, ROTATION PEAKS AND INVERSION PEAKS IN THE PATTERSON OF SPACE GROUP *Pbca*

Coordinates of equivalent positions

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

	Vectors	Coordinates of Patterson peaks				Weight	Number of peaks
Reflection peaks	$1-\bar{2}$, $2-\bar{1}$, $\bar{3}-4$, $\bar{4}-3$	$\frac{1}{2}+2x$	$\frac{1}{2}$	0		4	6
	$3-\bar{4}$, $4-\bar{3}$, $\bar{1}-2$, $\bar{2}-1$	$\frac{1}{2}-2x$	$\frac{1}{2}$	0	*		
	$1-\bar{3}$, $3-\bar{1}$, $\bar{2}-4$, $\bar{4}-2$	0	$\frac{1}{2}+2y$	$\frac{1}{2}$			
	$2-\bar{4}$, $4-\bar{2}$, $\bar{1}-3$, $\bar{3}-1$	0	$\frac{1}{2}-2y$	$\frac{1}{2}$	*		
	$1-\bar{4}$, $4-\bar{1}$, $\bar{2}-3$, $\bar{3}-2$	$\frac{1}{2}$	0	$\frac{1}{2}+2z$			
	$2-\bar{3}$, $3-\bar{2}$, $\bar{1}-4$, $\bar{4}-1$	$\frac{1}{2}$	0	$\frac{1}{2}-2z$	*		
Rotation peaks	$1-4$, $\bar{4}-\bar{1}$	$\frac{1}{2}+2x$	$2y$	$\frac{1}{2}$		2	12
	$2-3$, $\bar{3}-\bar{2}$	$\frac{1}{2}+2x$	$-2y$	$\frac{1}{2}$			
	$\bar{2}-\bar{3}$, $3-2$	$\frac{1}{2}-2x$	$2y$	$\frac{1}{2}$	*		
	$\bar{1}-\bar{4}$, $4-1$	$\frac{1}{2}-2x$	$-2y$	$\frac{1}{2}$			
	$1-2$, $\bar{2}-\bar{1}$	$\frac{1}{2}$	$\frac{1}{2}+2y$	$2z$			
	$3-4$, $\bar{4}-\bar{3}$	$\frac{1}{2}$	$\frac{1}{2}+2y$	$-2z$			
	$\bar{3}-\bar{4}$, $4-3$	$\frac{1}{2}$	$\frac{1}{2}-2y$	$2z$	*		
	$\bar{1}-\bar{2}$, $2-1$	$\frac{1}{2}$	$\frac{1}{2}-2y$	$-2z$			
	$1-3$, $\bar{3}-\bar{1}$	$2x$	$\frac{1}{2}$	$\frac{1}{2}+2z$			
	$\bar{2}-\bar{4}$, $4-2$	$-2x$	$\frac{1}{2}$	$\frac{1}{2}+2z$			
	$2-4$, $\bar{4}-\bar{2}$	$2x$	$\frac{1}{2}$	$\frac{1}{2}-2z$	*		
	$\bar{1}-\bar{3}$, $3-1$	$-2x$	$\frac{1}{2}$	$\frac{1}{2}-2z$			
Inversion peaks	$1-\bar{1}$	$2x$	$2y$	$2z$	*	1	8
	$2-\bar{2}$	$2x$	$-2y$	$-2z$			
	$3-\bar{3}$	$-2x$	$2y$	$-2z$			
	$4-\bar{4}$	$-2x$	$-2y$	$2z$			
	$\bar{1}-1$	$-2x$	$-2y$	$-2z$			
	$\bar{2}-2$	$-2x$	$2y$	$2z$			
	$\bar{3}-3$	$2x$	$-2y$	$2z$			
	$\bar{4}-4$	$2x$	$2y$	$-2z$			

cell are marked with asterisks, from which it can be seen that one inversion peak of weight 1 must necessarily be accompanied by six satellite peaks, three of weight 2 and three of weight 4.

(c) <u>Image-seeking functions</u>

After examination of the Patterson, all possible reflection and rotation peaks were listed and combinations of values of $2x$, $2y$, $2z$ given by three reflection and three rotation peaks were sought.

A satisfactory combination appeared to be $2x = 16$, $2y = 8$, $2z = 20$, which was arrived at from the following peak positions:-

Rotation peaks were found at

$(\frac{1}{2}-2x,\ 2y,\ \frac{1}{2})$:	(34, 6, 50)	(Height, 43)
$(\frac{1}{2},\ \frac{1}{2}-2y,\ 2z)$:	(50, 40, 20)	(" 30)
$(2x,\ \frac{1}{2},\ \frac{1}{2}-2z)$:	(16, 50, 30)	(" 36)

Reflection peaks were found at

$(\frac{1}{2}-2x,\ \frac{1}{2},\ 0)$:	(34, 50, 0)	(59)
$(0,\ \frac{1}{2}-2y,\ \frac{1}{2})$:	(0, 42, 50)	(107)
$(\frac{1}{2},\ 0,\ \frac{1}{2}-2z)$:	(50, 0, 30)*	(137)

(* although not a specific peak, this position was a continuous "rod" of high values along the $x = 50$, $y = 0$ line)

The corresponding inversion peak, of height 52, was found in the location $2x = 16$, $2y = 8$, $2z = 20$.

At this stage all seven peaks were located; the heights and geometrical relations of the peaks were considered sufficiently close to the calculated values to warrant a vector shift to the inversion peak. The corresponding three-dimensional minimum function (M_2) was calculated with the use of the programme "Minimum Function".
As every M_2 function is inherently centro-

symmetrical, one half only of the unit cell was computed, contoured and transferred to glass sheets by a similar method as used for the Patterson.

In the case of a shift to a vector point corresponding to a pair of atoms which are centrosymmetrically situated in the crystal structure, the resulting M_2 map should give the "image" only, without its inverse, and should exhibit the symmetry of the crystal lattice, i.e. the minimum function as calculated above should have been a picture of the unit cell.

The selection of inversion peak (16,8,20), based on an apparently sound foundation as explained above, proved to be a most unfortunate one. Despite being incorrect, the M_2 map showed many features which were to be expected in this particular problem, such as twelve well-defined peaks, each appearing in the eight equivalent positions, and one strong peak at an appropriate distance (6.25 Å) from the supposed $C\ell$ peak to suggest interpretation as a S peak. The ultimate solution of the structure disclosed that the orientation of the phenothiazine group was correct, the y- and z-coordinates of the "$C\ell$" and "S" peaks of the minimum function were very nearly correct, and that the x-coordinates were incorrect.

Thus, owing to the deceptive coincidences, much time was consumed in calculating structure factors and Fouriers based on various possible positions of the phenothiazine group. After many attempts, the lowest R attained was 52%, and it was then decided that the trial structure was basically incorrect.

Subsequently, further minimum functions were calculated and various other techniques were applied , but as they led to a reasonably thorough understanding of the <u>properties</u> of the Patterson, but not to its <u>solution</u>, they need not be described.

(d) Sharpened Patterson function

In order to obtain better definition of the peaks, the Patterson coefficients were sharpened in accordance with the formula

$$|F|^2 = \frac{(\sin^2 \theta/\lambda^2 + 0.16)\, F_o^2 \exp(B \sin^2 \theta/\lambda^2)}{(\sum f_i)^2}$$

REFER ADDENDA (3-10-1969), P.169.

and used in the calculation of a sharpened Patterson function. As before, the sections $x = \frac{1}{2}$ and $y = \frac{1}{2}$ were calculated. The sharpened function was found to have considerably greater clarity than the unsharpened function.

Because the origin of the sharpened Patterson was 1020 units, the expected heights of Harker peaks were again calculated, as described in sub-section (a).

H_{ii} for a single weight Cℓ-Cℓ ≈ 30 units, and for peaks of weight 2 and 4,

H_{ii} = 60 and 120 units respectively.

(e) The benzene ring

Examination of the peaks of the sharpened Patterson led to the discovery of a feature which, due to the spread of the origin peak, had not been noticeable on the unsharpened Patterson. A nearly perfect benzene ring with two attached atoms was clearly visible. A theoretical Patterson was then drawn for a benzene ring + Cℓ + S + N, and on comparison a remarkable agreement was disclosed with the actual Patterson, as illustrated in Figure 5.

The following substantive inferences could be drawn:-

(1) The orientation of the benzene ring (i.e C(1)-C(6); see Figure 8) was established,

(2) The difference in the y-coordinates of S and S' was close to 2 (where S may be chlorine or sulphur),

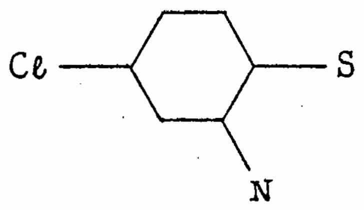
(3) The difference in the x-coordinates of S and S' was close to 25,

(4) The orientation of the phenothiazine group was confined to a limited number of possibilities (four,

Figure 5

The benzene ring.

A. Theoretical Patterson of a benzene ring and three attached atoms:



B. The Patterson of chlorpromazine, drawn to the scale of 1 Å = 4 cm.

The full contours represent the $z = o$ section;
the dotted contours represent the $z = 6$ section.

FIGURE 5(A)

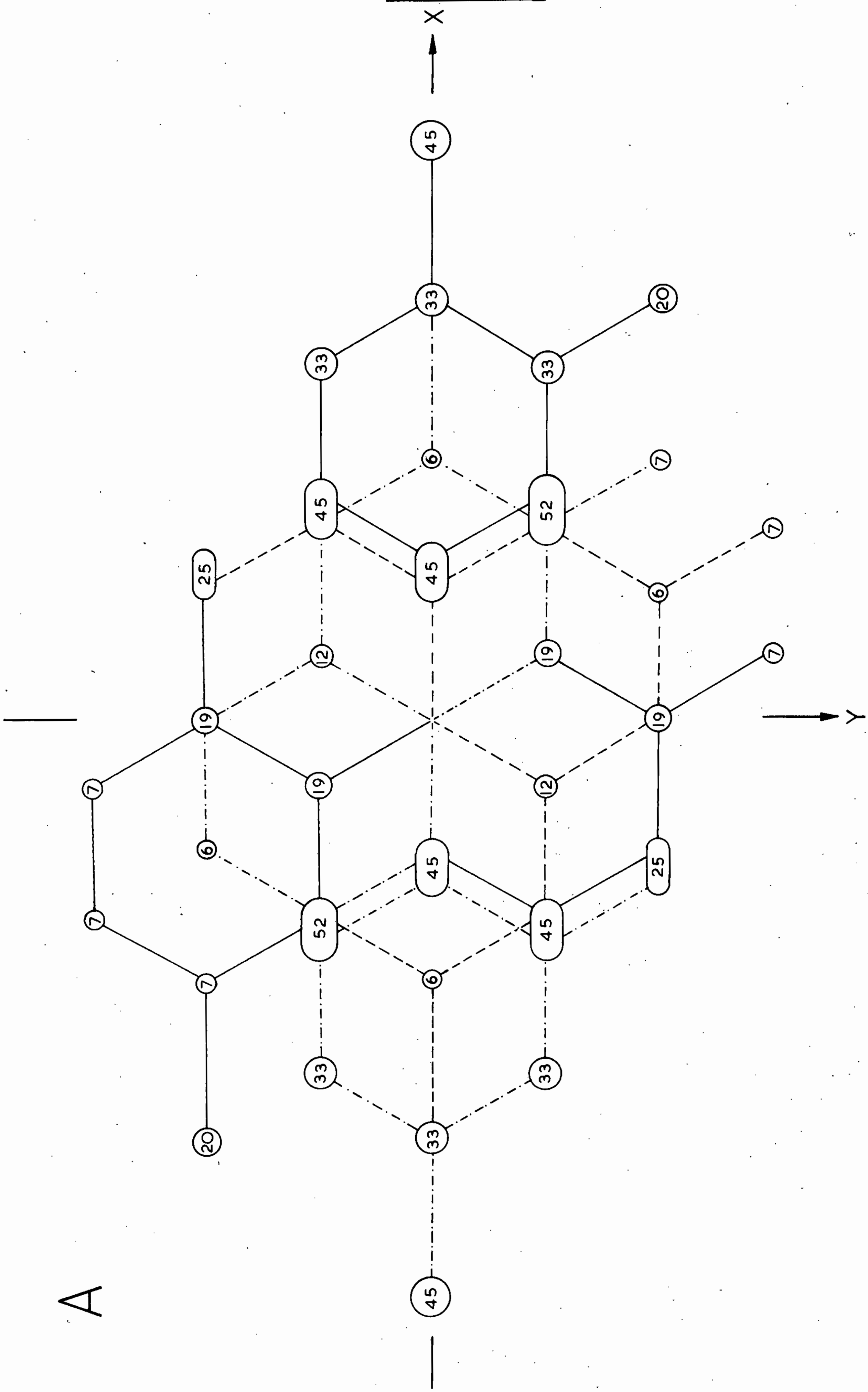
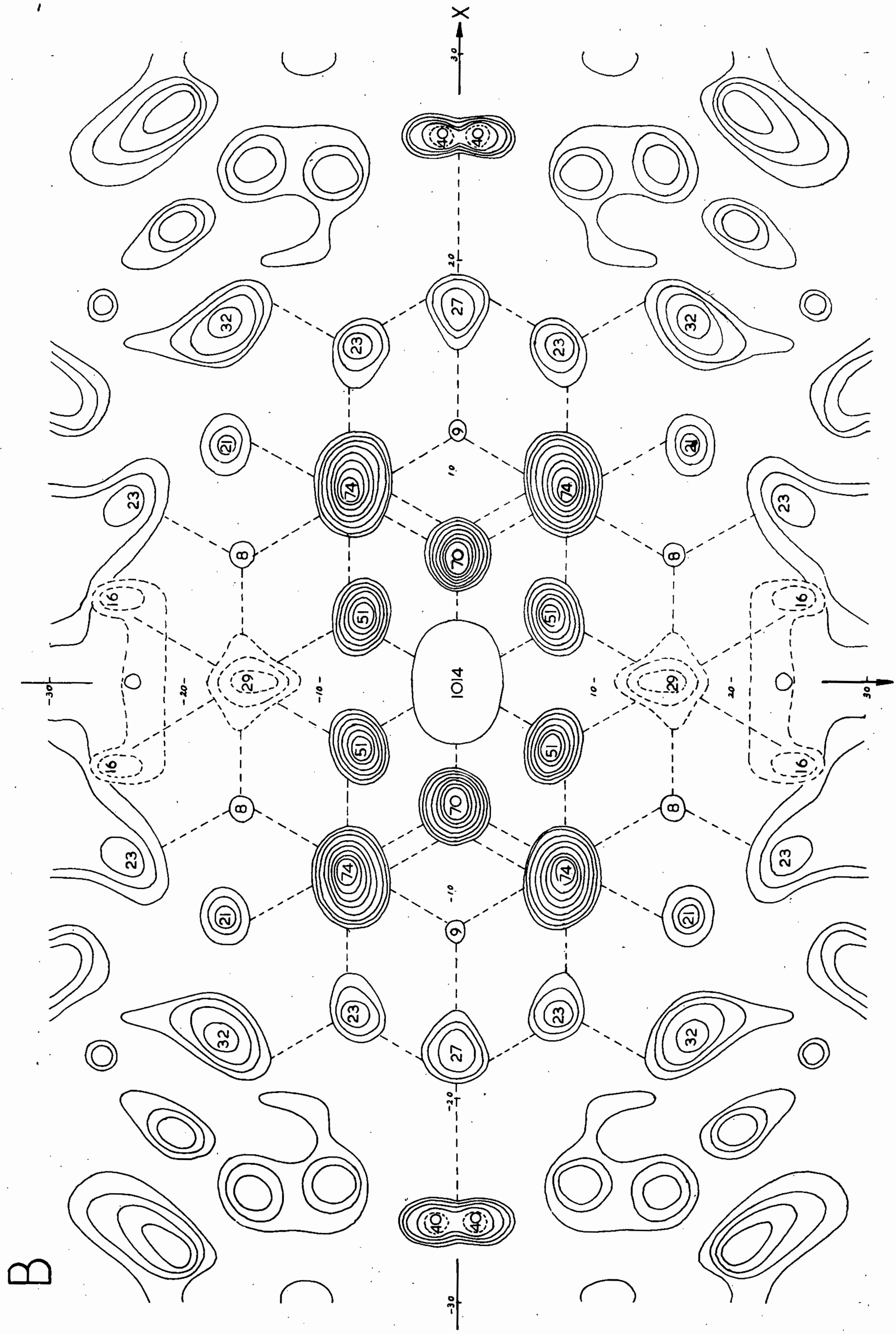

X
Y
A
45
33
33
20
33
6
7
45
52
7
25
45
6
12
19
7
19
19
7
19
12
6
45
25
7
52
45
7
6
33
33
33
20
45

FIGURE 5(B)



if the tricyclic group was planar, and eight if it was folded about the S-N axis).

When the structure was ultimately solved, the above interpretation was proved to be basically sound. However it is plain that although deductions as to the relative positions of the sulphur and chlorine atoms could be made, their absolute locations in the unit cell were still undetermined. Nevertheless, the inferences were borne in mind and assisted in the successful solution of the Patterson by Fourier methods, discussed in the following sub-section:-

(f) Solution of the Patterson by Fourier methods

The reflection and rotation peaks of the sharpened function were listed as for the unsharpened Patterson, and it was found that the number of peaks was nearly doubled. For the purpose of calculating a meaningful Fourier, it was considered that both S and Cℓ must be correctly located. Thus in addition to two sets of seven peaks each, eight S-Cℓ peaks had to be found.

Possible sets of seven Harker peaks were listed as described in sub-section (c); the inversion peaks were taken in pairs, i.e. $(2x_A, 2y_A, 2z_A)$ and $(2x_B, 2y_B, 2z_B)$, and the corresponding atoms were initially assumed to be situated at $(\pm x_A, \pm y_A, \pm z_A)$ and $(\pm x_B, \pm y_B, \pm z_B)$ respectively. (The positions $(\pm x_A \pm \frac{1}{2}, \pm y_A, z_A)$ or $(\pm x_A \pm \frac{1}{2}, \pm y_A \pm \frac{1}{2}, \pm z_A)$, etc. were of course alternatively permissible because the Patterson peak for $x_A + \frac{1}{2}$ is indistinguishable from the Patterson peak for x_A.)

The signs of the coordinates of one atom, A say, could be chosen as positive, because a change of any of the signs represents merely a change of choice of the origin; when two atoms were simultaneously considered however, the signs of the second atom, B, had to be correctly allocated, as follows:-

The coordinates of atom A in its first equivalent position taken in combination with each of the eight possible permutations of signs of the coordinates of atom B would produce eight possible locations, at one of which the A-B peak would be found in the Patterson. Similarly, each of the equivalent positions of atom A would yield eight locations, one of which in each case would be the correct position of a Patterson peak.

In total therefore, for a unit cell containing eight equivalent positions, 64 locations in the Patterson should be examined, and eight A-B peaks arising from one particular permutation of signs of B must be found. A modification arises in a centrosymmetric cell, because the centrosymmetrically related atoms, i.e. A(1) and A($\bar{1}$), produce the indentical set of eight positions, with the result that 32 locations only need be examined.

The procedure described above was followed for each pair of possible inversion peaks in the Patterson of chlorpromazine. Dr. G. Gafner, head of the crystallography division of the C.S.I.R., supplied the valuable information that the absence of even one of the eight S-Cℓ peaks would invalidate the whole set, which considerably narrowed the field of possibilities. The information as to coordinate differences (described in sub-section (e)) further reduced the number of pairs which it was necessary to investigate.

Details of the peaks which finally revealed the long sought positions of the elusive sulphur and chlorine atoms will render clearer the application of the technique.

Cℓ-Cℓ inversion peak of height (26) at $(2x,2y,2z)$:(10,6,26).

Corresponding satellite peaks at

$(\frac{1}{2}-2x,\ 2y,\ \frac{1}{2})$	: (40,4-6,50)	(36)*
$(\frac{1}{2},\ \frac{1}{2}-2y,\ 2z)$	: (50, 44,26)	(28)
$(2x,\ \frac{1}{2},\ \frac{1}{2}-2z)$	: (10, 50,24)	(50)
$(\frac{1}{2}-2x,\ \frac{1}{2},\ 0)$	: (41, 50, 0)	(100)
$(0,\ \frac{1}{2}-2y,\ \frac{1}{2})$	: (0, 46,50)	(85)*
$(\frac{1}{2},\ 0,\ \frac{1}{2}-2z)$	: (50, 0,22)	(206)*

S-S inversion peak of height (26) at $(2x,2y,2z)$:(43,10,13)

Corresponding satellite peaks at

$(\frac{1}{2}-2x,\ 2y,\ \frac{1}{2})$	: (6, 10,50)	(51)*
$(\frac{1}{2},\ \frac{1}{2}-2y,\ 2z)$	: (50, 40,12)	(61)
$(2x,\ \frac{1}{2},\ \frac{1}{2}-2z)$	: (43, 50,36)	(88)
$(\frac{1}{2}-2x,\ \frac{1}{2},\ 0)$	: (7, 50, 0)	(177)
$(0,\ \frac{1}{2}-2y,\ \frac{1}{2})$	: (0, 40,50)	(138)*
$(\frac{1}{2},\ 0,\ \frac{1}{2}-2z)$	: (50, 0,36)	(226)*

(Labels on Fig. 6 indicate six of the 14 Harker peaks which were located by the technique on the y = 0 and the z = 50 sections of the sharpened three-dimensional Patterson.)

The coordinates of the S atom were chosen as positive, i.e. the S atom was placed at $(+21\frac{1}{2},\ +5,\ +6\frac{1}{2})$.

Therefore, due to the symmetry of space group *Pbca*, S atoms must be situated at the equivalent positions:-

(1):	$(21\frac{1}{2},\ 5,\ 6\frac{1}{2})$	$(\overline{1})$:	$(\overline{21\frac{1}{2}},\ \overline{5},\ \overline{6\frac{1}{2}})$
(2):	$(71\frac{1}{2},\ 45,\ \overline{6\frac{1}{2}})$	$(\overline{2})$:	$(28\frac{1}{2},\ 55,\ 6\frac{1}{2})$
(3):	$(\overline{21\frac{1}{2}},\ 55,\ 43\frac{1}{2})$	$(\overline{3})$:	$(21\frac{1}{2},\ 45,\ 56\frac{1}{2})$
(4):	$(28\frac{1}{2},\ \overline{5},\ 56\frac{1}{2})$	$(\overline{4})$:	$(71\frac{1}{2},\ 5,\ 43\frac{1}{2})$

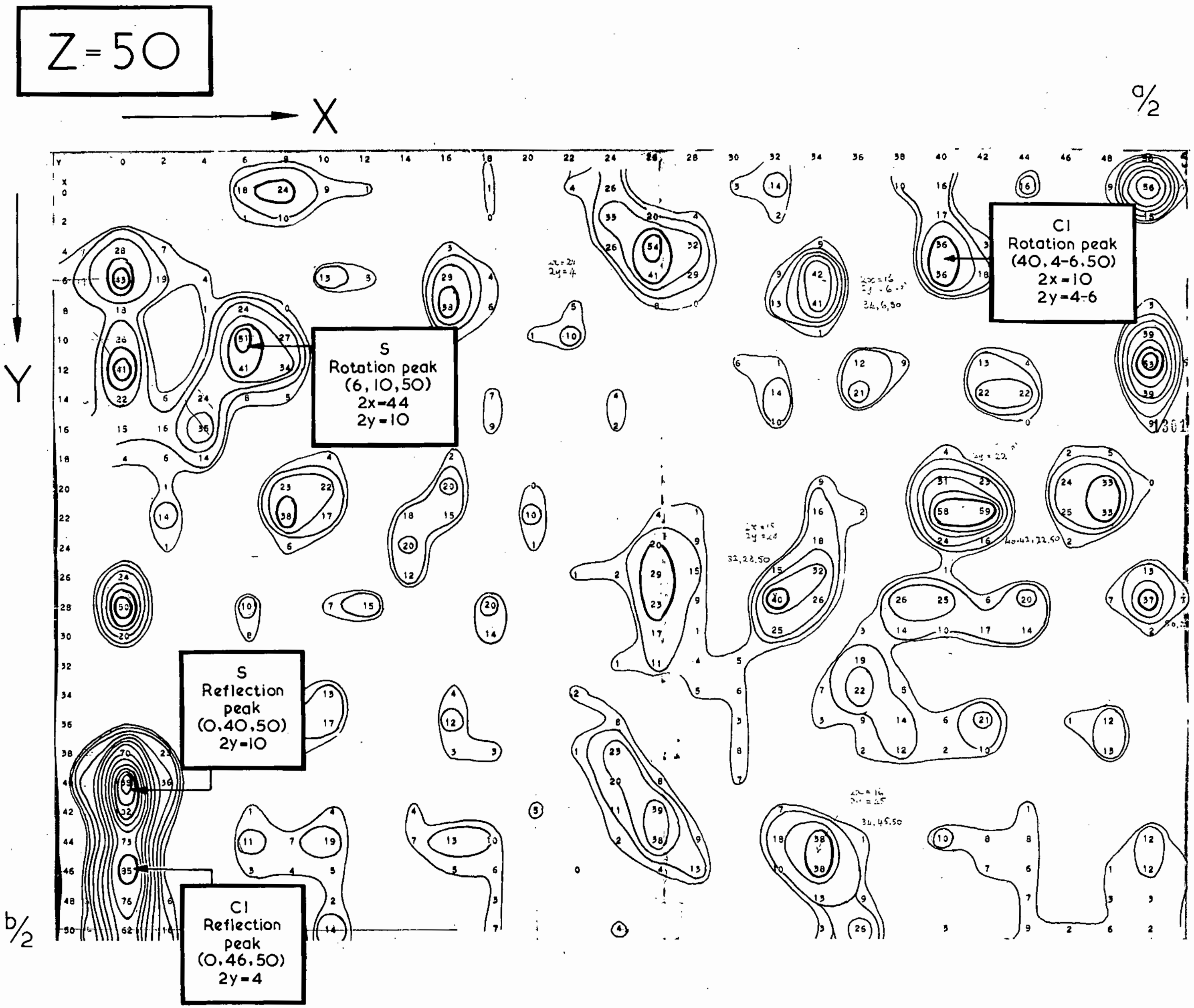


FIGURE 6

SECTIONS OF THE THREE-DIMENSIONAL SHARPENED PATTERSON FUNCTION SHOWING SIX OF THE CHOSEN HARKER PEAKS

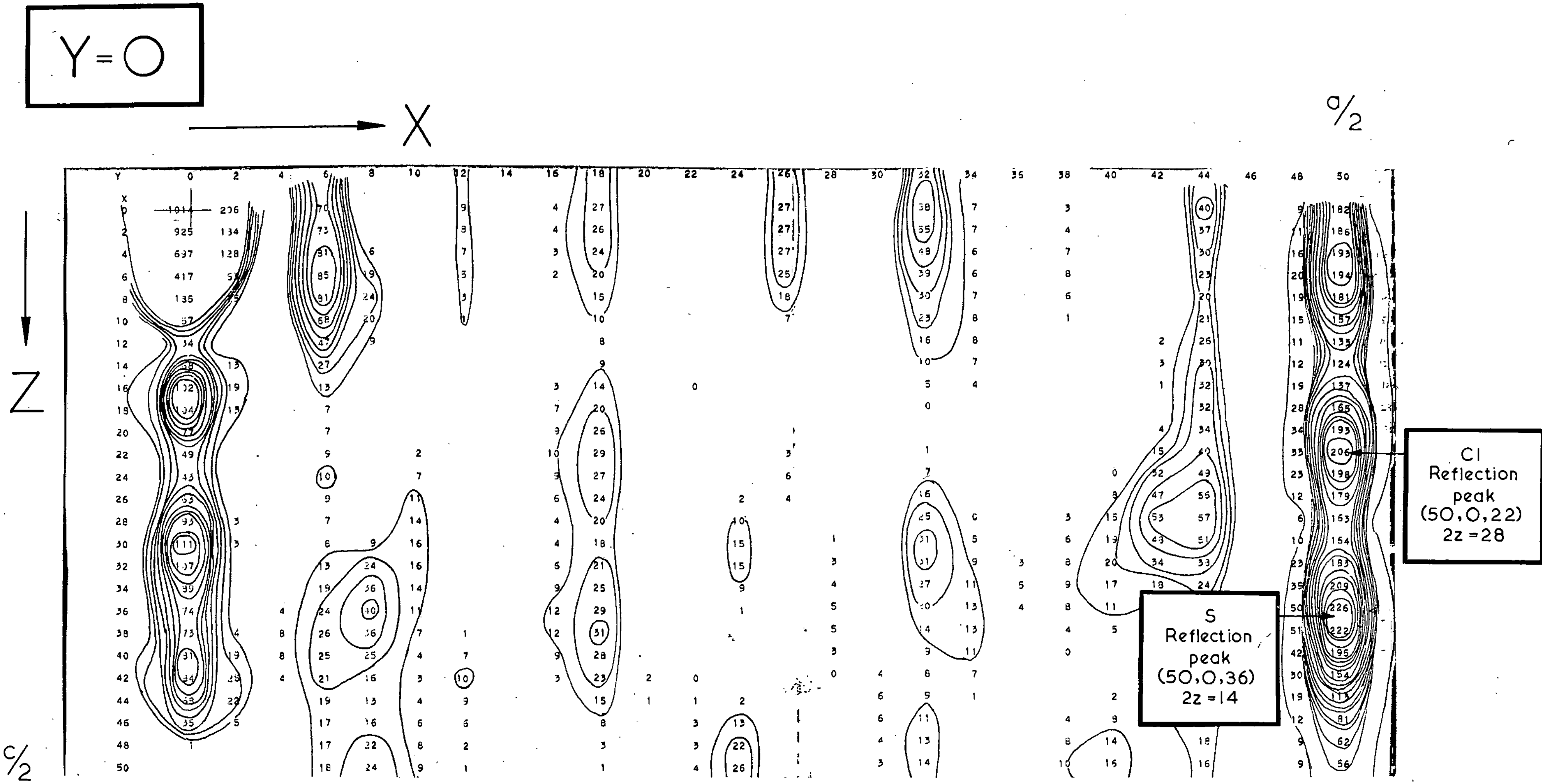


FIGURE 6 (cont.)

The Cℓ atom was assumed to be at (±5, ±3, ±13); i.e. at one of the eight possible positions represented by the permutations of the signs of x, y, and z.

The first equivalent position of the S atom, i.e. S(1), taken in conjunction with each of the sign combinations of the coordinates of the Cℓ atom, led to eight positions in the Patterson at which S-Cℓ peaks could be sought:-

(+++) :	($16\frac{1}{2}$,	2,	$6\frac{1}{2}$)	(10)	(---) :	($26\frac{1}{2}$,	8,	$19\frac{1}{2}$)	(0)
(-++) :	($26\frac{1}{2}$,	2,	$6\frac{1}{2}$)	(40)*	(+--) :	($16\frac{1}{2}$,	8,	$19\frac{1}{2}$)	(63)*
(+-+) :	($16\frac{1}{2}$,	8,	$6\frac{1}{2}$)	(23)	(-+-) :	($26\frac{1}{2}$,	2,	$19\frac{1}{2}$)	(4)
(--+) :	($26\frac{1}{2}$,	8,	$6\frac{1}{2}$)	(-)	(++-) :	($16\frac{1}{2}$,	2,	$19\frac{1}{2}$)	(10)

The centrosymmetrically equivalent atom, S($\overline{1}$), combined with each of the sets of signs of the coordinates of the Cℓ atom, led to the identical set of eight positions to those above, but each possible S-Cℓ position was obtained from a set of Cℓ coordinates with signs reversed. e.g. S(1) with Cℓ(-++) gave a peak of (40), while S($\overline{1}$) with Cℓ(+--) gave a peak of (63), (see * above). It can be deduced therefore that these were two of the required Patterson S-Cℓ peaks, and consequently allocated the signs (-++) to the coordinates of the Cℓ atom.

The second equivalent position of the S atom, i.e. S(2), taken in conjunction with each of the sign combinations of the coordinates of the Cℓ atom, plus the centrosymmetrically equivalent position, S($\overline{2}$), combined with Cℓ , defined another eight locations:-

(+++) :	($33\frac{1}{2}$,	42,	$19\frac{1}{2}$)	(-)	(---) :	($23\frac{1}{2}$,	48,	$6\frac{1}{2}$)	(1)
(-++) :	($23\frac{1}{2}$,	42,	$19\frac{1}{2}$)	(52)*	(+--) :	($33\frac{1}{2}$,	48,	$6\frac{1}{2}$)	(43)*
(+-+) :	($33\frac{1}{2}$,	48,	$19\frac{1}{2}$)	(-)	(-+-) :	($23\frac{1}{2}$,	42,	$6\frac{1}{2}$)	(23)
(--+) :	($23\frac{1}{2}$,	48,	$19\frac{1}{2}$)	(3)	(++-) :	($33\frac{1}{2}$,	42,	$6\frac{1}{2}$)	(-)

As before, Patterson S-Cℓ peaks were found at the two locations required by the (-++) signs of the Cℓ coordinates.

Similarly, S(3) and S($\overline{3}$) defined eight locations:-

(+++) :	(26½, 48, 30½)	(2)	(---) :	(16½, 42, 43½)	(1)
(-++) :	(16½, 48, 30½)	(45)*	(+--) :	(26½, 42, 43½)	(55)*
(+-+) :	(26½, 42, 30½)	(1)	(-+-) :	(16½, 48, 43½)	(-)
(--+) :	(16½, 42, 30½)	(15)	(++-) :	(26½, 48, 43½)	(-)

And S(4) and S($\overline{4}$):-

(+++) :	(23½, 8, 43½)	(-)	(---) :	(33½, 2, 30½)	(-)
(-++) :	(33½, 8, 43½)	(58)*	(+--) :	(23½, 2, 30½)	(39)*
(+-+) :	(23½, 2, 43½)	(13)	(-+-) :	(33½, 8, 30½)	(34)
(--+) :	(33½, 2, 43½)	(6)	(++-) :	(23½, 8, 30½)	(6)

Hence, out of a total of 32 locations, eight S-Cℓ peaks were found which assigned (-++) to the coordinates of the Cℓ atom. It was therefore assumed that S was at (21½, 5, 6½) and Cℓ at (-5, +3, +13).

The two atoms were placed at these positions, structure factors were calculated and a three-dimensional Fourier was computed.

As had been hoped, the two atoms, although not accurately placed, governed the phases of the scattered waves to an extent sufficient for the dramatic disclosure in the Fourier of <u>all</u> the remaining non-hydrogen atoms of the structure.

11. Refinement of the structure

Using the analytical *f*-values of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955), structure factors were calculated with all 21 atoms placed and, after adjustment of the scale factors, the value of R was 35.8%, where

$$R = 100 \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

FIGURE 7

THE MOLECULE AS IT APPEARED IN FOURIER 4 (R = 27.4%)

Three successive three-dimensional Fourier and difference Fourier syntheses brought the value of R down to 27.4%, at which stage one molecule in Fourier 4 contoured on glass sheets is shown in Figure 7. An I.C.T. 1301 computer was used for the calculations; the formulae used are given in Appendix A.

The refinement was continued on an I.B.M. 360/40 computer. Using the Busing, Martin & Levy (1962) programme ORFLS, and the scattering factor values of Hanson, Herman, Lea & Skillman (1964), five least-squares cycles were computed. The function minimised was

$$R_1 = \sum w_{(hkl)} \{|F_o(hkl)| - |F_c(hkl)|\}^2 \quad \text{with}$$

equal weight given to each term. Initially an overall temperature factor of 3.8 was applied; subsequently individual isotropic temperature factors for each atom were used. The value of R for observed reflections dropped to 18.9%. At this stage 675 unobserved reflections, estimated as $\frac{1}{3}$ $|F_{min}|$ of the appropriate layer line, were included and a further four cycles with anisotropic temperature factors for all atoms (excluding hydrogen atoms) were computed. In the last cycle the average parameter shifts expressed as fractions of the e.s.d.'s were about 0.3 for x-coordinates, 0.5 for y and z-coordinates. The final R value for 2560 reflections was 13.5%. Subsequently a further two cycles were carried out on the 1885 observed reflections and the final R was 11.4%. The progress of the least-squares refinement is summarised in Table 8; Table 9 lists the observed and calculated structure factors; final atomic coordinates and thermal-motion parameters with associated e.s.d.'s are given in Table 10.

TABLE 8

LEAST-SQUARES REFINEMENT

Operation number	Number of cycles	Data	Parameters varied	Number of parameters varied	Remarks		Cycle number	R before (%)	R after (%)
1	1	1893 $F_{obs.}$	8 scale factors	8	Overall B = 3.8	Isotropic cycles	1	27.4	26.4
2	2	1893 "	8 scale factors 1 overall B 63 coords.	72			2	26.4	22.9
							3	22.9	22.3
3	2	1893 "	8 scale factors 21 indiv. B's 63 coords.	92	Individual isotropic B's		4	22.4	19.3
							5	19.3	18.9
4	1	2568 (1893 $F_{obs.}$ +675 $F_{unobs.}$)	63 coords 126 β's	189	Individual anisotropic β's	Anisotropic cycles $F_{obs.}$ + F_{unob}	6	21.6	15.5
5	1	2563	"	189	5 $F_{obs.}$ omitted		7	15.2	14.1
6	1	2563	8 scale factors 63 coords.	71	"		8	14.1	14.0
7	1	2560	63 coords. 126 β's	189	8 $F_{obs.}$ omitted		9	14.1	13.5
8	2	1885 $F_{obs.}$	"	189	"	Anisotropic cycles $F_{obs.}$ only	10	11.5	11.4
							11	11.4	11.4

Table 9

Observed and calculated structure factors.

Within each group the columns, reading from left to right, contain the values of h, $K|F_o|$ and F_c.

* indicates a reflection with $I_o = 0$, $|F_o| = \frac{1}{3}|F_{min}|$ of the appropriate layer line for these reflections.

† indicates $|F_o|$ omitted for these reflections in the last three refinement cycles because the intensities were too high to measure accurately.

TABLE 9

h00		
4	70	-55
6	47	-44
8	102	-106
10	45	31
12	174	-177
14	18	16
16	11	-13
18*	37	35
20	4	-5
22	25	22
24*	23	20
26*	3	4
28	3	-3
30	12	-14
h10		
4	81	82
6	85	78
8	67	46
10	24	14
12	65	-55
14*	30	27
16	3	5
18	15	-17
20	14	-13
22	13	13
24	27	-25
h20		
0†	67	108
2	29	27
4	37	41
6	54	-44
8	28	-24
10	56	-53
12	102	-103
14*	25	22
16	3	4
18	46	46
20	21	18
22	16	22
h30		
2	7	10
4	110	116
6	65	-58
8	59	58
10*	28	-26
12	3	2
14	35	-36
16*	21	-20
18	4	1
20	9	-8
22	15	15
h40		
0*	68	70
2	2	7
4	100	103
6	11	9
8	47	-42
10	41	-45
12	67	-65
14	18	-17
16	7	-7
18	31	33
20	10	10
22	13	11
h50		
2	61	-55
4	110	114
6	33	28
8	59	50
10	11	-11
12	27	27
14	11	-9
16	35	-27
18	38	-38
20	7	-5
22*	11	11
24	3	-5
26	7	9
h60		
2	67	67
4	26	12
6	95	-93
8	11	-17
10	28	-22
12	31	30
14	10	-9
16	13	-16
18*	20	19
20	4	7
22*	11	12
24*	3	6
26	3	-1
28	8	-10
h70		
4	82	86
6	28	-23
8	41	45
10	18	-19
12	8	7
14	23	21
16	68	-66
18	26	27
20	16	-16
22*	11	-8
24	3	-3
26	6	6
28	13	15

h80		
0	35	-35
2	85	82
4	77	-71
6	40	35
8	25	-20
10	16	-17
12	7	-7
14	49	-48
16	61	62
18	8	-8
20	15	19
h90		
4*	48	46
6*	3	-3
8	3	-3
10	35	33
12	20	19
14	45	-45
16	11	-10
18	21	-22
20	11	10
22*	6	-6
24	3	1
26	10	10
h,10,0		
0	19	-14
2	36	39
4	29	-29
6*	29	24
8	4	2
10	51	-51
12	16	15
14	21	-20
16*	31	31
18	4	5
20	8	12
22	8	-9
24	5	-7
h,11,0		
2*	34	38
4	4	-4
6*	44	38
8	4	1
10	32	33
12*	22	-22
14*	4	-7
16*	4	-4
18*	32	-30
20	3	3
22	7	5
h,12,0		
0	67	-67
2	49	47
4	9	-7
6	24	-23
8*	15	-16
10	4	-7
12	35	33
14*	4	5
16	8	8
18	11	-10
20	13	13
h,13,0		
2	26	25
4	7	-4
6	27	28
8	11	-13
10	7	8
12	20	-21
h,14,0		
0	60	-51
2	37	33
4*	11	-11
6*	4	1
8	4	4
10	8	-7
12	13	14
14	8	-6
h,15,0		
2	13	11
4	12	-11
6	24	25
8	7	-8
10*	11	10
12	3	-4
14*	9	-11
16	3	4
18	10	-12
h,16,0		
2	18	-17
4*	13	13
6*	3	-1
8*	3	1
10*	3	-1
12	3	1
14	10	8
h,17,0		
2	20	19
4	10	-8
6	5	-3
8	5	-6
10	12	10

h,18,0		
0	22	22
2*	15	-13
4*	3	1
6*	3	2
8	11	-8
10	13	13
h,19,0		
4	5	6
h11		
5	63	64
6	48	48
7	45	-43
8	63	68
9	19	14
10	34	33
11	79	-81
12	40	-41
13	13	-15
14	43	-39
15	14	-14
16*	18	-22
17	3	1
18	13	-13
19	27	32
20*	16	-17
21	3	1
22	20	26
23	15	17
h21		
4*	52	-44
5†	103	-80
6	9	7
7	9	7
8	10	8
9	45	43
10	47	-43
11	8	-9
12	50	41
13*	29	31
14	2	-3
15	27	-25
16*	14	13
17	3	3
18	11	-10
19	16	-18
20*	8	-8
21	3	3
22	10	-10
h31		
1†	159	124
2†	216	264
3	49	37
4	81	73
5	23	-13
6	21	14
7	100	
8	15	14
9	4	3
10	12	-9
11	43	-44
12	36	37
13	11	-13
14	48	-46
15	4	-3
16*	20	-20
17	3	1
18	14	-15
19*	18	19
20*	3	6
21	3	3
22	14	-17
23	14	16
24*	7	9
25	3	3
26	9	12
h41		
0†	99	-81
1†	160	-106
2	48	-47
3	87	88
4	12	-3
5	17	-7
6	27	-18
7	28	30
8	35	35
9	21	25
10	10	11
11	32	-31
12	25	29
13*	34	34
14	2	-1
15	30	-32
16	26	28
17	20	23
18	9	-7
19	28	-32
20*	5	-7
21	3	-2
22*	6	10
23	3	1
24*	11	-14
25	2	-4
26	5	-8
27	7	9
h51		
1	27	18
2	3	-1
3	89	78
4	85	73
5	12	-12
6	19	-11
7	22	-22

8	15	-13
9	56	-54
10	36	34
11	38	-37
12*	21	-20
13	3	
14	27	-28
15	7	-6
16	55	-64
17	12	14
18	30	34
19*	20	24
20	3	-1
21*	9	13
22*	3	5
23	3	1
24*	10	13
25*	2	1
26	2	4
27	4	-5
28	6	8
h61		
0	7	-4
1*	29	-13
2	2	-1
3	99	93
4	64	-63
5	52	-38
6	109	97
7	58	49
8	47	-39
9*	26	21
10	2	2
11	22	-19
12	39	40
13*	26	-27
14	3	1
15	58	-66
16	16	16
17	11	13
18	40	-46
19	14	-15
20*	10	10
21*	3	-1
22*	3	-8
23*	3	2
24*	2	-7
25*	2	2
26	2	-3
27	6	10
h71		
1	31	29
2	31	27
3	16	17
4	17	-11
5	21	-21
6	56	59
7	26	19
8	32	31
9	42	-40
10*	12	8
11*	2	-3
12	3	-3
13	27	-28
14	33	-33
15	7	7
16	5	-7
17	25	28
18*	11	-13
19	3	-4
20	14	15
21	7	11
h81		
0	32	-23
1	31	-26
2	24	-22
3	48	45
4	76	-70
5	19	22
6	45	38
7	40	37
8	15	17
9*	6	9
10*	2	7
11	3	-2
12*	34	34
13*	3	3
14	3	-2
15	30	-33
16*	39	42
17	3	-1
18	20	-21
19	19	-20
20	14	-16
21*	4	8
22*	3	-1
23	2	2
24	8	-9
h91		
2	19	-17
3	27	23
4	29	27
5	54	-48
6	31	25
7	24	24
8	39	-33
9	37	-37
10	19	-22
11	24	21
12	21	-23
13	6	7
14*	11	10
15	3	4
16*	22	24
17	3	4
18	22	-27
19	4	-7
20	9	9
21	11	16

22	6	9
h,10,1		
0	15	-15
1	15	18
2	27	-27
3	29	28
4*	23	23
5	3	5
6	11	-7
7	12	12
8*	17	17
9	3	0
10*	18	16
11	3	-1
12	11	-9
13	7	-8
14	18	18
15	13	-15
16*	10	-12
17	3	1
18*	8	-7
19*	3	-2
20*	3	3
21	2	-3
22	5	-10
h,11,1		
2	9	9
3	6	-9
4	10	-9
5	12	-12
6	14	16
7	33	31
8	11	-10
9	26	-23
10	10	11
11*	16	16
12	3	-7
13*	14	-16
14*	3	-1
15	3	6
16	6	-8
17*	9	12
18	3	4
19	10	-8
h,12,1		
0	43	-51
1	18	19
2	15	14
3	14	-15
4	6	-7
5	18	18
6	5	8
7	6	8
8*	6	-8
9*	3	-1
10	3	1
11	13	11
12	29	32
13*	16	-18
14	3	-1
15*	11	12
16	3	-4
17	14	-17
h,13,1		
1	12	-13
2	19	-20
3	10	13
4	10	11
5	5	-6
6*	16	-17
7	3	3
8*	15	18
9	3	-6
10*	9	-9
11*	3	2
12*	3	-5
13*	3	-1
14*	3	1
15*	3	7
16*	2	-6
17*	2	2
18*	2	2
19	2	3
20	12	15
h,14,1		
1	22	26
2	20	-24
3	15	-17
4	27	34
5	11	13
6*	11	-11
7	3	2
8*	11	-11
9	3	-5
10	13	15
11*	10	13
12	3	-2
13	11	-13
14*	10	12
15	2	2
16	5	-7
17	8	-12
h,15,1		
1	4	8
2	6	-6
3*	11	-13
4	3	6
5	9	10
6	7	7
7	10	-12
8*	10	-12
9	3	-1
10	6	-6

11*	7	8
12*	2	1
13*	2	1
14	2	1
15	6	6
h,16,1		
0	16	20
1	12	17
2	15	-19
3*	8	-10
4	3	3
5*	10	15
6*	3	6
7*	2	-2
8*	2	1
9	2	-3
10*	7	7
11*	2	5
12	2	-5
13*	6	-12
14	2	4
15	4	8
h,17,1		
2*	8	-11
3	2	-6
4	8	12
5	5	8
6	8	-11
7	6	-10
8	6	8
9*	6	9
10*	2	-3
11	2	-4
12	4	7
h,19,1		
6	5	-1
h02		
2†	76	90
3†	216	273
4	120	121
5	102	110
6	43	-40
7	39	35
8	48	-39
9	29	24
10	29	-34
11	33	-32
12*	42	35
13	3	-1
14	20	27
15	58	-59
16*	16	-13
17	3	-2
18	16	20
18*	33	-33
20*	4	-3
21*	4	3
22*	4	5
23*	4	5
24	3	-4
25	8	9
26	9	-10
27	12	14
h12		
1	37	-40
2	60	-61
3	38	-47
4	64	61
5	18	-11
6	45	-45
7	41	49
8*	19	7
9	2	7
10	55	-54
11	24	22
12*	27	20
13	3	-3
14	15	-13
15*	16	-17
16	3	2
17	19	21
18	7	3
19*	6	4
20*	4	5
21*	4	-3
22*	4	-3
23	4	-2
24*	13	14
25*	3	-3
26	3	-2
27	6	-4
h22		
0	85	89
1	168	-159
2	70	-70
3	126	135
4	129	131
5	52	60
6	38	-33
7	46	46
8	47	-49
9	92	87
10	10	14
11	83	-75
12	20	-6
13	8	-5
14	28	26
15	53	-54
16	46	-47
17	30	-32
18	12	8
19*	18	-19
20	4	-1

21*	18	20
22	4	-2
23*	12	12
24*	4	4
25*	3	6
26	3	-1
27	9	13
h32		
1	128	-128
2	43	27
3	127	113
4	64	53
5	25	-28
6	18	-13
7	10	-3
8	61	61
9	19	20
10	30	-32
11	37	31
12	16	13
13	30	29
14*	8	-7
15	3	-2
16	21	-17
17	12	-16
18*	20	21
19	4	-3
20*	15	-16
21*	4	-3
22	4	2
23	14	-15
h42		
0	71	62
1	28	20
2	59	-51
3	53	52
4	60	-50
5*	22	22
6	2	9
7	74	69
8	22	18
9	6	17
10	38	32
11	25	21
12	11	1
13*	5	-10
14	3	2
15*	72	-74
16	3	5
17	7	-7
18*	8	-6
19*	4	1
20*	4	-7
21*	4	4
22*	4	4
23*	3	3
24	3	-1
25	8	8
h52		
1	55	-52
2*	36	-28
3	2	4
4	43	39
5	70	-57
6	84	-83
7	47	45
8	66	64
9	14	-13
10	36	-29
11*	41	45
12	3	-2
13	37	33
14	6	-6
15*	10	5
16	3	-2
17	23	20
18	26	27
19	27	-29
20	17	-18
21	6	-7
22	11	12
23	6	-8
24	6	8
25	6	-3
h62		
0	66	-61
1	27	22
2	20	16
3	62	55
4	37	-26
5	67	65
6	67	56
7*	27	-15
8	3	1
9	24	-22
10*	17	-10
11*	3	-2
12	3	5
13	23	-21
14*	10	-10
15	3	1
16	18	17
17	18	-14
18*	20	-20
19	4	-4
20	4	9
21*	4	8
22*	3	-3
23*	3	4
24	3	-2
25	10	13
h72		
1*	42	-39
2	2	2
3	19	-15
4	13	-13

5*	3	-12
6	23	-25
7	42	41
8*	24	28
9	3	7
10	23	-20
11	18	14
12	25	24
13	20	20
14*	30	-32
15	4	2
16*	41	43
17	4	-1
18*	19	-19
19	4	1
20*	10	-10
21	3	-5
22	7	9
23	11	-14
h82		
0	30	-30
1	56	61
2	11	11
3	25	-19
4	24	20
5	12	14
6	11	-8
7	26	26
8	12	9
9	4	6
10	32	-32
11	4	5
12	29	28
13*	34	-38
14*	4	-1
15	4	2
16	14	-11
17*	16	-19
18*	4	-2
19	4	4
20	5	1
21	8	7
h92		
1*	31	-34
2	3	-8
3	10	6
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12*	3	-1
13	3	-4
14	26	-22
15	8	6
16*	8	8
17	3	2
18	13	-12
19	17	15
20*	16	14
21*	2	4
22*	2	2
23	2	-5
24	6	6
h75		
1	14	-11
2	13	-7
3	7	-5
4	21	-17
5	24	24
6	24	22
7	14	-11
8	30	-32
9	21	21
10*	8	8
11*	3	-1
12*	3	-1
13	3	-5
14	12	11
15	9	8
16	24	20
17	15	-14
18*	12	-9
19*	3	-3
20	2	2
21	7	-7
22	10	-10
h85		
0	19	-20
1	42	40
2	25	19
3	4	-3
4*	2	1
5*	12	-11
6	2	3
7	19	-19
8	15	11
9	24	-24
10	18	-13
11	35	34
12*	15	-12
13	3	-1
14*	12	-9
15*	3	-3
16	3	-2
17*	12	11
18	3	1
19	12	12
20*	12	13
21*	2	-3
22	2	-1
23	10	-8
h95		
1	24	20
2	8	3
3	45	-43
4*	67	-68
5	3	2
6	48	45
7	16	16
8	32	-30
9	12	12
10	23	19
11	7	-6
12*	7	7
13*	3	-1
14*	3	3
15	3	1
16*	10	9
17	2	-2
18	13	-10
19	4	-4
20*	9	9
21	2	-3
22	8	-7
23	10	9
h,10,5		
0	42	42
1*	31	-31
2*	3	-6
3	3	4
4	13	11
5	13	-9
6	15	-12
7*	32	-29
8	3	-4
9	16	16
10	7	-7
11	11	-10
12*	16	-15
13*	3	6
14	3	5
15	10	9
16*	8	-8
17	2	-1
18	11	8
19*	6	6
20*	2	-2
21	2	1
22	6	6
h,11,5		
1	14	12
2	22	18
3	13	-12
4	29	-26
5	13	12
6*	24	22
7	3	-4
8	34	-31
9	8	7
10	27	26
11	15	-14
12*	10	-10
13	3	4
14*	14	16
15*	2	3
16	2	-5
17	15	-14
18	4	-1
h,12,5		
1	12	10
2*	15	10
3	3	-4
4	12	9
5*	15	-13
6*	3	-4
7	3	2
8*	8	-7
9	3	2
10*	8	-6
11	2	1
12*	13	-13
13	2	2
14	9	9
15	4	4
16*	8	-8
17	2	1
18	3	3
h,13,5		
1*	3	-4
2*	9	8
3	3	3
4	5	-4
5	8	8
6	8	6
7	9	-8
8	8	-6
9	9	9
10	8	8
11	12	-11
h,14,5		
0	26	22
1	15	-16
2	20	-19
3	8	7
4*	20	18
5*	2	1
6	2	-2
7	11	-11
8*	13	-10
9*	2	2
10	2	-1
11	6	-6
12	6	-7
13*	13	12
14*	2	5
15*	2	-3
16	1	-7
17	5	2
h,15,5		
1*	2	-1
2*	2	-4
3	2	1
4	4	-5
5	12	9
6	9	5
7*	7	-8
8*	2	3
9*	2	1
10*	2	4
11*	2	-2
12	2	-7
13	7	2
h,16,5		
0*	16	17
1	2	2
2*	10	-9
3	2	1
4*	9	9
5	5	-6
6	5	-6
7	5	5
8*	5	-6
9	2	-5
10*	4	8
11	1	1
12	6	-9
h,17,5		
1*	1	-1
2	2	-2
3	5	5
h06		
1	30	-43
2	36	40
3	16	-14
4	32	-34
5	21	-23
6	19	24
7	28	-25
8	17	-22
9	14	-11
10	26	-25
11	16	15
12	51	52
13	13	11
14	16	-12
15*	18	16
16	2	-1
17	17	15
18	15	-13
19	15	-14
20	6	5
21	22	22
22	10	10
23	7	-7
24	7	-7
25	9	-9
h16		
1	13	-15
2	11	12
3	25	29
4	6	-8
5	15	-15
6	6	-3
7*	11	-11
8	1	1
9*	7	-7
10	2	-2
11	13	11
12	9	-9
13	15	16
14	4	4
15	4	-4
16	19	17
17	14	-13
18	13	-13
19	4	5
20*	12	12
21	2	1
22*	10	-10
23*	2	-1
24	2	3
25	5	7
h26		
1*	21	-21
2	1	1
3	11	10
4	8	7
5*	53	-57
6	2	-4
7	24	-25
8	5	8
9	12	-14
10	13	-15
11*	17	-17
12	2	3
13	44	43
14	16	-14
15	7	-6
16	11	12
17*	23	21
18	2	2
19*	17	12
20*	2	-3
21	2	1
22*	9	10
23	2	-4
24	7	-8
25	11	13
h36		
1	13	-12
2	9	-12
3	34	34
4	8	-3
5	14	14
6	20	16
7	10	-10
8	29	-27
9	22	-22
10	29	30
11	26	28
12	26	-29
13	34	-34
14*	19	18
15*	2	-1
16	2	2
17	7	-6
18*	13	-12
19	2	-3
20	7	8
21	10	10
22*	7	-7
23	2	-3
24	7	8
25	9	11
h46		
0*	17	13
1	1	-1
2	6	-4
3	28	-27
4	7	8
5*	25	-23
6	2	3
7	22	-17
8	11	-10
9	29	-29
10	9	7
11	33	29
12	15	-13
13	18	18
14	8	-6
15	8	4
16	8	5
17	18	16
18	6	5
19	6	4
20*	7	7
21	2	1
22	8	-9
23	16	-15
h56		
1	17	-18
2	25	24
3	46	47
4	32	-32
5	12	-9
6	27	29
7	26	29
8	36	-37
9	44	-47
10	39	40
11	8	5
12	10	-8
13	21	-17
14	5	-5
15*	11	-9
16	2	1
17	9	8
18*	8	-7
19	2	1
20	9	9
21	15	15
22*	7	-6
23	2	-2
24	4	3
h66		
0	11	11
1	13	13
2	12	13
3*	34	-31
4	2	-8
5*	20	-23
6	2	-4
7	20	-20
8	23	-20
9	12	-8
10	9	7
11*	29	31
12	2	-2
13*	11	8
14*	2	1
15	2	4
16*	4	1
17	2	1
18*	2	-1
19*	10	9
20	2	5
21	6	-6
h76		
1	36	35
2*	23	22
3	2	-3
4	24	-24
5	10	9
6*	32	32
7	2	-6
8	26	-26
9	42	-42
10*	13	10
11*	2	8
12	2	-2
13	17	-15
14*	9	-8
15	2	3
16*	9	10
17	2	-3
18*	13	-12
19	2	1
20	15	14
21	9	9
22	13	-12
h86		
0	15	15
1	16	13
2	22	-21
3	8	-6
4*	34	33
5	2	-2
6	12	-12
7*	17	-18
8	2	-5
9*	10	13
10*	2	1
11	2	1
12	13	-14
13	9	-7
14	15	16
15	22	22
16	9	-9
17	6	-6
18*	6	4
19*	2	2
20*	2	-1
21	1	-5
22	4	4
h96		
1	9	7
2	8	-3
3*	24	23
4	2	-3
5	4	-4
6*	24	25
7	2	-3
8	19	-20
9	19	-17
10	18	18
11	8	-6
12	15	-15
13	8	-7
14*	8	5
15*	2	1
16	2	-3
17*	3	-3
18*	2	-1
19*	2	3
20	1	-2
21	10	9
h,10,6		
0	9	8
1	9	9
2	6	-7
3*	11	-10
4	2	-5
5	9	7
6*	10	10
7*	2	-4
8	2	-1
9*	12	10
10*	2	-2
11	2	2
12	7	-7
13	13	-13
14	9	11
15	17	18
16*	4	-5
17	2	-3
18	5	6
h,11,6		
1*	2	-3
2*	7	-7
3	2	3
4	15	15
5	24	24
6	17	-19
7	15	-16
8*	14	13
9*	2	-4
10*	2	1
11	10	-11
12*	9	-11
13	2	0
14*	8	10
15	2	1
16	6	-6
17*	5	-5
18	1	-1
19	9	9
h,12,6		
0	16	11
1*	17	16
2	2	1
3*	9	-9
4	2	-2
5	6	-5
6*	11	-11
7	2	1
8	6	5
9	7	6
10*	7	8
11	2	2
12	9	-9
13*	3	-2
14*	2	3
15*	2	4
16	1	-1
17	5	-5
h,13,6		
1*	8	8
2*	2	-1
3	2	-3
4	11	10
5	17	16
6	11	-10
7	19	-21
8	7	8
9*	7	7
10	2	3
11	7	-9
h,14,6		
1	5	-5
2*	6	-6
3	2	3
4*	10	10
5*	2	3
6*	2	-5
7*	2	-1
8*	2	2
9*	2	2
10*	2	1
11*	2	-1
12	1	-4
13	5	5
h,15,6		
6*	5	-7
7	2	-2
8*	7	7
9	1	1
10	5	-6
11	8	-10
h,16,6		
0	14	-13
1	8	-9
2*	8	9
3	1	4
4*	5	-4
5	1	-1
h17		
1	5	4
2	10	-9
3	45	51
4	9	-6
5	25	-24
6	37	-41
7*	17	19
8	2	2
9*	44	-45
10	2	3
11	10	-10
12	7	4
13*	16	-17
14*	3	3
15	3	8
16*	15	13
17*	3	3
18*	3	-1
19	2	-1
20	7	6
21	18	20
h27		
0	8	3
1	19	18
2	5	-2
3	21	-24
4	19	20
5*	15	14
6	2	1
7	20	22
8	20	-21
9	13	-10
10	4	-1
11*	21	20
12	3	2
13*	8	-8
14	3	-4
15*	16	-14
16	3	-1
17*	7	-7
18*	3	-1
19	2	5
20*	9	8
21	2	-1
22	5	-6
h37		
1*	18	17
2	2	1
3	31	31
4	25	-26
5	36	-39
6	7	7
7	27	25
8	12	-10
9	49	-51
10	14	-14
11*	7	3
12*	3	5
13	3	4
14*	21	18
15*	3	-3
16	3	3
17*	11	10
18	3	2
19*	9	-9
20	2	-2
21	14	13
h47		
0	37	-38
1	33	31
2	42	45
3	19	-16
4	14	-9
5	31	34
6	4	2
7	18	15
8	20	-17
9*	26	-28
10	2	-1
11*	14	11
12	2	-1
13	19	-17
14	16	-13
15	14	13
16	14	12
17	13	-12
18*	13	-13
19	2	1
20	11	12
h57		
1	11	10
2*	9	7
3	2	-1
4	14	-11
5	12	10
6*	14	16
7	2	-1
8	15	-15
9	11	-8
10	12	-11
11	15	-17
12*	23	21
13	3	-5
14	14	-14
15	4	4
16	9	8
17*	4	-4
18	2	5
19*	8	9
20	2	2
21	4	3
h67		
0	28	28
1*	20	16
2	2	2
3	23	-22
4	21	-23
5	27	28
6	18	20
7*	21	20
8	3	3
9	12	-12
10	18	-16
11*	9	6
12	3	3
13	13	-9
14	13	-11
15*	11	11
16	3	6
17*	12	-13
18	2	-3
19	9	-6
h77		
1*	8	5
2	3	3
3	8	-5
4	12	-12
5*	16	16
6	3	2
7	17	-15
8*	12	-11
9	3	-1
10	15	14
11	9	-9
12*	8	-9
13	3	2
14*	11	10
15*	2	-1
16*	2	2
17*	2	1
18	2	-1
19	11	12
h87		
0	15	-12
1	11	-8
2	13	12
3*	10	-13
4	3	1
5	7	7
6	10	8
7*	11	13
8	3	2
9	11	9
10	15	-14
11	8	-8
12*	4	-2
13*	3	-4
14*	2	-1
15*	2	3
16	2	-1
17	10	-11
18*	6	-4
19	2	-3
20	2	3
h97		
1*	11	9
2*	3	2
3*	3	-3
4	3	6
5	25	26
6	17	-18
7*	39	-45
8	2	-2
9	18	16
10	14	14
11	8	-9
12*	8	-8
13	2	2
14	10	13
15	4	6
16	6	-8
17*	8	-8
18	2	5
19	10	10
h,10,7		
1*	18	18
2*	3	7
3*	3	-4
4	3	3
5*	9	9
6	3	4
7	19	20
8	14	-14
9*	12	-12
10*	2	2
11	2	2
12*	6	-6
13*	2	-1
14	2	-2
15	6	-3
h,11,7		
1*	3	2
2	12	-12
3*	12	-12
4	3	4
5*	25	27
6	3	4
7*	25	-29
8	2	2
9*	11	11
10	2	2
11*	5	-6
12	2	-2
13*	4	3
14*	2	2
15	2	-2
16	6	8
h,12,7		
0	13	11
1*	17	-16
2	3	-6
3	14	15
4*	14	14
5	2	2
6*	12	-12
7*	2	-1
8	2	1
9*	9	10
10	2	-2
11*	12	-11
12	2	-2
13*	8	8
14	2	2
15	10	11
h,13,7		
1*	2	5
2	2	2
3	11	-10
4	6	-8
5	8	8
6	5	7
7*	8	-10
8	2	5
9	5	6
h,14,7		
1*	8	-10
2	2	-3
3*	7	7
4*	2	4
5	2	-2
6*	6	-2
7*	2	6
8	2	-3
9	5	5
h,15,7		
4	7	10

TABLE 10

FINAL ATOMIC FRACTIONAL COORDINATES (x 10^4) AND THERMAL PARAMETERS (x 10^4) WITH ESTIMATED STANDARD DEVIATIONS

Temperature factor = $\exp\{-(h^2\beta_{11} + k^2\beta_{22} + \ell^2\beta_{33} + 2hk\beta_{12} + 2h\ell\beta_{13} + 2k\ell\beta_{23})\}$ with $\beta_{11} = 2\pi^2a^{*2}U_{11}$, $\beta_{12} = 2\pi^2a^*b^*U_{12}$, etc.

The least-squares standard errors are given in parentheses.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cℓ	4520 (1)	0199_5(2)	3710 (3)	23 (0_4)	102 (2)	176 (4)	20 (1)	4 (1)	11 (2)
S	2164 (1)	0515 (1)	0643 (2)	28 (0_4)	41 (1)	107 (3)	- 6 (0_5)	-16 (1)	-13 (1)
N(1)	2687 (2)	1874 (3)	2481 (6)	17 (1)	29 (2)	107 (9)	- 1 (1)	- 0 (2)	- 9 (3)
N(2)	4192 (2)	3325 (4)	3565 (7)	19 (1)	58 (3)	122 (10)	- 5 (1)	10 (3)	- 5 (4)
C(1)	3855 (3)	0261 (5)	2893 (8)	23 (2)	58 (4)	88 (12)	7 (2)	10 (3)	14 (5)
C(2)	1344 (4)	4537 (5)	2131 (9)	27 (2)	55 (4)	92 (13)	- 5 (2)	-17 (4)	11 (5)
C(3)	1870 (4)	4617 (5)	1478 (9)	34 (2)	36 (3)	138 (14)	- 1 (2)	-21 (4)	1 (5)
C(4)	2802 (3)	0398 (4)	1597 (8)	24 (2)	32 (3)	88 (11)	- 1 (2)	5 (3)	- 5 (4)
C(5)	3020 (3)	1111 (4)	2379 (7)	20 (1)	42 (3)	50 (10)	3 (2)	6 (3)	- 5 (4)
C(6)	3548 (3)	1045 (5)	3073 (7)	21 (1)	52 (4)	58 (11)	5 (2)	11 (3)	-11 (4)
C(7)	1807 (3)	1156 (5)	1926 (8)	21 (2)	45 (3)	102 (12)	- 2 (2)	-15 (3)	15 (5)
C(8)	1206 (3)	1052 (5)	2119 (11)	23 (2)	48 (4)	232 (17)	- 3 (2)	-19 (4)	27 (6)
C(9)	0921 (4)	1579 (6)	3109 (13)	22 (2)	53 (5)	281 (20)	5 (2)	4 (5)	27 (8)
C(10)	1214 (4)	2194 (6)	3942 (11)	24 (2)	53 (4)	233 (18)	9 (2)	15 (5)	20 (7)
C(11)	1807 (3)	2288 (5)	3780 (9)	22 (2)	39 (3)	145 (13)	6 (2)	8 (3)	17 (5)
C(12)	2097 (3)	1782 (4)	2747 (8)	18 (1)	36 (3)	104 (12)	- 0_4(2)	- 7 (3)	21 (4)
C(13)	2973 (3)	2709 (4)	2992 (8)	20 (1)	34 (3)	91 (11)	- 4 (2)	2 (3)	-17 (4)
C(14)	3394 (3)	3028 (4)	1840 (8)	26 (2)	42 (3)	80 (11)	-10 (2)	1 (3)	- 6 (4)
C(15)	3802 (3)	3713 (5)	2522 (9)	27 (2)	43 (3)	112 (13)	- 8 (2)	- 3 (4)	2 (5)
C(16)	4662 (4)	2836 (7)	2845 (15)	24 (2)	83 (6)	395 (26)	5 (3)	28 (6)	-62 (11)
C(17)	4426 (4)	4024 (7)	4476 (11)	35 (2)	89 (6)	161 (16)	-17 (3)	-15 (5)	-28 (8)

TABLE 11

BOND LENGTHS AND ANGLES AND ESTIMATED STANDARD DEVIATIONS

Bond	ℓ	Angle	θ
C(1) - C(2)	1.39 Å	C(6) - C(1) - C(2)	124.1(7)°
C(2) - C(3)	1.38	C(1) - C(2) - C(3)	117.0(7)
C(3) - C(4)	1.42	C(2) - C(3) - C(4)	121.7(7)
C(4) - C(5)	1.40	C(3) - C(4) - C(5)	119.3(7)
C(5) - C(6)	1.40	C(4) - C(5) - C(6)	120.3(6)
C(6) - C(1)	1.40	C(5) - C(6) - C(1)	117.5(7)
C(7) - C(8)	1.43	C(12) - C(7) - C(8)	119.4(7)
C(8) - C(9)	1.39	C(7) - C(8) - C(9)	119.5(8)
C(9) - C(10)	1.39	C(8) - C(9) - C(10)	120.9(8)
C(10) - C(11)	1.41	C(9) - C(10) - C(11)	119.9(8)
C(11) - C(12)	1.40	C(10) - C(11) - C(12)	119.8(8)
C(12) - C(7)	1.39	C(11) - C(12) - C(7)	120.4(7)
C(7) - S	1.75	C(4) - S - C(7)	97.3(3)
C(4) - S	1.75	S - C(7) - C(12)	120.9(6)
C(12) - N(1)	1.41	C(7) - C(12) - N(1)	116.9(6)
C(5) - N(1)	1.40	C(12) - N(1) - C(5)	118.4(5)
		N(1) - C(5) - C(4)	118.1(6)
N(1) - C(13)	1.51	C(5) - C(4) - S	119.7(5)
C(13) - C(14)	1.53		
C(14) - C(15)	1.55	C(12) - N(1) - C(13)	117.7(5)
C(15) - N(2)	1.45	C(5) - N(1) - C(13)	117.8(5)
N(2) - C(16)	1.49	C(1) - C(13) - C(14)	109.7(5)
N(2) - C(17)	1.46	C(13) - C(14) - C(15)	109.3(6)
		C(14) - C(15) - N(2)	112.7(6)
Cℓ - C(1)	1.74	C(15) - N(2) - C(16)	112.0(8)
Cℓ - C(16)	4.10	C(15) - N(2) - C(17)	108.9(7)
Cℓ - S	6.24	C(16) - N(2) - C(17)	109.9(7)
Cℓ - Cℓ($\bar{1}$)	3.34	Cℓ - C(1) - C(2)	118.7(6)
Cℓ - S(4)	4.47	Cℓ - C(1) - C(6)	117.1(6)
Cℓ - S($\bar{4}$)	6.26		
N(2) - S($\bar{3}$)	5.37		
N(2) - S($\bar{2}$)	5.45		
N(2) - Cℓ(3)	4.71		
N(2) - Cℓ($\bar{3}$)	5.28		

TABLE 12

MEAN PLANE PARAMETERS AND DEVIATIONS OF ATOMS FROM THE PLANE

I Benzene ring, C(1) - C(6)

$$-0.4353x - 0.3576y + 0.8262z = -1.8684$$

Atom	Displacement	Atom	Displacement
C(1)	-0.011 Å	S	-0.135
C(2)	0.004	N(1)	-0.007
C(3)	0.001	Cℓ	-0.035
C(4)	0.003		
C(5)	-0.011		
C(6)	0.014		

II Benzene ring, C(7) - C(12)

$$0.1603x - 0.6920y + 0.7038z = 0.7144$$

Atom	Displacement	Atom	Displacement
C(7)	0.001	S	-0.023
C(8)	0.010	N(1)	-0.062
C(9)	-0.009		
C(10)	-0.004		
C(11)	0.015		
C(12)	-0.014		

12. Discussion

Figure 8 shows the structure of the molecule and bond lengths and angles; Table 11 gives interatomic distances and angles with associated e.s.d.'s, which were calculated from the results of the ninth refinement cycle by the Busing, Martin & Levy (1964) programme ORFFE. The quoted errors include allowance for errors in cell dimensions. The C-C bond lengths in the tricyclic group are all between 1.38 and 1.43 Å; the average value for each benzene ring is 1.40 Å which is in good agreement with the values reported for benzene (1.397 Å, Stoicheff, 1954; 1.392 Å, Cox, Cruickshank & Smith, 1958; 1.394 Å, Sutton, 1965).

The C-Cℓ bond length is 1.74 ± 0.01 Å; this is an average C (aromatic)-Cℓ bond distance, although the value given by Sutton in the *Tables of Interatomic Distances and Configuration in Molecules and Ions* (1965) is 1.70 ± 0.01 Å. Palenik, Donohue and Trueblood (1968) tabulated twenty-six C-Cℓ bond distances reported between the years 1959 and 1968 in various aromatic molecules. Each distance involves a chlorine atom bonded to only one other atom. Of the bond lengths tabulated, four are equal to or greater than 1.76 Å, six have values between 1.71 and 1.72 Å, and sixteen have values between 1.73 and 1.75 Å. The average value of the twenty-six bonds reported is 1.737 ± 0.016 Å, which is in excellent agreement with the result reported above.

The S-C bonds are 1.75 ± 0.01 Å, which implies double-bond character of about 13%. This is close to other values in similar aromatic substances, e.g. Thianthrene, 1.76 Å (Lynton & Cox, 1956), Phenoxthionine, 1.75 Å (Hosoya, 1966), Phenothiazine, 1.77 Å (Bell, Blount, Briscoe & Freeman, 1968). The C-S-C angle (97.3°) is much less than the C-N-C angle (118.4°). The implication of the difference in angles and the contraction of the S-C bond will be discussed in a succeeding paragraph.

The best planes for the two benzene rings were obtained by the method of Schomaker, Waser, Marsh & Bergman (1959), using the program LSPLANE. The equations for the planes, together with the displacements of the atoms from these planes are given in Table 12. The deviations from planarity of the C atoms are not significant; the Cℓ atom is very close to the plane of the attached benzene ring. The fact that S is not in plane I, and N not in plane II may indicate that the steric effects of the "tail" have slightly distorted the ring portion of the molecule so that it has no plane of symmetry through the S-N axis, as it could be expected to have in Phenothiazine.†

The dihedral angle between the two planes of the benzene rings is 139.4°, and is very close to that found by Hosoya for Phenoxthionine (1966). The folding of the molecule, the difference in the angles of the type C-N-C and C-S-C and the shortening of the C-S bond are characteristic of a number of heterocyclic compounds derived by replacing anthracene meso-CH groups by atoms A and B. It has been found that molecules are planar if both A and B are any of C, N or O, but folded if at least one of A and B is S, Se or Te. The X-S(Se,Te)-X angles which have been determined are in the range 93° - 100°. e.g. Thianthrene (Lynton & Cox, 1956), Phenothiazine (Cullinane & Rees, 1940; Wood, McCale & Williams, 1940; Bell, Blount, Briscoe & Freeman, 1968), Phenoxthionine (Cullinane & Rees, 1940; Hosoya, 1966). According to Lynton & Cox (1956), and Hosoya (1963), this is explained by assuming the participation of *d* orbitals in the bonding of S and S-like atoms. The valence orbitals in atoms of the second period such as C, N and O are limited to 2*s* and 2*p* or hybrids of the two, but sulphur can be converted to the excited configuration $(3s)^2(3p)^3(3d)$. The folding of the molecule enables the sulphur atom to retain its "natural" valency angle. The quantum mechanical treatment of Craig &

†This however is not the case. The author has just received a communication from Drs. Bell, Blount, Briscoe & Freeman who have recently accurately determined the structure of Phenothiazine (1968). It is also not symmetrical.

Magnusson (1956) lends support to the above theory.

A few intermolecular distances are given at the end of Table 11. The only noteworthy distance is Cℓ - Cℓ($\overline{1}$), which is 3.34 Å implying that the effective van der Waals radius of chlorine is less than the ionic radius, 1.81 Å.

The molecular packing in the unit cell is given in Figures 9 and 10. Four of the molecules are "left-handed", while the other four are "right-handed" enantiomorphs. Fig. 10, which represents half the contents of the unit cell from 0 to $a/2$, shows clearly that the molecules are arranged in layers of width $b/2$, with the axis of the fold alternately left and right in the z-direction.

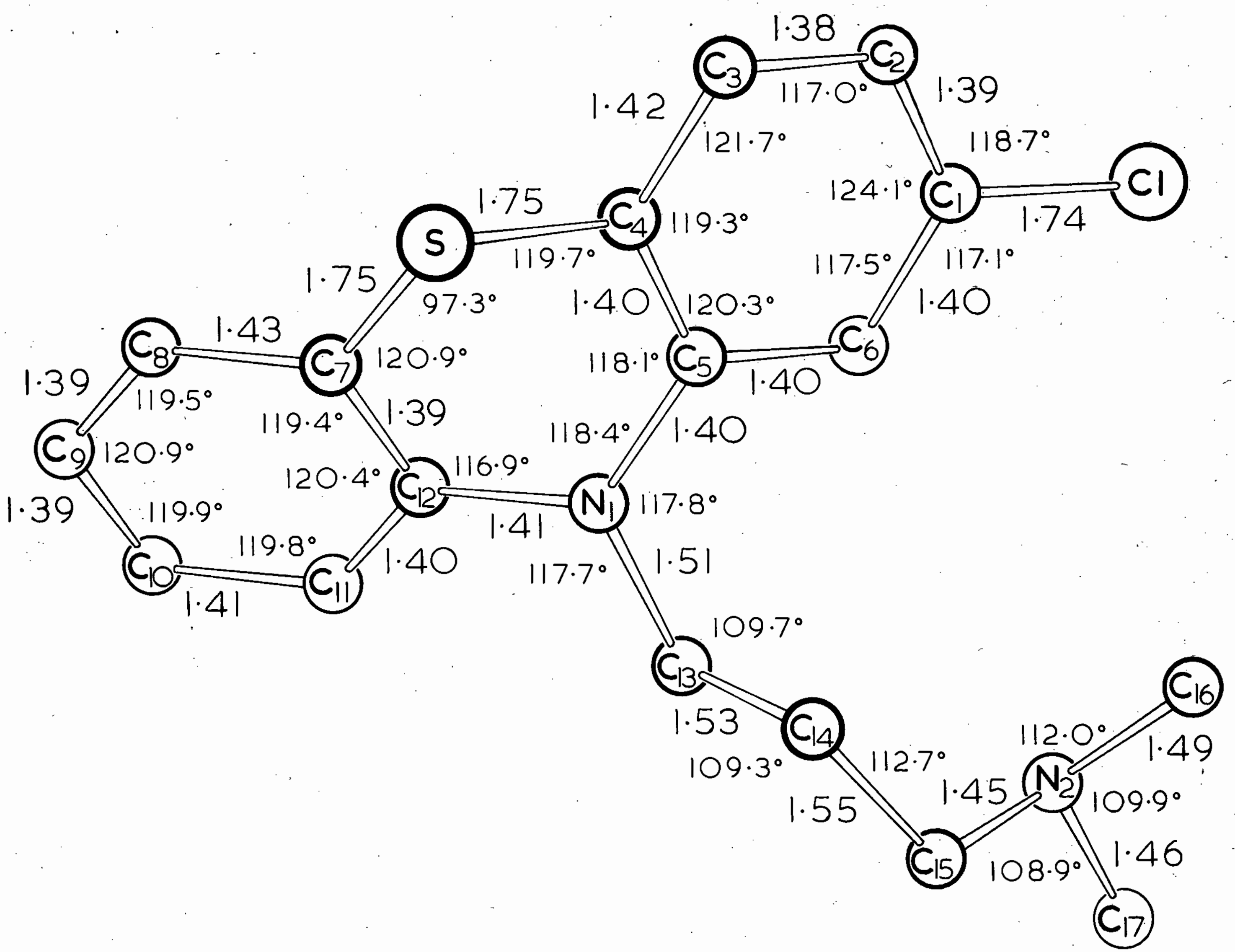


FIGURE 8

BOND DISTANCES AND ANGLES

FIGURE 9

THE STRUCTURE VIEWED DOWN THE c - AXIS

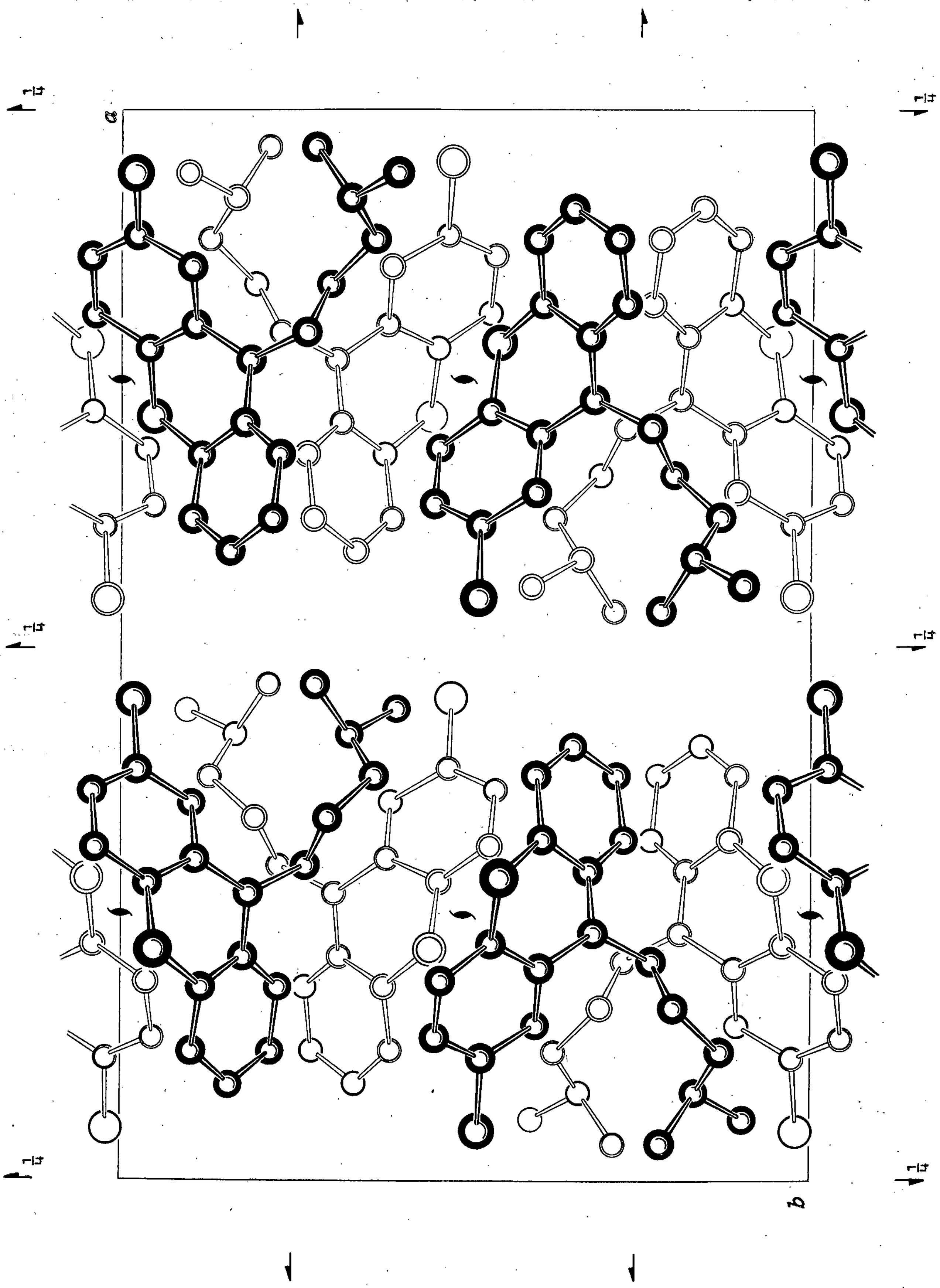


Figure 10(A)

Perspective drawing of half the contents of the unit cell (from 0 to *b*/2) viewed down the *b* axis. All molecules from 0 to *a*/2 are folded downwards about the S-N axis (dashed lines); all molecules from *a*/2 to *a* are folded upwards.

Figure 10(B)

Similar to Fig. 3(A), except that the $-(CH_2)_3N(CH_3)_2$ "tail" has been omitted in order to show the fold of the molecule more clearly.

FIGURE 10 (A)

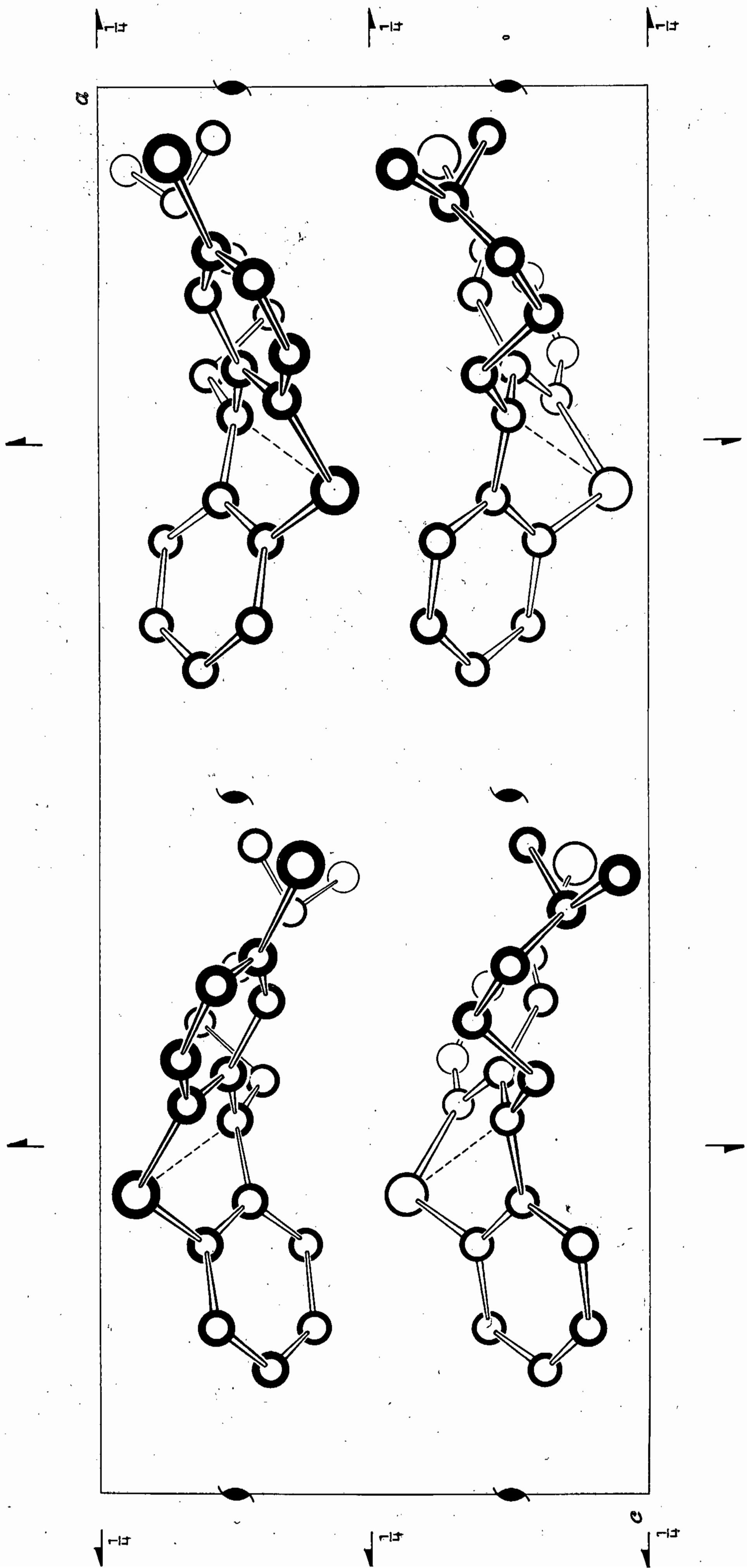
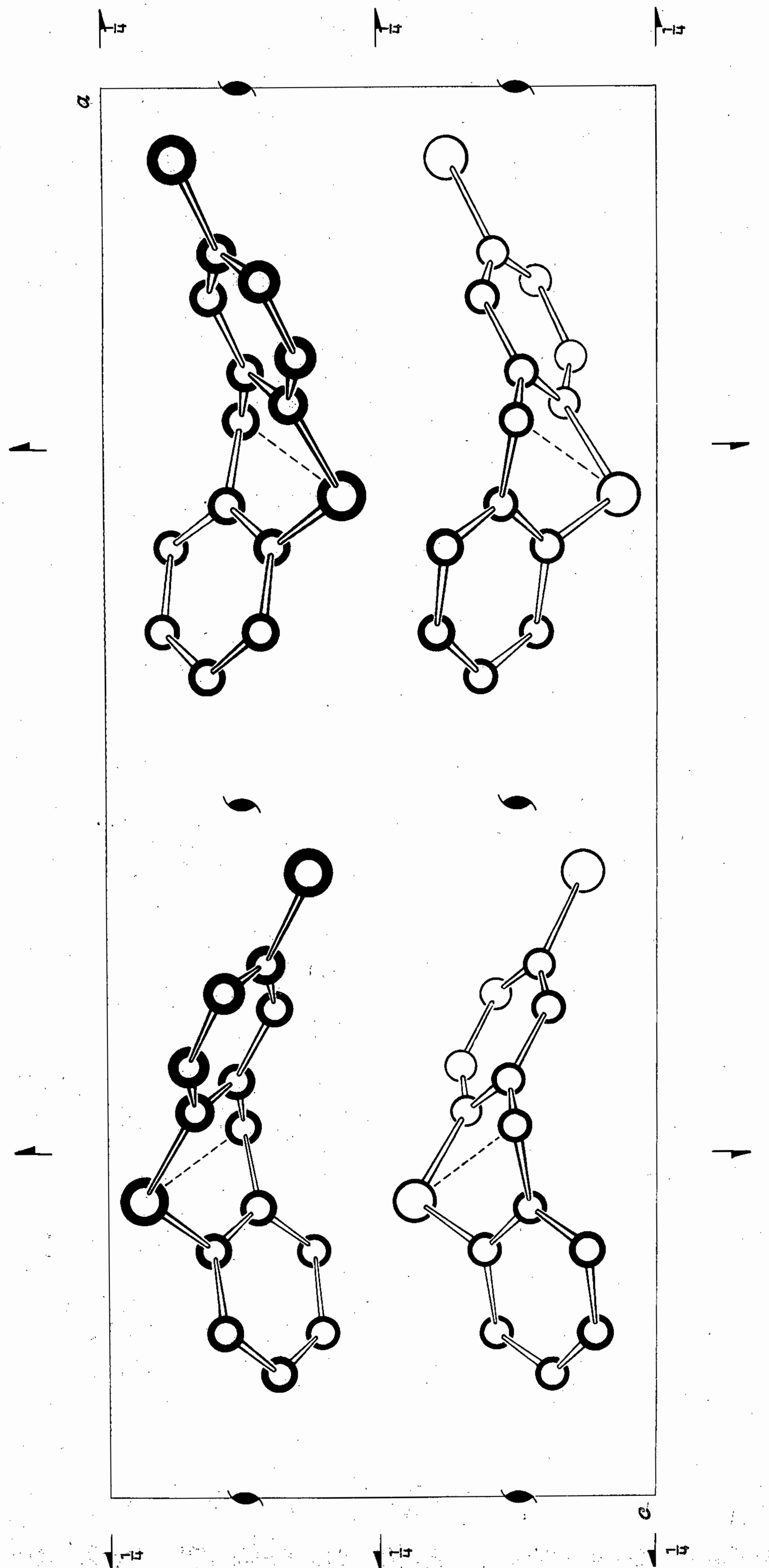


FIGURE 10 (B)



SECTION C

THE CRYSTAL AND MOLECULAR STRUCTURE OF THIETHYLPERAZINE

1. Crystals

Sandoz, Basle, Switzerland, supplied the powdered substance; colourless transparent prismatic crystals were prepared by evaporation from a warmed solution of thiethylperazine in petrol ether. As crystals exposed to air turned yellow within a few hours, single crystals were sealed in nitrogen-filled capillary tubes.

2. Cell dimensions and space group

X-ray oscillation and equi-inclination Weissenberg photographs, with the use of Ni-filtered Cu$K\alpha$ radiation, taken about the x and z axes gave an orthorhombic system with $a = 12.056 \pm 0.02$, $b = 19.952 \pm 0.03$, $c = 9.204 \pm 0.01$ Å, in close agreement with the diffractometer values obtained subsequently: $a = 12.057 \pm 0.01$, $b = 19.953 \pm 0.01$, $c = 9.215 \pm 0.01$ Å. The latter values were considered more accurate and were used in all calculations. The conditions for non-extinction were found to be $h00$, $h = 2n$; $0k0$, $k = 2n$; $00l$, $l = 2n$, which uniquely determined the space group as $P2_12_12_1$.

3. Density

The measured density = 1.187 g.cc^{-1}.

The number of molecules per unit cell, calculated by the method described in section B4,

$$N = \frac{1.187 \times (2216.88 \times 10^{-24}) \times (6.023 \times 10^{23})}{399.6}$$

$$= 3.97,$$

from which result it was concluded that there were 4 molecules in the unit cell.

The calculated density for 4 molecules = 1.198 $g.cc^{-1}$.

4. Spherical crystals

By comparison with the chlorpromazines, the crystals were not as fragile and difficult to handle, and therefore it was practicable to grind cubic-cut crystals into near-perfect spheres; single crystals were driven by a carefully controlled jet of air round the perimeter of a plastic "pill-box" which had been lined with fine emery paper. The directions of the crystallographic axes were then located as the directions of extinction under a polarising microscope; the spheres were mounted on glass rods in alignment with one of these axes.

To prevent discolouration on exposure to air, the spherical crystals were coated immediately with a thin layer of low-absorbent polyvinylacetate; in addition, it was considered advisable to expedite the entire procedure.

Photographs were taken of all the processed crystals and the best of a dozen was selected for intensity measurements.

5. Intensity measurements

Dr. G. Gafner kindly offered to undertake the data collection. Three carefully packed spherical crystals were taken to the Council of Scientific and Industrial Research in Pretoria; as the selected crystal had not been damaged in transit, it was mounted on the Hilger & Watts automatic diffractometer and intensity and background measurements were carried out by Dr. Gafner.

Using Zr-filtered Mo$K\alpha$ radiation, the integrated intensities were collected over 120 seconds involving 60 steps of 0.02° in ω. After each set of five readings the intensity of the strong reference reflection (020) was measured, but as the variation in the values of the reference intensity was small, no scaling was applied. The measured data extended to h,k,l (max)= 14,23,10 respectively; subsequently it was found that over 98% of the reflections with h,k,l > 12,17,8 respectively, were less than I_{min}, therefore the 2200 reflections originally recorded were reduced to about 1400 in the refinement, i.e. about 56% of the Cu$K\alpha$ sphere was utilised.

The raw data was sent to the author in Cape Town, who carried out the subsequent analysis.

6. Background correction

Individual background intensities left and right were measured, but as they were subject to random fluctuations a more accurate estimate of the background correction was obtained and applied as follows:- for several different values of ω the background radiation was measured for values of θ from 0.05° up to about 20° in steps of 0.05°, each measurement occupying 4 seconds. Each set of values of I plotted against θ gave erratic curves as shown in Figure 11. The full curve suitably scaled gave the best average background intensity for any particular θ. Figure 11 shows that the background could be taken as constant for values of θ greater than about 17°.

The standard deviation was calculated and I_{min} was estimated to be approximately $3 \times \sqrt{\frac{\Sigma\sigma^2}{n(n-1)}}$. Peak intensities which were less than I_{min} were recorded as $\frac{1}{2} I_{min}$ and the corresponding F's are listed in the structure factor table as F_{unobs}.

FIGURE 11

GRAPH FROM WHICH BACKGROUND AND STREAK CORRECTIONS WERE DETERMINED

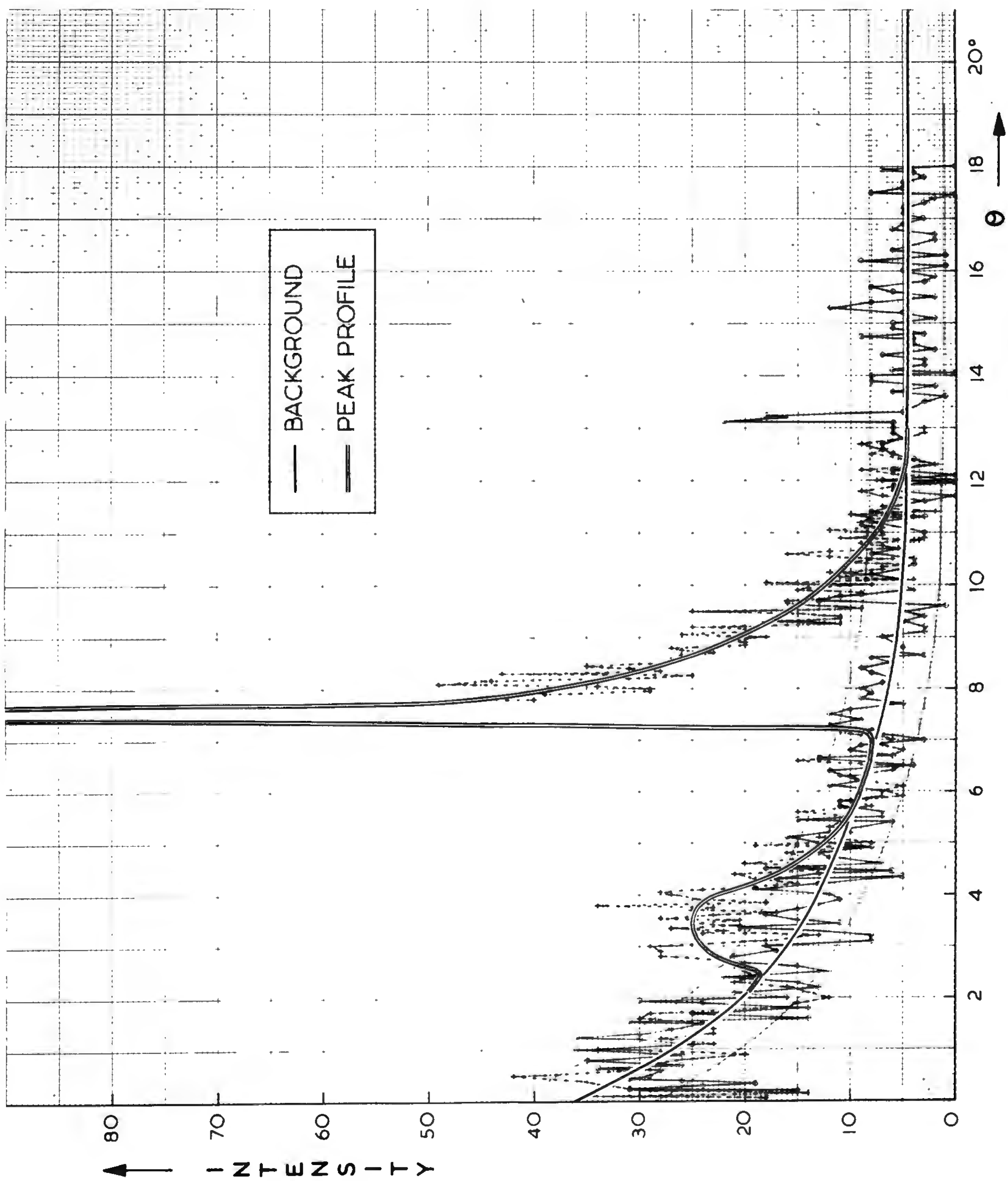
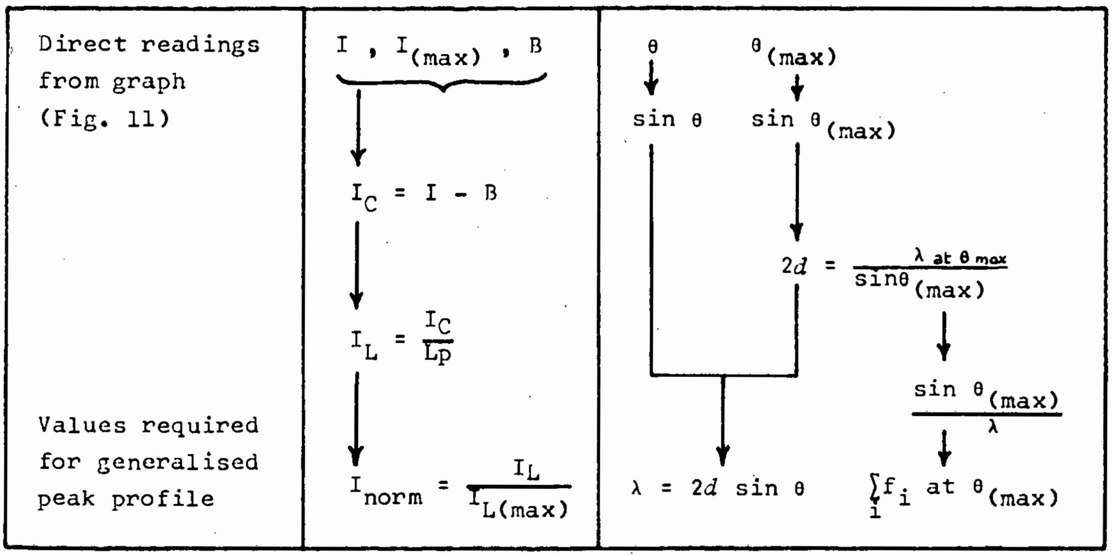


TABLE 13

PROCEDURAL DIAGRAM: CALCULATION OF GENERALISED PEAK PROFILE

B	=	intensity of background
I_C	=	intensity corrected for background
I_L	=	intensity corrected for Lp factor
I_{norm}	=	normalised value of intensity (= 1 at $I_{L(max)}$)
$\theta_{(max)}$	=	value of θ at which $I = I_{(max)}$
λ	=	wavelength of *MoKα* radiation
Lp	=	Lorentz polarisation factor (Int. Tables II, P.268).
d	=	interplanar spacing of (5,2,0) planes



<u>Values obtained for the peak (5,2,0)</u>

$I_{(max)}$ = 1132.0

$I_{L(max)}$ = 303.398

$\theta_{(max)}$ = 7.55°

$2d = \frac{\lambda}{\sin\theta_{(max)}} = \frac{.70926}{.13139} = 5.398$ Å

$\frac{\sin\theta_{(max)}}{\lambda}$ = .18524 Å^{-1}

$\sum_{i=1}^{108} f_i$ = 495.00 at $\theta_{(max)}$

7. Lorentz and polarisation factors and streak correction

Corrections for the Lorentz and polarisation factors were applied as discussed in section B7 and a correction for peak spread was applied to the Lp corrected data. On Figure 11 can be seen the graph of the peak (5,2,0) which was scanned in steps of 0.05° in θ by the same method as the background scan. From the graph normalised values of I as a function of λ were calculated so that the peak profile obtained was common to any selected peak. The manner in which this was done can be readily seen by reference to the procedural diagram, Table 13.

From the scattering factor values of Hanson, Herman, Lea & Skillman (1964), tables were drawn up for the unit cell contents of thiethylperazine, i.e. $\sum_{i=1}^{108} f_i$ was calculated for each value of $\frac{\sin\theta}{\lambda}$ from 0 to 1.55, in steps of 0.05 Å^{-1}. Using the programme STREACOR the overlap of peaks occurring as a result of peak spread was corrected by searching the intensity data so that all peaks affected by any particular peak were reduced by a factor which is dependent on the relative positions of the peaks concerned.

REFER ADDENDA (3-10-1969), P.168.

8. Absorption

The diameter of the selected crystal was 0.04 cm. The linear absorption coefficient, μ, was calculated by the method described in section B5.

Table 14

Calculation of linear absorption coefficient of thiethylperazine

Atom	Atomic weight	Total weight	P Fraction of total weight	$\frac{\mu}{\rho}$ for Mo*K*α radiation	$P\left(\frac{\mu}{\rho}\right)$
S	32.066	64.132	0.1731	9.55	1.654
N	14.008	42.024	0.1135	.916	.104
C	12.010	264.220	0.7134	.625	.446

$$\mu = D \times \sum P\left(\frac{\mu}{\rho}\right)$$

$$= 1.187 \times 2.204 \quad \text{(from Table 14)}$$

$$= 2.62\ \text{cm}^{-1}$$

$$\text{and } \mu R = 2.62 \times 0.02 = 0.05$$

The corresponding absorption correction factor A^* for Mo*K*α radiation is 1.16 throughout the range of θ, hence absorption corrections need not be applied.

9. Preliminary temperature factor (B) and scale factor (K).

Preliminary values for K and B were obtained by Wilson's method applied to the corrected intensity data, as described in section B8. The top left graph (Figure 12) was based on values calculated from the full data set; also illustrated are the graphs of the $0kl$, $1kl$ and $2kl$ sets, each of which comprised more than 200 reflections. As the $3kl$, $4kl$, etc. each consisted of less than 200 reflections it was considered that the number was insufficient to justify the averaging over a large number of terms implied by the equation

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

Therefore from the four most reliable graphs, shown in Figure 12, values for B and K, listed in Table 15, were calculated.

Table 15

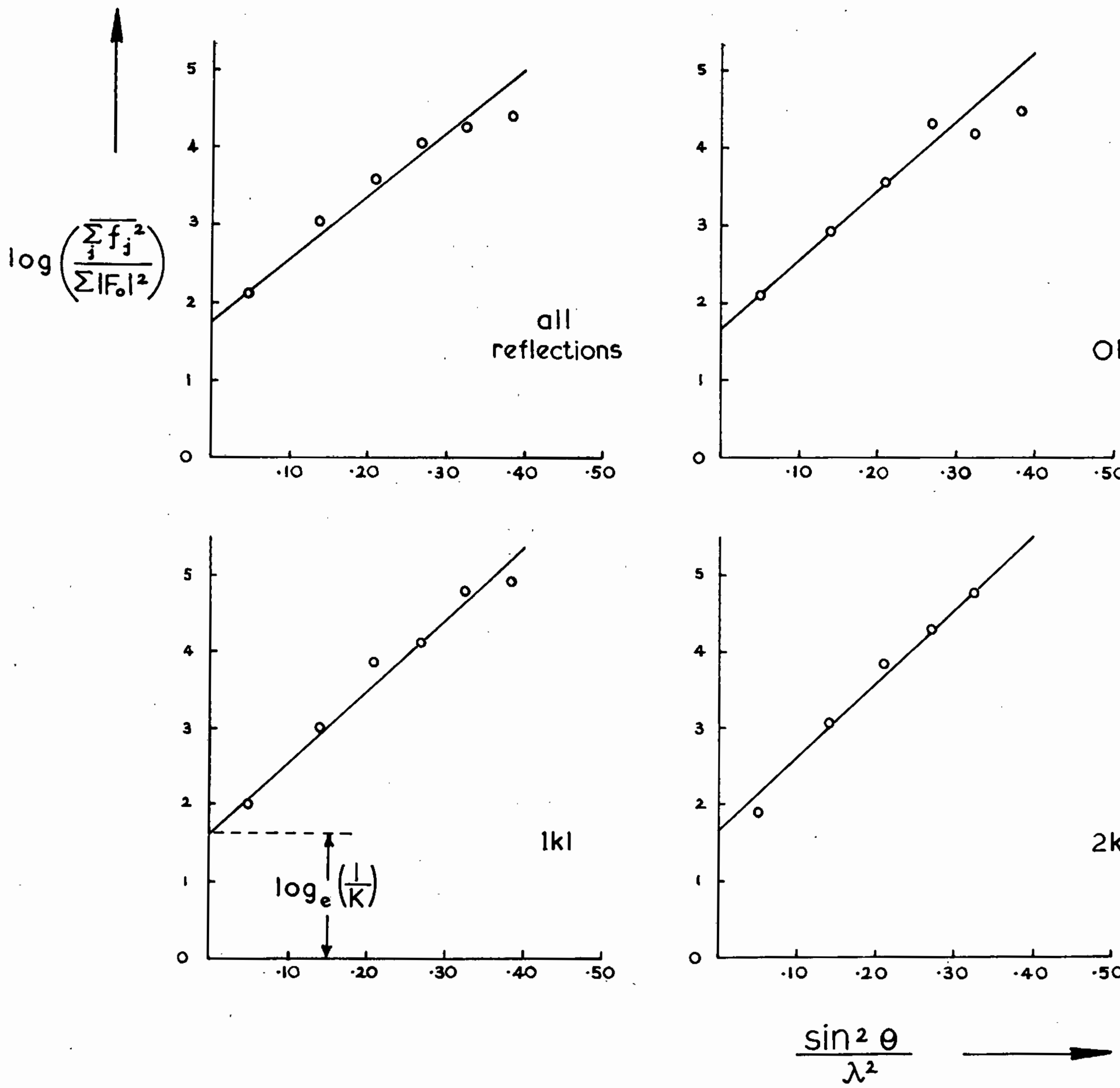
Temperature and scale factors

		$\frac{1}{K}$	K	B
Wilson's method	$0kl$	5.21	.192	4.44
	$1kl$	5.21	.192	4.67
	$2kl$	5.21	.192	4.75
	$0kl$, $1kl$, $2kl$	5.21	.192	4.62
	All reflections	5.75	.174	4.17
	Average	5.48	.183	4.40
Least-squares refinement		5.04	.198	4.94

The B values of the 27 atoms gave an average of 4.94 in the final isotropic least-squares refinement cycle (see Table 19), or 4.40 if the most thermally agitated atoms C(18), C(21) and C(22) were omitted; the refined scale factor was 0.198. It will be noted therefore that there was excellent agreement between the least-squares and Wilson's method which is apparently very reliable for this type of structure.

FIGURE 12

THIETHYLPERAZINE : WILSON PLOT



10. The unsharpened and sharpened Patterson functions.

The three-dimensional unsharpened Patterson function P(u) was calculated as described in section B9. The symmetry of the Patterson of space group $P2_12_12_1$ is *Pmmm* so that, as previously, it was necessary to calculate 1/8th only of the unit cell. Table 16 shows that rotation peaks could be expected on the $x = \frac{1}{2}$ and $y = \frac{1}{2}$ sheets of the Patterson, therefore these particular Patterson sections were computed as well as all sections perpendicular to the *z*-axis.

The three-dimensional sharpened Patterson function P(s) which had proved so useful in the study of chlorpromazine was computed immediately after P(u), as described in section B10(d). Figure 13 depicts the $z = 0$ sections of the unsharpened and sharpened three-dimensional Patterson functions with the positive contours drawn in steps of 20 units; the superior resolution of peaks on P(s) can be clearly seen. In particular, at the origin the peaks of P(s) are most satisfactorily disclosed. However, it was considered that both functions should be calculated and used in collaboration, as the peaks of P(s) should be "weighted" by P(u); e.g. peaks occurring in regions of P(s) corresponding to valley regions in P(u) were not considered to be meaningful.

REFER ADDENDA (3-10-1969), P.169.

11. Interpretation of the Patterson

(a) Calculated heights of Patterson peaks

The heights of peaks to be expected were calculated as described in section B10(a). For thiethylperazine, the size of the Patterson origin was 1439 units; the size of the sharpened Patterson origin was 1591 units.

$$\sum_j z_j = 4 \quad \{22 \times 6^2 + 3 \times 7^2 + 2 \times 16^2\}$$
$$= 5804$$

TABLE 16

THEORETICAL POSITIONS OF ROTATION PEAKS IN THE PATTERSON OF SPACE GROUP $P2_12_12_1$

Coordinates of equivalent positions

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

	Vectors	Coordinates of Patterson peaks				Weight	Number of peaks
Rotation peaks	1-2	$\frac{1}{2}+2x$	$2y$	$\frac{1}{2}$		1	4
	2-1	$\frac{1}{2}-2x$	$-2y$	$\frac{1}{2}$			
	3-4	$\frac{1}{2}+2x$	$-2y$	$\frac{1}{2}$			
	4-3	$\frac{1}{2}-2x$	$2y$	$\frac{1}{2}$	*		
	1-3	$\frac{1}{2}$	$\frac{1}{2}+2y$	$2z$		1	4
	3-1	$\frac{1}{2}$	$\frac{1}{2}-2y$	$-2z$			
	2-4	$\frac{1}{2}$	$\frac{1}{2}-2y$	$2z$	*		
	4-2	$\frac{1}{2}$	$\frac{1}{2}+2y$	$-2z$			
	1-4	$2x$	$\frac{1}{2}$	$\frac{1}{2}+2z$		1	4
	4-1	$-2x$	$\frac{1}{2}$	$\frac{1}{2}-2z$			
	2-3	$-2x$	$\frac{1}{2}$	$\frac{1}{2}+2z$			
	3-2	$2x$	$\frac{1}{2}$	$\frac{1}{2}-2z$	*		

Z = 0

Unsharpened Patterson

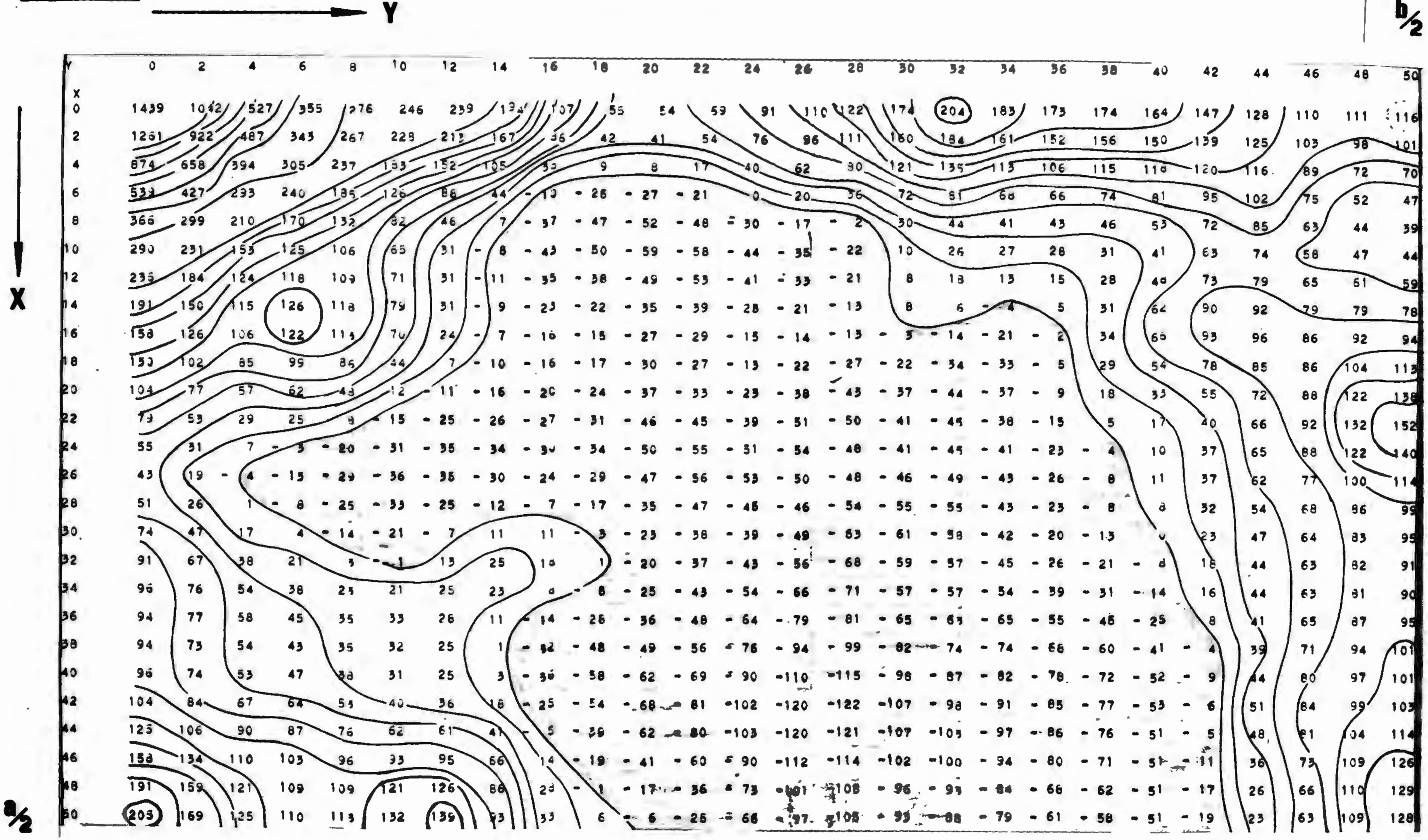
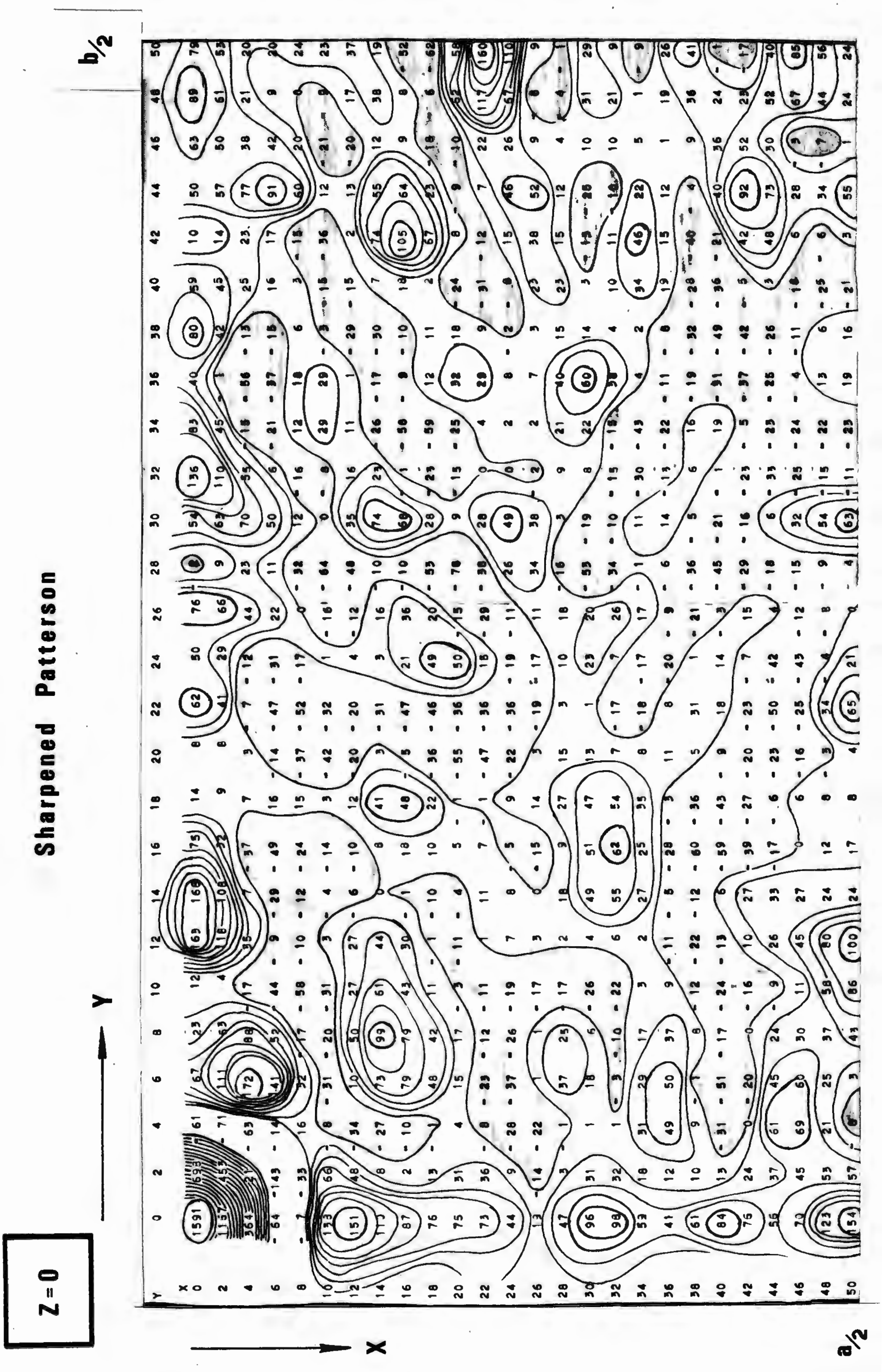


FIGURE 13

z = 0 SECTIONS OF THE THREE-DIMENSIONAL UNSHARPENED AND SHARPENED PATTERSON FUNCTIONS

FIGURE 13 (cont.)



For a S-S peak, $z_i z_i = 16^2 = 256$
Therefore the expected height of a S-S peak of single weight on P(u),

$$H_{ii} = \frac{256}{5804} \times 1439 \approx 65 \text{ units},$$

and on P(s),

$$H_{ii} = \frac{256}{5804} \times 1591 \approx 70 \text{ units}.$$

(b) Calculated positions of Harker peaks

Table 16 shows that one atom together with its three symmetry-equivalent atoms produce 12 single weight rotation peaks in the Patterson of space group $P2_12_12_1$, of which the three marked with asterisks occur in the relevant 1/8th of the unit cell.

(c) Solution of the Patterson by Fourier methods

All possible rotation peaks in the Patterson of thiethylperazine were listed and combinations of values of $2x$, $2y$, $2z$ were sought. Thirty possible Harker peaks were provided by P(u) and 63 by P(s). Figure 14 illustrates the x = 50, y = 50 and z = 50 sections of P(s) which must necessarily feature all the Harker peaks for all 27 atoms (see Table 16). A similarity in two of the coordinates of the light atoms would produce an overlap of peaks which would make the sulphur peaks difficult to distinguish and, of course, no inversion peaks existed to provide a check on chosen sets of coordinates.

Combinations of three rotation peaks produced 34 possible sets of coordinates. One combination appeared to be sufficiently promising as regarded peak positions and peak heights for interpretation as sulphur to be possible. This set is marked S(1) on Figure 14; the coordinates were given by the following three peaks:-

Patterson section	$2x$	$2y$	$2z$	Height
x = 50	-	38	22	126
y = 50	34	-	20	125
z = 50	34-36	40-42	-	92

Patterson coordinates ($2x$, $2y$, $2z$):(36,40,20) were then deduced, and the atom was assumed to be at (± 18,± 20, ±10).

The intention was to apply the methods which had proved rewarding for chlorpromazine, i.e. to attempt to locate both S atoms, which are designated for present purposes as S_A and S_B†. With this object in view, two procedures were simultaneously followed:-

(1) structure factors were calculated from single atoms placed at possible coordinate sets derived as described above, in the hope of reducing the large number of possible sets;

(2) the sets were combined in pairs by the method described in section B10(f), and S_A - S_B peaks were sought in the Patterson.

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†For the purpose of clarity, S_A and S_B are used in the text to designate the two sulphur atoms of the structure, whose positions are undetermined; S(1) and S(2) are used to designate the sulphur atoms as placed in the specific positions corresponding to the Patterson coordinates marked on Figure 14.

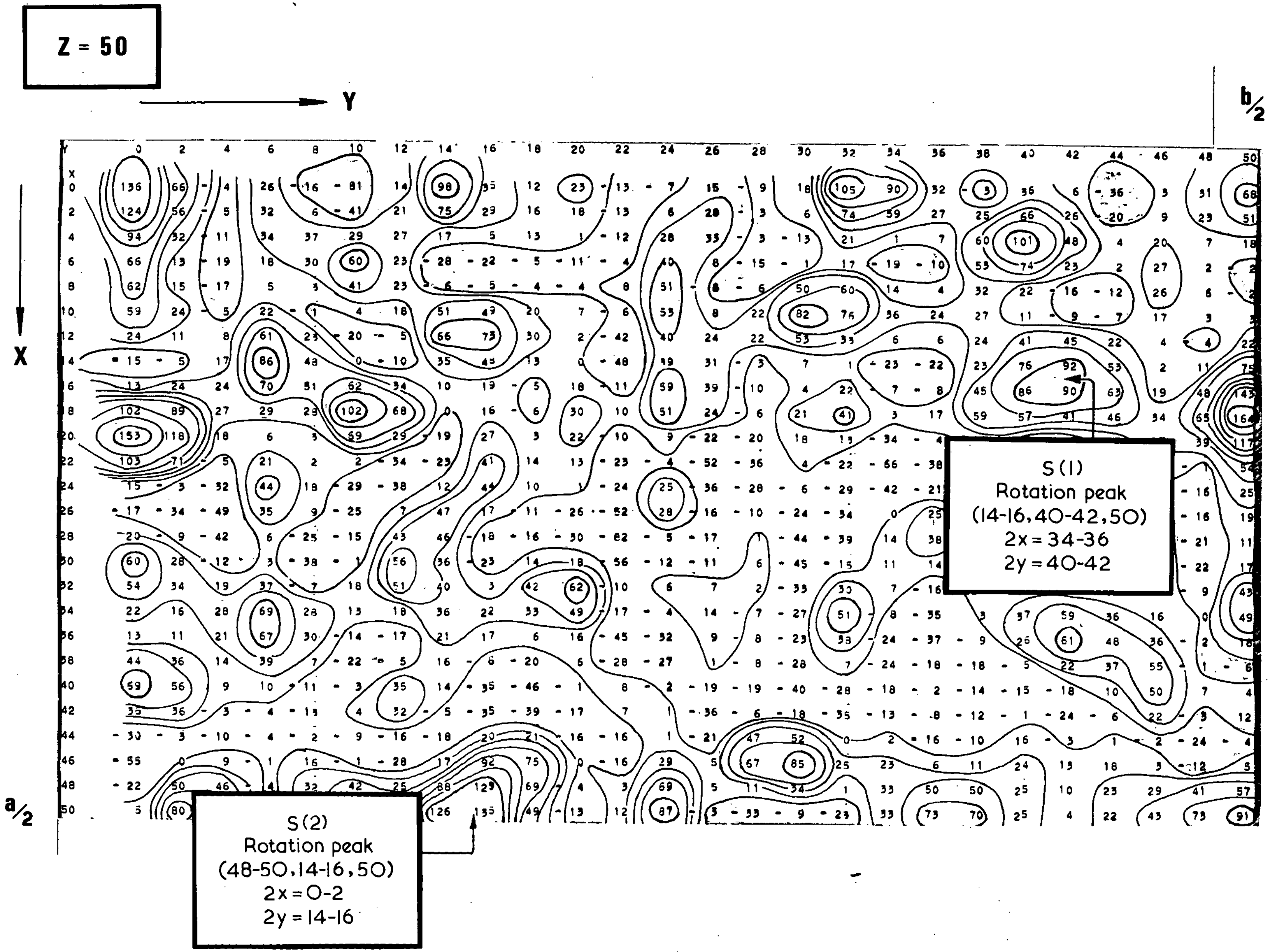


FIGURE 14

SECTIONS OF THE THREE-DIMENSIONAL SHARPENED PATTERSON FUNCTION SHOWING HARKER PEAKS

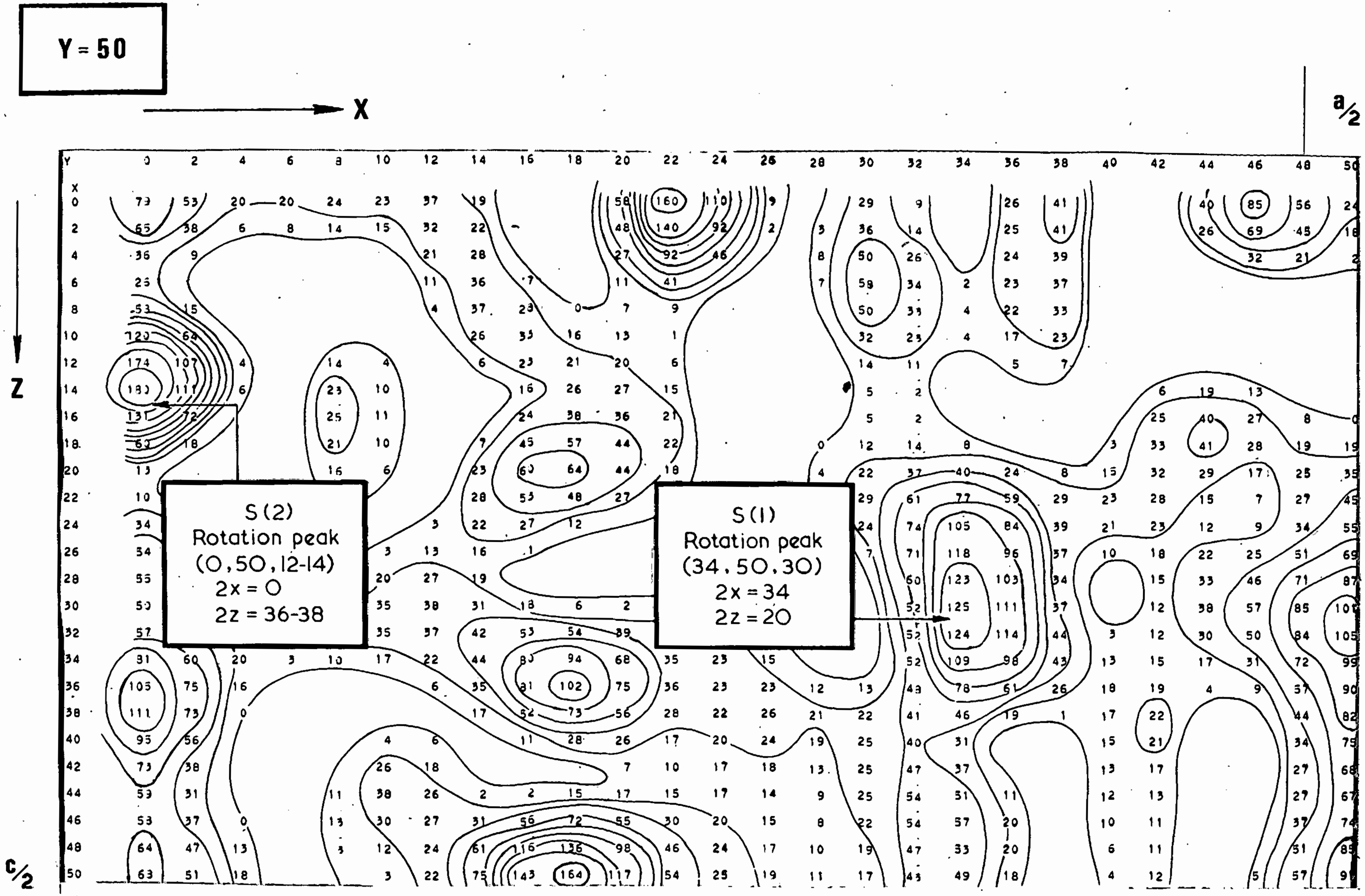


FIGURE 14 (cont.)

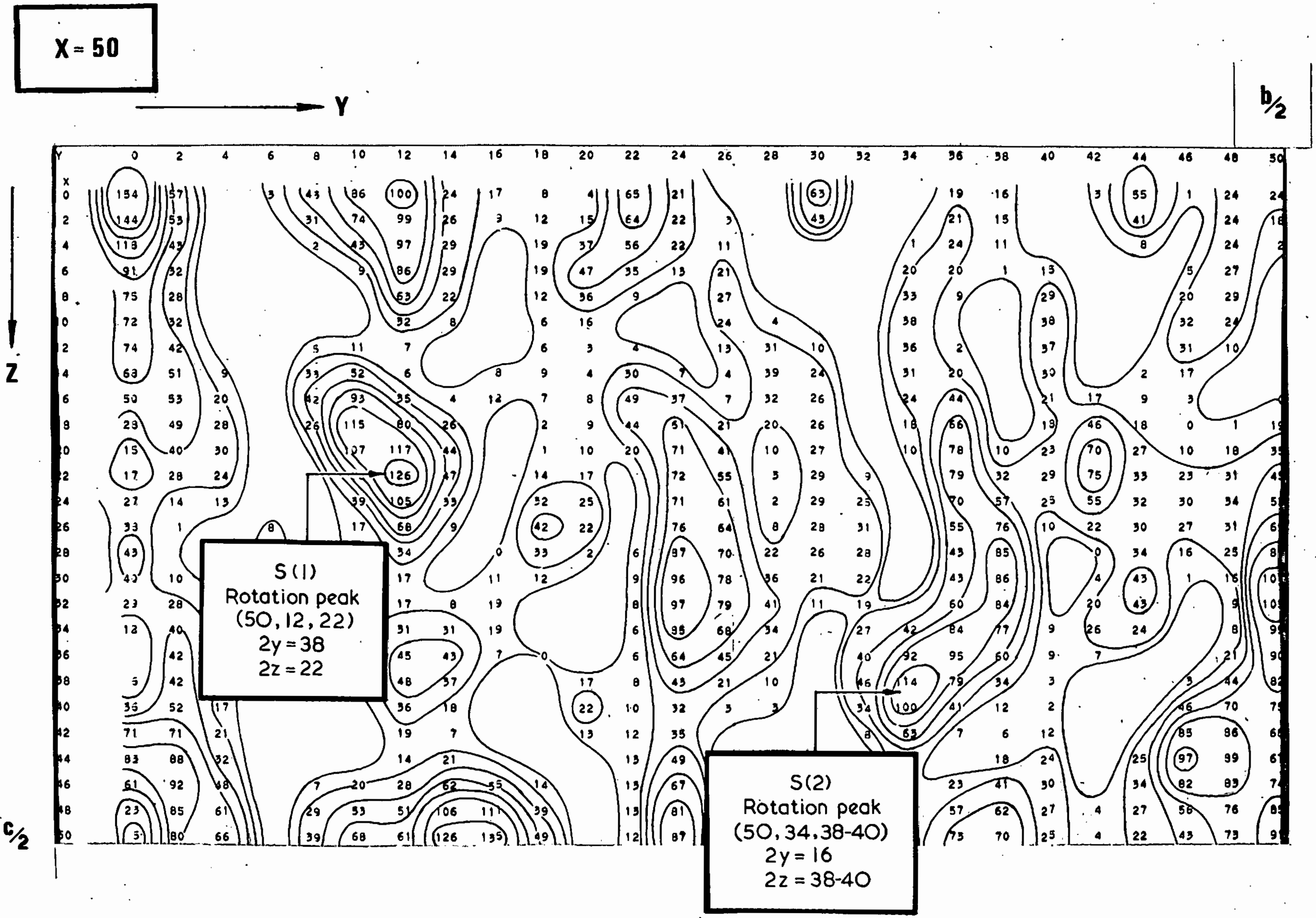


FIGURE 14 (cont.)

Although procedure (1) gave an R-value of 49.7% for S(1), it gave values of 45 and 49% for coordinate sets which proved ultimately to be C atoms, while the value of 65% was obtained for the set which proved to be the second S atom; it follows that method (1) alone proved not to be very reliable, but it did give a few leads.

Procedure (2) differed in detail from that followed in the case of chlorpromazine, because $P2_12_12_1$ is non-centrosymmetric and has only four equivalent positions.

If the signs of S_A are chosen as positive, the first equivalent position of S_A, i.e. $S_A(1)$, taken in combination with the eight possible permutations of signs of S_B would yield eight locations in the Patterson at one of which a peak should be found, thus giving the correct signs of the coordinates of S_B. $S_A(2) - S_B$ would give one correct peak from the same set of signs of the coordinates of S_B, and similarly $S_A(3) - S_B$, $S_A(4) - S_B$ would give one peak each. There are thus four $S_A - S_B$ peaks to be found out of a total of 32 locations.

The application of procedure (2) was extremely tedious, and examination of the symmetry relationships between the coordinates of possible $S_A - S_B$ Patterson peaks eventually suggested the improvisation of a device which resulted in considerable time saving and increased accuracy. The device is described in Appendix B.

Another promising set of rotation peaks appeared to be as follows:-

Patterson section	$2x$	$2y$	$2z$	Height
x = 50	-	16	38-40	114
y = 50	0	-	36-38	180
z = 50	0-2	14-16	-	135

This set is marked S(2) on Figure 14; Patterson coordinates ($2x$, $2y$, $2z$) : (2,16,36) were deduced, and the atom was assumed to be at (± 1,± 8,± 18).

S(1) and S(2) were tested with each other and each was tested with numerous other sets. A complete blank was drawn; in no case were four correctly situated Patterson peaks found.

It was then decided to work "backwards", i.e. to start with suitable Patterson peaks regarded as possible $S_A - S_B$ peaks, and to see whether S_A and S_B rotation peaks could be deduced from these.

The general Patterson peaks were listed and the rather formidable number of 105 was obtained. However, only 47 had heights greater than 70 units, and it was decided to concentrate on the larger peaks first. At this stage, the "coordinate difference" cards (see Appendix B) provided an invaluable jumping-off point. For instance, if four Patterson $S_A - S_B$ peaks could be found with x-coordinates having the values corresponding to the numbers 1-4 on any particular card, then the x-coordinates of atoms S_A and S_B would be directly ascertainable from the card, and similarly for the y- and z-coordinates. In this manner, four large Patterson peaks having nearly "matching" coordinates were soon selected:-

$2x$	$2y$	$2z$	Height
16	28	24	111
18	22	10	78
32	12	26	85
34	38	42	100

Temporarily disregarding the signs of the coordinates, the x-coordinates of the atoms which could produce the above set of $S_A - S_B$ peaks (from the "coordinate difference" cards) were x = 18, and x = 0-2; similarly the y-coordinates were y = 30 and y = 8, and the z-coordinates were z = 10 and z = 16-18. The corresponding Patterson coordinates were (36,40,20) and (0-4,16,36). Therefore, the atoms which have been detailed on pages 75 and 79 , and designated S(1) and S(2) on Figure 14 were definitely indicated, but with the one very significant difference - that S(1) was not situated at (x_1, y_1, z_1) but at (x_1 , $\frac{1}{2}-y_1$, z_1).

It is clear to the author in retrospect that the above result might have been attained by an easier route,i.e. by extending the comparison of pairs of atoms to include the sets ($x \pm \frac{1}{2}$, $y \pm \frac{1}{2}$, $z \pm \frac{1}{2}$). However, working "backwards" certainly proved more stimulating.

Atom S(1) was now placed at (18,30,10) and the signs of the coordinates of S(2) were determined by the use of the cards (Appendix B) to be (-++), therefore S(2) was assumed to be at (-1,8,18). The distance between S(1) and S(2) was calculated and found to be approximately 6.3 A.

Other pairs of positions of S(1) and S(2) would also have given the correct results, e.g. S(1) at (18,20,10) and S(2)' at (49,8,-18), or the z-coordinate of S(2) could have been changed such that S(2)' was at (1,-8,32). These permissible changes represented only changes in the choice of an origin; but S(1) and S(2) as originally placed represented a different and unacceptable structure.

A three-dimensional Fourier of $\frac{1}{4}$ of the unit cell was computed with the two sulphur atoms placed at (18,30,10) and (-1,8,18). As the space group is non-centrosymmetric, it was not to be expected that the phases would be determined by the sulphur atoms to the extent that the revelation of all other atoms in the Fourier would follow. However, nine atoms did show up reasonably clearly, and the R dropped from 46.7% for two atoms to 40.5% for eleven atoms.

Six successive Fourier and difference Fourier syntheses led to the location of all 27 atoms. Following standard

FIGURE 15

ONE MOLECULE IN FOURIER 6 (R = 19.8%)

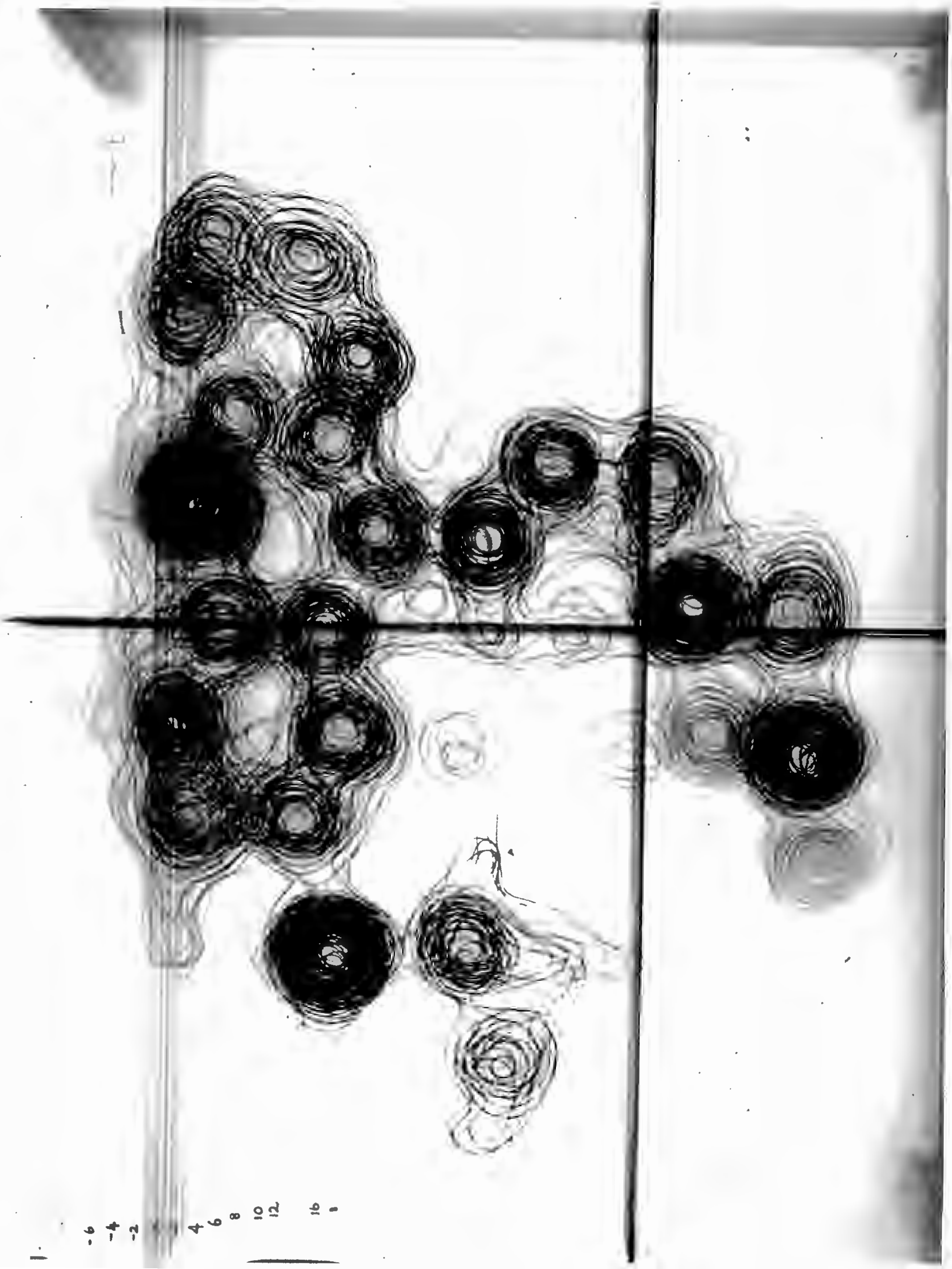


TABLE 17

PROGRESS OF THE REFINEMENT

A. Fourier refinement

Overall B = 4.1

Data : 892 $F_{obs.}$ only

Fourier number	Number of atoms	Height of S(1) peak	Height of S(2) peak	R
1	1	462	-	49.7
2	2	521	484	46.7
3	11	543	539	40.5
4	19	577	579	31.2
5	26	602	617	21.8
6	27	648	667	19.8
-	27	-	-	18.7

B. Least-squares refinement

Operation number	Number of cycles	Parameters varied	Number of parameters varied	Data	Type of cycle	Cycle number	R before (%)	R after (%)
1	1	1 scale factor 81 coords. 27 indiv. B's	109	2192 $F_{obs.}$ + $F_{unobs.}$ h,k,l (max) = 14,23,10	Isotropic	1	-	25.4
2	3	"	109	"		2 3 4	25.4 19.0 18.1	19.0 18.1 17.9
3	3	1 scale factor 81 coords. 162 β's	244	1418 $F_{obs.}$ + $F_{unobs.}$ h,k,l (max) = 12,17,8	Anisotropic	5 6 7	17.9 15.7 14.2	15.7 14.2 13.0
4	3	1 scale factor 81 coords. 27 indiv. B's	109	892 $F_{obs.}$ only	Isotropic	8 9 10	11.5 11.2 10.9	11.2 10.9 10.8
5	3	1 scale factor 81 coords. 162 β's	244	1418 $F_{obs.}$ + $F_{unobs.}$	Anisotropic	11 12 13	13.0 11.8 11.3	11.8 11.3 11.3
6	3	1 scale factor 81 coords. 27 indiv. B's	109	892 $F_{obs.}$ only	Isotropic	14 15 16	10.8 10.6 10.5	10.6 10.5 10.5

procedure, all Fouriers were carefully analysed; the values of ρ for individual atoms were plotted for each of the three directions and improved positions were determined for insertion into the next Fourier. The difference Fouriers gave evidence of considerable thermal motion among some of the atoms, notably C(22), C(21), C(18), C(10) and C(11), as well as of the anisotropic character of the sulphur atoms. Table 17 tabulates the progress of the refinement; Figure 15 is a photograph of one molecule in Fourier 6 (at which stage R was 19.8%) contoured in steps of 20 units and traced on to glass sheets.

12. Least-squares refinement

The structure was refined by four least-squares cycles with the use of the Busing, Martin & Levy (1962) programme ORFLS. The function minimised was

$$R_1 = \sum w(hkl)\{|F_o(hkl)|-|F_c(hkl)|\}^2$$

with equal weight given to each term. Individual isotropic temperature factors was assigned and $F_{unobs.}$ were included. The number of $F_{obs.}$ was only 892, which was unfortunately insufficient to carry out a meaningful anisotropic cycle in which there were 244 parameters to be varied. From this point therefore the refinement was continued along two separate lines:- Six cycles were carried out using 1418 F's and anisotropic temperature factors, resulting in a final R index for all reflections of 0.113; six cycles were carried out using 892 $F_{obs.}$ and isotropic temperature factors, resulting in a final R index of 0.105. The refinement was terminated when the average parameter shifts were approximately 10% of the e.s.d.'s.

Observed and calculated structure factors are listed in Table 18. The analytical *f* values used in all calculations are those given by Hanson, Herman, Lea & Skillman (1964). Table 19 gives the final atomic positional parameters and anisotropic thermal-motion parameters with their standard deviations which were obtained in the thirteenth cycle. The last column of Table 19 lists the isotropic temperature factors obtained at the end of the sixteenth cycle.

Patterson and Fourier syntheses were carried out on an I.C.T. 1301 computer. An I.B.M. 360/65 computer was used for the correction calculations and the least-squares refinements.

TABLE 18

OBSERVED AND CALCULATED STRUCTURE FACTORS

Within each group the columns, reading from left to right, contain the values of l , $K|F_o|$, F_c , A_c and B_c

* indicates F_{unobs}.

00ℓ

-8*	7	5	-5	0
-6	50	46	46	0
-4	68	69	-69	0
-2	95	95	-95	0

01ℓ

-8*	7	3	0	3
-7	14	14	0	-14
-6	10	11	0	-11
-5	24	21	0	-21
-4	23	23	0	-23
-3	12	8	0	8
-2	113	112	0	112
-1	27	15	0	-15

02ℓ

-9*	10	11	-11	0
-8	6	2	2	0
-7	23	24	24	0
-6	25	24	24	0
-5	24	26	-26	0
-4	42	41	-41	0
-3	37	34	-34	0
-2	165	178	-178	0
-1	19	22	22	0
0	108	115	115	0

03ℓ

-8*	7	5	0	5
-7	6	3	0	3
-6	11	6	0	6
-5	18	23	0	23
-4	27	29	0	-29
-3	16	16	0	16
-2	42	40	0	-40
-1	49	42	0	-42

04ℓ

-9	11	11	-11	0
-8	11	15	15	0
-7	16	16	16	0
-6	19	19	-19	0
-5	5	5	-5	0
-4	10	10	10	0
-3	28	27	27	0
-2	61	55	55	0
-1	62	60	60	0
0	8	4	4	0

05ℓ

-8*	7	6	0	-6
-7	6	7	0	7
-6*	13	12	0	12
-5*	5	8	0	8
-4*	5	3	0	3
-3	8	6	0	-6
-2	42	42	0	42
-1	9	8	0	8

06ℓ

-8	15	17	17	0
-7	10	8	8	0
-6	15	14	-14	0
-5*	25	25	-25	0
-4*	5	2	2	0
-3	28	31	-31	0
-2	22	25	25	0
-1	12	10	-10	0
0	53	53	-53	0

07ℓ

-8*	7	2	0	2
-7*	6	1	0	-1
-6	30	28	0	28
5	27	26	0	-26
4	55	52	0	-52
3	20	19	0	19
2	7	7	0	-7
1	9	8	0	8

08ℓ

-8*	7	3	3	0
-7*	7	7	-7	0
-6*	6	4	4	0
-5*	5	2	2	0
-4	28	27	27	0
-3	22	21	21	0
-2	18	16	-16	0
-1	6	5	5	0
0	44	41	-41	0

09ℓ

-8*	7	3	0	-3
-7	12	13	0	13
-6*	10	9	0	9
-5*	6	8	0	-8
-4	19	19	0	-19
-3	16	18	0	18
-2	34	30	0	30
-1	49	47	0	-47

0,10,ℓ

-7*	7	9	-9	0
-6*	6	6	-6	0
-5*	6	3	3	0
-4	6	8	-8	0
-3	11	10	10	0
-2	22	21	-21	0
-1	20	17	17	0
0	42	42	42	0

0,11,ℓ

-7*	10	7	0	7
-6	7	8	0	-8
-5	14	17	0	-17
-4	18	19	0	19
-3*	12	14	0	14
-2	5	4	0	-4
-1	23	24	0	24

0,12,ℓ

-7*	7	4	-4	0
-6*	25	25	25	0
-5	6	5	-5	0
-4	15	15	15	0
-3	15	15	-15	0
-2	21	20	-20	0
-1	20	20	20	0
0	8	5	5	0

0,13,ℓ

-7*	7	2	0	2
-6*	7	4	0	-4
-5	6	6	0	-6
-4*	10	11	0	11
-3	6	1	0	-1
-2*	44	46	0	-46
-1	6	1	0	-1

0,14,ℓ

-6*	7	8	8	0
-5	7	9	9	0
-4*	13	15	-15	0
-3*	6	4	4	0
-2	6	6	-6	0
-1	30	29	29	0
0	30	30	30	0

0,15,ℓ

-6*	7	7	0	-7
-5*	7	2	0	-2
-4	7	5	0	5
-3	14	13	0	-13
-2*	28	28	0	28
-1	6	3	0	-3

0,16,ℓ

-6*	7	4	-4	0
-5	7	6	-6	0
-4	23	21	-21	0
-3*	24	19	-19	0
-2*	6	5	-5	0
-1	6	5	5	0
0	29	31	31	0

0,17,ℓ

-5*	7	3	0	3
-4*	16	16	0	-16
-3	7	4	0	-4
-2	17	18	0	18
-1	23	23	0	23

10ℓ

-8*	7	5	-5	0
-7	6	3	0	-3
-6	19	17	-17	0
-5	13	10	0	-10
-4	7	1	1	0
-3	39	31	0	31
-2	153	161	161	0
-1	71	83	0	-83

11ℓ

-8*	6	6	-6	-3
-7	13	15	-14	-7
-6	12	12	11	5
-5	44	44	37	23
-4	25	25	-24	6
-3	43	43	-18	39
-2	44	42	35	-23
-1	32	29	-26	-12
0	59	66	0	-66

12ℓ

-8*	12	12	4	-11
-7	6	7	-6	-3
-6	24	22	-4	21
-5	24	26	-14	-21
-4	24	23	-19	-12
-3	62	57	-19	54
-2	23	18	6	17
-1	29	19	15	12
0	19	22	0	22

13ℓ

-8*	7	5	1	5
-7*	6	6	-2	-6
6	22	21	21	-4
5	16	11	7	9
4	55	55	-55	-5
3	39	38	-20	-32
2	97	95	82	48
1	98	95	49	-82
0	96	94	0	94

14ℓ

-8*	12	15	0	-15
-7	6	7	3	6
-6	10	6	2	5
-5	31	29	20	-21
-4	25	23	15	-17
-3	27	26	25	8
-2	33	30	-30	0
-1	51	49	-29	39
0	35	27	0	-27

15ℓ

-8*	7	8	1	8
-7*	6	5	2	-5
-6	6	6	2	6
-5	18	18	-15	9
-4	24	25	-22	-12
-3	27	29	29	2
-2	52	54	41	-35
-1	51	51	-50	-15
0	45	45	0	-45

16ℓ

-8*	6	5	3	-4
-7	13	13	-12	7
-6	15	15	6	14
-5	16	15	-15	-3
-4	7	6	4	4
-3*	8	8	5	-6
-2	4	9	-7	6
-1	29	28	26	12
0	6	4	0	4

17ℓ

-8*	7	6	-2	6
-7	7	4	-1	-3
-6	14	16	-8	-14
-5	32	33	-32	8
-4	39	43	35	-25
-3	51	52	50	15
-2	35	32	-14	29
-1	16	16	1	16
0	35	36	0	36

18ℓ

-8*	7	6	5	3
-7	7	3	-2	1
-6	12	10	9	-5
-5	10	9	5	-7
-4*	23	22	-21	-5
-3	5	5	-1	5
-2	37	33	-31	10
-1	16	18	-17	6
0	35	28	0	-28

19ℓ

-8*	7	8	-2	8
-7	7	10	0	10
-6	11	8	-8	3
-5	13	13	-1	-12
-4	13	14	14	-3
-3	32	33	4	-33
-2	38	39	-37	15
-1	22	22	-22	2
0	17	15	0	-15

1,10,ℓ

-7*	7	9	5	7
-6*	18	19	9	-17
-5	6	7	5	-5
-4	8	10	7	8
-3	9	9	0	-9
-2	35	35	3	35
-1	18	19	-12	-15
0	49	45	0	-45

1,11,ℓ

-7*	7	7	-2	6
-6	14	15	13	7
-5	15	19	15	-12
-4	10	10	0	-10
-3*	21	22	-10	20
-2	5	5	-3	-4
-1	44	43	18	39
0	9	9	0	9

1,12,ℓ

-7*	7	9	3	-8
-6*	19	19	11	-15
-5	6	7	4	-6
-4	15	16	-13	10
-3	17	19	-2	19
-2	24	24	-23	6
-1	27	24	-24	1
0	39	41	0	-41

1,13,ℓ

-7*	7	2	1	2
-6	12	13	12	-4
-5	14	15	-5	-14
-4	31	33	-24	-23
-3*	23	19	-19	0
-2*	6	3	3	-1
-1	10	11	6	9
0	32	32	0	31

1,14,ℓ

-6*	7	6	-1	-6
-5	7	7	7	1
-4	14	14	-3	14
-3	18	23	-21	11
-2	11	9	9	-2
-1	25	27	-16	-21
0	16	16	0	16

1,15,ℓ

-6*	7	8	7	4
-5*	7	2	-2	-1
-4	16	15	-9	12
-3*	19	20	19	4
-2*	6	7	6	3
-1	10	10	-10	2
0	25	25	0	-25

1,16,ℓ

-6*	11	8	-4	7
-5*	7	7	-5	4
-4*	7	4	2	3
-3	7	5	-4	4
-2	30	30	21	-21
-1	29	29	20	-21
0	13	13	0	13

1,17,ℓ

-5*	11	12	-12	-1
-4	7	8	3	8
-3	15	15	12	8
-2	11	10	-3	10
-1	11	9	-6	7
0	11	14	0	-14

20ℓ

-8*	14	14	-14	0
-7*	6	6	0	6
-6*	6	3	3	0
-5	5	0	0	0
-4	50	50	50	0
-3	33	35	0	-35
-2	113	111	-111	0
-1	64	74	0	74
0	31	32	32	0

21ℓ

-8*	7	7	1	-7
-7	6	4	-3	-1
-6	23	23	13	19
-5	42	46	41	21
-4	38	36	36	0
-3	30	28	-26	-11
-2	85	77	45	-62
-1	135	141	-137	-32
0	9	1	1	0

22ℓ

-9*	12	12	-12	-3
-8	7	3	-2	2
-7	28	27	26	4
-6	15	14	-14	0
-5	36	37	-29	22
-4	34	33	33	-4
-3	33	30	12	-27
-2	34	31	-29	-12
-1	99	96	93	-26
0	55	52	52	0

23ℓ

-8	13	13	-2	-13
-7	9	8	-7	-3
-6	15	14	-9	10
-5	19	17	6	16
-4	36	34	-5	34
-3	36	37	24	-28
-2	70	56	-17	-53
-1	62	62	-27	56
0	77	68	-68	0

24ℓ

-9	12	12	-11	-2
-8	16	16	16	-4
-7	25	25	22	-10
-6	13	13	-12	3
-5	24	24	-19	15
-4	16	16	9	13
-3	35	38	-37	-7
-2	35	33	29	15
-1	8	8	7	-2
0	9	8	-8	0

25ℓ

-9*	11	11	0	-11
-8*	7	3	-2	-2
-7*	6	8	7	3
-6*	6	10	4	9
-5	5	8	-6	5
-4	25	26	22	-14
-3	35	34	0	-34
-2	7	9	-6	-7
-1	27	29	-24	-15
0	6	1	-1	0

26ℓ

-8*	7	9	9	2
-7	7	5	-3	-4
-6	15	17	-12	12
-5*	12	13	6	12
-4	29	30	-14	-26
-3	29	31	27	-16
-2	34	32	-4	-31
-1	23	26	16	21
0	48	45	-45	0

27ℓ

-8	10	5	-1	-5
-7	13	16	-3	16
-6*	14	16	12	10
-5	6	5	5	0
-4	31	31	17	-26
-3	25	25	18	18
-2	64	60	-34	49
-1	15	16	-15	-6
0	8	7	-7	0

28ℓ

-8*	7	2	-1	-2
-7	12	11	-10	5
-6*	11	10	-1	10
-5*	6	8	3	7
-4	5	3	1	-3
-3	23	24	-7	-23
-2	21	22	5	21
-1	36	35	-34	8
0	51	48	48	0

29ℓ

-8*	7	2	-2	1
-7*	13	13	8	11
-6	6	8	-2	8
-5	34	36	4	-35
-4	14	16	-11	-12
-3	16	14	-8	11
-2	24	23	-2	23
-1	36	30	-22	20
0	64	59	59	0

2,10,ℓ

-7	12	10	-10	0
-6	15	14	14	1
-5*	22	26	15	-21
-4	6	5	-4	-3
-3	8	10	4	-9
-2	23	23	-23	-1
-1	40	38	-25	29
0	31	27	27	0

2,11,ℓ

-7*	7	2	2	0
-6	11	10	3	-9
-5*	12	12	4	-12
-4	6	9	-9	2
-3	16	17	-1	17
-2	12	12	-11	-5
-1*	25	27	-12	-24
0	5	1	1	0

2,12,ℓ

-7*	7	7	-5	5
-6*	7	5	-3	4
-5*	6	6	4	5
-4*	6	9	-9	0
-3*	6	7	-3	7
-2	6	8	-1	-8
-1	24	23	15	-17
0	17	17	17	0

2,13,ℓ

-7*	7	9	-8	-4
-6*	7	8	-3	-7
-5*	7	7	7	-1
-4	27	27	-11	24
-3	13	13	13	0
-2*	10	10	7	-7
-1	6	11	-9	7
0	26	28	28	0

2,14,ℓ

-6*	7	1	-1	0
-5*	7	5	-3	4
-4	6	6	6	-1
-3	16	18	-18	-3
-2	17	16	0	16
-1	26	27	25	12
0	15	13	-13	0

2,15,ℓ

-6*	7	4	4	1
-5*	13	11	6	9
-4	7	6	-4	4
-3	12	13	-11	-7
-2	23	26	-5	-26
-1	25	25	-23	10
0	16	17	17	0

2,16,ℓ

-5*	7	9	-9	-4
-4	18	17	12	-11
-3*	18	19	5	-18
-2	7	4	-3	-3
-1	28	28	27	6
0	11	11	-11	0

2,17,ℓ

-5*	7	6	6	3
-4*	7	3	-1	3
-3	7	7	1	-7
-2	11	13	-9	-10
-1*	11	9	-4	-8
0	7	0	0	0

30ℓ

-8*	7	1	-1	0
-7*	22	22	0	-22
-6	6	3	-3	0
-5	8	8	0	-8
-4	8	8	8	0
-3	56	56	0	56
-2	18	13	13	0
-1	84	76	0	-76

31ℓ

-8*	7	7	-1	7
-7	6	4	-4	2
-6	15	12	11	-3
-5	21	21	20	-6
-4	35	36	-33	-17
-3	46	48	-47	-3
-2	52	50	-42	26
-1	45	53	52	7
				5

32ℓ

-8*	7	9	-1	-9
-7	10	11	5	10
-6	11	13	-13	0
-5*	5	3	2	-2
-4	30	28	9	-26
-3	9	8	0	8
-2	6	4	3	-2
-1	38	38	2	-38
0	8	3	0	-3

33ℓ

-8*	7	5	0	-5
-7	10	8	-6	5
-6	23	22	19	10
-5	25	28	25	-13
-4	32	31	-21	-23
-3	13	10	-9	-3
-2	62	57	51	-26
-1	47	45	-42	15
0	60	61	0	61

34ℓ

-9*	14	15	-4	-14
-8	7	6	4	-4
-7	17	16	2	16
-6	20	19	-11	15
-5	8	7	5	-4
-4	22	25	19	15
-3	42	40	-27	-29
-2	20	18	-1	18
-1	38	38	30	23
0	22	25	0	-25

35ℓ

-8	10	10	8	-5
-7	15	16	-12	11
-6	13	13	7	11
-5	15	15	-11	-10
-4	38	39	-38	-10
-3	47	46	45	-12
-2	24	21	1	-21
-1	16	18	-10	14
0	36	39	0	39

36ℓ

-9*	13	12	-2	-12
-8	7	7	6	3
-7	19	19	-6	18
-6	12	14	-8	-12
-5	10	11	11	1
-4	35	36	-10	-35
-3	33	32	-28	-16
-2	25	20	-8	19
-1	38	39	-3	39
0	47	45	0	45

37ℓ

-8*	7	8	7	-2
-7*	11	11	8	7
-6	6	8	6	6
-5	9	7	-7	-4
-4	16	15	6	13
-3	34	34	32	-11
-2	49	48	-43	20
-1	38	35	-32	15
0	32	27	0	-27

38ℓ

-8*	7	7	5	4
-7*	16	15	-8	13
-6	6	4	2	3
-5	20	21	10	-18
-4	20	20	-20	-5
-3	21	18	15	-10
-2	34	33	33	-1
-1	29	28	12	25
0	33	32	0	-32

39ℓ

-8*	11	11	-11	-3
-7	7	6	-2	-5
-6	11	10	-10	1
-5	9	9	-9	0
-4*	32	32	30	-10
-3*	5	6	-1	6
-2*	5	4	1	4
-1	15	14	7	12
0	49	47	0	-47

3,10,ℓ

-7*	7	7	-7	-3
-6*	6	4	-2	4
-5	6	3	2	-3
-4	12	9	-9	3
-3	23	23	0	23
-2	12	14	8	11
-1	22	20	-17	11
0	8	7	0	-7

3,11,ℓ

-7*	7	7	-6	-3
-6	7	9	4	8
-5*	15	15	15	0
-4	6	4	1	-4
-3	17	20	-20	2
-2*	26	26	-22	14
-1*	5	5	5	2
0*	5	3	0	-3

3,12,ℓ

-7*	7	3	-3	-1
-6	7	4	-2	-3
-5	9	5	3	4
-4	9	9	9	-3
-3*	9	9	2	-9
-2	6	5	-5	-2
-1	26	27	0	-27
0	8	9	0	9

3,13,ℓ

-6*	7	5	5	-1
-5*	27	24	24	-2
-4	6	6	5	-3
-3	11	13	-12	5
-2*	20	19	18	5
-1	6	10	3	9
0	9	9	0	-9

3,14,ℓ

-6*	7	3	3	0
-5*	7	7	3	7
-4*	17	17	-3	17
-3	6	8	7	4
-2	15	15	-6	-14
-1	12	11	-3	-11
0	15	15	0	-15

3,15,ℓ

-6	4	4	3	-3
-5	14	12	-12	-1
-4*	12	12	-10	-5
-3*	7	5	-4	2
-2	6	9	6	7
-1*	12	10	9	3
0*	6	2	0	-2

3,16,ℓ

-5*	7	6	4	-4
-4*	7	7	-7	-3
-3*	7	10	6	8
-2*	7	8	7	-5
-1	6	6	-6	3
0	23	24	0	24

40ℓ

-8	12	10	-10	0
-7	19	19	0	-19
-6	14	17	17	0
-5	39	42	0	42
-4	24	23	23	0
-3	23	21	0	21
-2	68	71	-71	0
-1	52	55	0	-55
0	25	23	23	0

41ℓ

-8*	7	6	-6	-1
-7*	6	9	0	-9
-6*	6	6	-1	-6
-5	24	23	-20	13
-4	35	38	-29	24
-3	26	26	25	-4
-2	42	38	-15	-35
-1	29	25	7	-24
0	47	50	50	0

42ℓ

-8*	7	7	-7	0
-7*	27	29	18	-22
-6	6	7	-1	-7
-5	19	19	-19	2
-4	26	28	23	16
-3	23	23	15	18
-2	21	17	-8	16
-1	28	33	28	-18
0	30	31	31	0

43ℓ

-8*	7	8	-6	-5
-7	21	22	17	-14
-6	20	20	19	-3
-5	15	14	-10	9
-4	11	12	-5	11
-3	20	22	-8	-21
-2	34	31	-30	6
-1	43	41	-22	34
0	31	29	29	0

44ℓ

-8	10	8	8	-1
-7	19	19	17	-9
-6	13	13	-13	-3
-5*	22	24	-23	8
-4	5	6	-5	-4
-3	38	39	-15	36
-2	11	12	4	-11
-1	16	14	9	-11
0	44	44	-44	0

45ℓ

-8*	7	4	4	-1
-7*	7	3	2	3
-6*	6	6	0	6
-5*	6	9	-9	1
-4	18	17	6	-16
-3	29	25	18	-18
-2	15	15	0	15
-1	21	19	-8	17
0	52	55	55	0

46ℓ

-8	20	18	12	-13
-7	10	10	2	-10
-6*	12	14	-14	0
-5	6	1	1	1
-4	18	19	7	18
-3	22	23	20	-13
-2	55	55	36	42
-1	27	25	20	-14
0	37	37	-37	0

47ℓ

-8*	7	9	3	-8
-7	10	10	3	10
-6	18	22	-15	16
-5	9	9	1	-9
-4	18	16	-13	-10
-3	19	19	8	18
-2	28	23	-19	-13
-1	37	38	-37	-9
0	27	25	26	0

48ℓ

-7	12	10	-9	-5
-6*	23	23	-21	10
-5	6	7	6	3
-4	26	25	11	-23
-3	11	8	-4	-7
-2	28	28	26	-10
-1	35	35	-29	20
0	47	43	-43	0

49ℓ

-7*	7	5	-4	1
-6	11	9	4	9
-5	20	19	-2	-19
-4	18	16	15	5
-3	19	18	16	8
-2	19	15	-6	-13
-1	16	15	-14	-6
0	13	15	-15	0

4,10,ℓ

-7*	7	7	-7	1
-6	16	17	-1	17
-5*	17	15	11	10
-4	6	9	4	-8
-3*	12	13	4	13
-2	6	4	4	-1
-1	31	31	-25	-17
0	16	15	-15	0

4,11,ℓ

-7*	7	7	7	-2
-6*	14	13	-7	-11
-5*	7	11	-4	10
-4	6	6	2	6
-3	17	14	4	13
-2	16	18	12	-13
-1*	8	9	8	-5
-0*	6	4	4	0

4,12,ℓ

-6*	7	6	6	1
-5*	13	14	2	-14
-4*	6	3	-3	-1
-3*	6	5	4	3
-2*	6	8	-3	-8
-1	6	7	3	7
0	27	27	27	0

4,13,ℓ

-6*	7	6	4	-5
-5	7	10	-8	5
-4	21	22	4	22
-3	11	11	-8	-8
-2*	10	10	-10	-3
-1	6	6	1	-5
0	14	10	-10	0

4,14,ℓ

-6*	7	7	2	7
-5*	7	6	6	0
-4	7	6	-6	-2
-3	14	14	-12	7
-2	21	21	-5	-20
-1	13	15	4	-14
0	12	11	11	0

4,15,ℓ

-5*	7	10	-6	9
-4*	7	5	-5	-1
-3	18	19	18	-7
-2	13	12	-9	-7
-1	13	14	13	6
0	16	16	16	0

4,16,ℓ

-5*	7	7	2	7
-4*	7	6	6	2
-3*	17	21	-3	21
-2*	7	6	-1	6
-1	15	15	12	-9
0	11	10	-10	0

50ℓ

-8*	7	6	6	0
-7*	7	6	0	6
-6*	6	5	5	0
-5*	5	5	0	-5
-4	5	3	-3	0
-3	8	8	0	-8
-2	35	32	-32	0
-1	73	71	0	-71

51ℓ

-8*	7	6	-5	4
-7*	7	7	3	-6
-6	6	6	5	-3
-5	8	8	4	-7
-4	24	23	-5	-22
-3	31	31	-12	-29
-2	24	24	21	10
-1	22	22	0	-22
-0	41	36	0	35

TABLE 18 (cont.)

52ℓ				
-8*	13	11	-4	-10
-7	7	5	-3	-3
-6*	32	34	-13	32
-5	6	7	7	2
-4	12	13	13	0
-3	24	22	-7	21
-2	25	24	2	-24
-1	18	21	-4	-21
0	58	56	0	56

53ℓ				
-8*	7	7	2	-6
-7	7	6	5	-4
-6	20	18	11	14
-5	17	17	-10	15
-4	30	28	-27	8
-3	27	27	-12	24
-2	26	24	11	-21
-1	36	36	33	13
0	16	15	0	-15

54ℓ				
-8*	22	18	5	-17
-7	7	9	-9	-1
-6	23	23	-14	18
-5	9	8	-5	6
-4	18	18	14	-11
-3	24	23	-13	-19
-2	36	33	11	-31
-1	34	30	30	-6
0	25	23	0	23

55ℓ				
-8*	15	14	2	-14
-7*	7	4	4	1
-6	6	5	0	5
-5*	11	10	-4	-10
-4	6	2	-2	0
-3	16	20	20	0
-2	12	9	9	0
-1	21	21	-19	9
0	31	35	0	35

56ℓ				
-7*	7	4	1	3
-6	19	20	-12	17
-5	18	19	19	4
-4	10	12	-11	5
-3	9	5	-3	-4
-2	13	14	9	-11
-1	25	30	-16	26
0	24	19	0	-19

57ℓ				
-7	10	8	5	6
-6	21	21	-14	16
-5	26	26	-26	-2
-4	17	16	14	-7
-3	10	11	0	11
-2	12	8	-3	-7
-1	8	6	1	-6
0	12	13	0	-13

58ℓ				
-7*	7	11	-9	-6
-6*	7	6	2	-5
-5*	13	13	-3	-12
-4	6	8	8	0
-3	15	15	5	15
-2	32	32	19	26
-1	28	26	0	26
0	8	5	0	-5

59ℓ				
-7	12	14	12	-6
-6*	16	16	-11	11
-5	6	9	1	9
-4	20	20	12	-16
-3	10	12	2	11
-2	21	18	-17	7
-1*	11	12	5	11
0	5	5	0	5

5,10,ℓ				
-7*	8	10	-9	-2
-6*	19	19	-2	-19
-5*	7	3	0	3
-4*	8	5	2	-5
-3	6	7	7	0
-2	22	25	-22	11
-1	11	10	0	-10
0	27	27	0	-27

5,11,ℓ				
-6*	10	10	-4	9
-5	7	6	3	-5
-4	14	14	13	-4
-3*	16	17	-5	-16
-2*	6	7	-4	6
-1*	6	8	4	8
0	6	4	0	4

5,12,ℓ				
-7	13	11	-4	-10
-6	12	12	-8	-10
-5	12	16	16	1
-4	16	15	13	6
-3*	12	10	-2	10
-2	6	9	9	-1
-1*	11	12	-10	6
0	6	4	0	4

5,13,ℓ				
-6*	7	6	1	6
-5	7	4	1	-4
-4	13	13	-12	5
-3*	18	18	-18	2
-2	6	6	4	-4
-1	17	15	5	15
0	26	29	0	-29

5,14,ℓ				
-6*	8	5	-1	-5
-5*	7	4	4	2
-4	7	5	-2	4
-3*	13	10	-7	-7
-2*	7	10	9	-5
-1	6	8	7	-3
0	24	25	0	25

5,15,ℓ				
-5	11	13	13	-3
-4*	14	14	-13	-5
-3	7	5	5	0
-2*	22	25	20	15
-1*	7	4	-4	-1
0	7	4	0	4

5,16,ℓ				
-5*	8	9	6	7
-4*	7	9	-9	2
-3	7	8	2	-7
-2	11	11	-6	-10
-1*	11	11	-7	-8
0	7	4	0	4

60ℓ				
-7*	7	5	0	-5
-6*	6	4	4	0
-5	6	8	0	8
-4	25	25	-25	0
-3*	9	8	0	-8
-2	5	1	1	0
-1	25	28	0	28
0	102	105	105	0

61ℓ				
-7	16	14	-10	-10
-6	34	36	10	-34
-5	17	18	17	6
-4	28	29	5	29
-3	20	17	9	-15
-2	33	33	0	33
-1	73	70	-65	26
0	15	10	10	0

62ℓ				
-7*	7	5	2	-4
-6	18	17	16	2
-5	12	13	-13	3
-4	11	15	-2	-15
-3	15	14	1	-14
-2	35	34	-28	18
-1	9	5	-5	-1
0	9	10	-10	0

63ℓ				
-8*	11	10	-1	10
-7	7	6	3	-5
-6	9	11	9	-6
-5	26	29	2	28
-4	15	14	-5	-13
-3	32	32	3	-32
-2	10	12	-10	-5
-1	10	6	-5	3
0	29	29	29	0

64ℓ				
-7*	7	4	4	-2
-6	7	3	2	-3
-5	9	7	4	-6
-4	13	12	-5	-11
-3	31	31	31	-1
-2	15	14	14	0
-1*	19	15	13	7
0	5	3	-3	0

65ℓ				
-7*	13	14	14	0
-6	6	6	-6	2
-5	14	14	-12	8
-4	13	15	-2	-15
-3	15	13	-9	-9
-2	47	50	-17	47
-1	13	14	13	7
0	9	4	4	0

66ℓ				
-7*	7	7	6	-5
-6	12	12	-7	9
-5	13	14	-11	7
-4	9	9	-7	6
-3	13	18	-16	7
-2	30	30	27	-14
-1	15	18	-13	-12
0	19	23	-23	0

67ℓ				
-7*	7	8	8	-1
6	10	9	-6	7
5	22	23	-17	-16
4	28	30	12	-27
3*	18	19	18	7
2	6	5	4	3
1	17	18	16	9
0	9	8	8	0

68ℓ				
-7*	7	12	-5	-11
-6	7	2	1	-1
-5*	19	22	8	20
-4	6	7	4	-6
-3	22	20	16	13
-2	10	8	7	4
-1	12	15	-11	-10
0	45	45	-45	0

69ℓ				
-7*	7	7	2	6
-6	7	5	1	-5
-5*	22	22	-21	5
-4	6	6	-2	-6
-3	15	15	13	8
-2	12	10	-6	9
-1	19	22	2	-21
0	13	14	14	0

6,10,ℓ				
-7*	13	12	-10	-7
-6*	7	5	4	3
-5	7	6	4	-4
-4	16	16	-16	-2
-3	9	8	8	-1
-2	9	10	3	9
-1	23	26	-19	-17
0	35	36	36	0

6,11,ℓ				
-7*	14	10	3	-10
-6*	7	4	2	-4
-5*	7	3	0	-3
-4	7	7	-6	3
-3	15	15	10	12
-2*	11	11	-10	5
-1*	6	5	-4	2
-0	6	5	5	0

6,12,ℓ				
-6*	17	20	20	0
-5*	7	2	-1	-2
-4	7	4	4	-2
-3	17	20	-10	18
-2*	17	17	-17	0
-1*	6	7	-7	1
0	6	3	3	0

6,13,ℓ				
-5*	7	7	5	6
-4*	7	5	-1	-5
-3	7	8	-5	6
-2	18	19	4	-18
-1*	13	15	-11	-10
0	6	10	10	0

6,14,ℓ				
-5*	7	9	4	-8
-4*	7	4	-3	3
-3*	7	3	-3	0
-2	7	7	-5	5
-1	12	12	12	1
0	12	12	12	0

6,15,ℓ				
-5*	8	6	4	4
-4*	7	7	4	6
-3	7	7	-5	-5
-2*	17	19	-1	19
-1	7	7	-7	0
0	7	3	-3	0

6,16,ℓ				
-4	12	10	-10	1
-3*	15	14	-13	-5
-2*	7	6	1	-6
-1	7	3	2	1
0	13	15	15	0

70ℓ				
-7*	7	7	0	-7
-6	7	4	-4	0
-5	9	13	0	13
-4	22	25	25	0
-3	12	12	0	12
-2	13	13	13	0
-1	52	56	0	-56

71ℓ				
-7*	7	8	6	-5
-6*	15	15	9	12
-5*	6	7	4	6
-4	6	7	-5	5
-3	26	26	-23	11
-2	16	18	10	-15
-1	22	22	20	10
0	16	15	0	-15

72ℓ				
-7*	14	14	-8	-11
-6	7	5	1	-5
-5*	10	11	11	2
-4	6	6	-5	3
-3	24	22	-18	13
-2	24	23	-22	-5
-1	22	24	11	-22
0	16	14	0	-14

73ℓ				
-7*	7	5	5	0
-6	7	4	0	-4

-5	17	19	-18	7
-4	25	29	-28	-6
-3	6	9	-4	-7
-2	21	23	20	13
-1	20	16	13	-9
0	25	27	0	27

74ℓ				
-7*	7	5	3	-3
-6	6	5	4	4
-5	20	23	23	4
-4	9	11	-3	10
-3*	13	13	-13	1
-2	6	6	6	1
-1*	17	15	-11	11
0	5	7	0	7

75ℓ				
-7*	7	8	7	-3
-6	7	5	-4	3
-5*	16	19	-18	-6
-4	6	4	-4	1
-3	18	18	17	6
-2	14	15	14	-5
-1	18	17	-16	-6
0	31	33	0	-33

76ℓ				
-7*	7	4	3	3
-6	11	11	5	9
-5*	12	10	-9	4
-4	6	8	-8	-2
-3	20	20	-7	-19
-2	12	15	14	-6
-1*	21	21	18	11
0	6	8	0	8

77ℓ				
-7*	7	3	3	1
-6	12	14	-10	-9
-5	12	8	-8	-2
-4	23	23	16	-17
-3	34	35	27	21
-2*	18	21	-5	20
-1	6	8	-4	7
0	15	13	0	13

78ℓ				
-6	10	9	8	-5
-5	11	9	-4	8
-4	14	14	-14	0
-3	15	16	10	-12
-2	12	12	-12	1
-1	15	14	-14	4
0	17	17	0	-17

79ℓ				
-6*	14	15	-13	6
-5*	7	8	-1	-8
-4	13	13	8	-11
-3	21	22	13	-18
-2	10	8	-5	7
-1*	22	24	-24	-4
0	6	2	0	2

7,10,ℓ				
-6*	7	5	2	-5
-5*	7	10	1	10
-4	7	10	10	2
-3	10	10	5	-9
-2	11	9	7	6
-1*	18	19	-6	-17
0	6	4	0	4

7,11,ℓ				
-6*	7	5	-5	2
-5	7	8	8	0
-4*	14	15	12	-10
-3*	7	4	1	4
-2	6	4	-4	2
-1*	18	21	-4	20
0	6	5	0	5

7,12,ℓ				
-5*	11	9	3	9
-4	7	7	-7	3
-3	10	9	-7	4
-2	20	17	-13	-10
-1	18	19	16	-10
0	18	20	0	20

7,13,ℓ				
-5*	7	8	5	-7
-4	11	11	6	-10
-3*	16	17	-15	-7
-2	7	10	-4	9
-1*	19	19	19	2
0	7	5	0	5

7,14,ℓ				
-5*	8	6	3	5
-4*	7	4	-3	-2
-3	7	11	-11	1
-2*	12	13	5	-12
-1	7	7	-6	4
0	16	16	0	16

7,15,ℓ				
-4*	8	8	-1	8
-3*	11	11	-9	5
-2*	7	4	1	4
-1	7	4	-1	-4
0	19	22	0	-22

80ℓ				
-7*	7	7	0	-7
-6*	7	3	3	0
-5	7	4	0	-4
-4	11	15	15	0
-3*	15	15	0	-15
-2	6	8	-8	0
-1	29	26	0	26
0	33	33	-33	0

81ℓ				
-7*	7	7	-7	1
-6	12	11	5	-10
-5	19	19	3	19
-4	12	13	1	13
-3	12	12	9	-8
-2	23	24	-6	-23
-1*	16	13	-13	-4
0	6	10	10	0

82ℓ				
-7*	7	7	6	3
-6	7	4	-4	0
-5*	12	8	-5	6
-4*	6	7	7	1
-3	6	8	5	-7
-2	21	18	10	-14
-1	18	20	17	-10
0	9	10	-10	0

83ℓ				
-7*	7	8	-7	-3
-6	7	2	-1	-2
-5	11	13	4	12
-4	15	15	-6	13
-3	26	29	10	-27
-2	11	13	-13	-1
-1	22	20	8	18
0	19	19	19	0

84ℓ				
-7*	18	16	15	3
-6	7	4	2	4
-5	11	12	-12	0
-4	12	10	4	9
-3	12	14	-12	7
-2*	15	16	16	-4
-1	6	8	6	5
0	24	25	-25	0

85ℓ				
-6*	7	1	-1	-1
-5	10	7	-1	7
-4	16	18	13	-13
-3*	13	13	-12	-3
-2*	6	5	3	-4
-1*	6	5	3	-3
0	6	8	8	0

86ℓ				
-6*	7	4	-3	2
-5	10	13	-13	-3
-4	12	10	-9	-2
-3	24	25	18	-17
-2	25	25	11	-22
-1	14	15	14	7
0	29	30	-30	0

87ℓ				
-6*	7	6	-6	0
-5*	7	6	5	1
-4	7	8	7	3
-3	11	13	0	13
-2	21	21	-5	20
-1	21	21	-14	-16
0	22	24	-24	0

88ℓ				
-6*	7	5	-3	4
-5*	7	8	5	7
-4	7	10	-10	4
-3	23	24	3	-24
-2	16	17	16	-3
-1*	29	31	-29	13
0	6	4	4	0

89ℓ				
-6	12	9	-7	-6
-5*	13	11	8	-8
-4*	7	5	1	-5
-3	7	6	-5	3
-2	12	11	8	8
-1*	37	37	-35	13
0	6	1	-1	0

8,10,ℓ				
-5*	11	14	14	0
-4	7	7	-3	-7
-3	15	14	1	-13
-2	12	11	-3	10
-1*	36	38	-32	21
0	6	0	0	0

8,11,ℓ				
-5*	7	8	8	1
-4*	7	5	4	3
-3*	7	5	-5	-2
-2	7	5	-1	4
-1*	25	24	-20	-13
0	7	7	-7	0

8,12,ℓ				
-5*	8	7	7	2
-4*	12	9	-3	-9
-3	7	6	2	-6
-2*	12	11	-1	11
-1*	7	7	-4	-6
0	7	5	5	0

8,13,ℓ				
-4*	7	9	-1	9
-3*	7	6	6	-1
-2*	7	8	-6	-6
-1	7	10	4	9
0	10	10	10	0

90ℓ				
-6*	7	3	3	0
-5*	14	15	0	15
-4	7	4	4	0
-3	14	13	0	13
-2	20	20	-20	0
-1	15	18	0	-18

91ℓ				
-6*	7	10	6	-8
-5	7	9	9	-4
-4	17	17	-15	9
-3	10	8	-5	-7
-2*	14	11	-3	11
-1	6	7	0	7
0	17	19	0	-19

92ℓ				
-6*	7	6	5	4
-5*	17	16	15	6
-4	7	7	0	-7
-3*	14	15	-12	-9
-2	6	4	-3	-2
-1	23	24	2	-24
0	22	23	0	23

93ℓ				
-6*	7	10	7	-7
-5*	7	9	5	-7
-4*	7	6	-5	3
-3	6	4	4	1
-2	18	18	18	1
-1	19	17	-12	12
0	15	14	0	-14

94ℓ				
-6*	14	14	8	12
-5	7	9	4	8
-4	12	12	-12	-3
-3	11	8	-6	-4
-2	11	13	2	-13
-1	10	6	5	-3
0	11	12	0	12

95ℓ				
-6*	7	3	2	0
-5*	12	13	-13	0
-4	7	6	6	-2
-3	10	13	12	3
-2	14	14	-14	1
-1*	13	12	5	-11
0	6	5	0	5

96ℓ				
-6*	7	6	3	5
-5	7	5	-2	-4
-4	25	23	-11	-20
-3	14	12	8	-8
-2	12	16	15	-6
-1	26	26	-17	20
0	37	40	0	40

97ℓ				
-5*	7	5	-4	3
4*	15	14	12	6
3	7	5	-3	3
2	24	25	-25	2
1*	19	19	-6	-18
0	6	3	0	-3

98ℓ				
-5*	7	8	-7	-5
-4	7	4	-3	-3
-3	17	17	14	-9
-2	19	19	19	1
-1*	23	21	4	20
0	6	3	0	3

99ℓ				
-5*	7	2	1	2
-4*	12	12	12	-3
-3*	7	8	-7	4
-2	7	6	5	-4
-1*	16	17	16	-4
0	7	9	0	-9

9,10,ℓ				
-5*	8	7	-5	5
-4*	7	6	4	3
-3*	7	4	-4	2
-2*	7	6	-1	5
-1	7	7	-3	7
0	17	16	0	-16

9,11,ℓ				
-4*	7	2	-1	2
-3*	11	12	-11	-5
-2*	7	9	-8	5
-1*	7	6	6	0
0	7	2	0	-2

9,12,ℓ				
-4*	8	8	8	1
-3*	7	7	-2	-7
-2*	7	4	-4	0
-1*	7	7	5	-5
0	7	2	0	2

10,0,ℓ				
-5*	7	2	0	2
-4*	7	3	-3	0
-3	7	4	0	4
-2*	10	10	-10	0
-1	7	5	0	-5
0	14	13	13	0

10,1,ℓ				
-5*	7	3	1	3
-4*	14	14	-4	14
-3	7	4	3	-4
-2*	19	18	5	-17
-1	7	3	2	2
0	15	15	15	0

10,2,ℓ				
-5*	7	9	1	-9
-4*	7	9	1	9
-3*	7	6	-6	-2
-2*	7	5	5	1
-1*	7	7	-1	7
0	7	5	5	0

10,3,ℓ				
-5*	7	6	-3	5
-4	7	8	-3	7
-3	16	16	-8	-14
-2*	12	12	-11	-5
-1*	7	10	10	4
0	7	6	6	0

10,4,ℓ				
-5*	7	5	-2	-4
-4	7	9	-8	-3
-3	11	11	-10	6
-2	12	11	9	-6
-1	9	8	-7	-5
0	22	23	-23	0

10,5,ℓ				
-5*	12	10	-8	6
-4*	7	8	-6	-2
-3*	7	6	4	-5
-2	7	8	-6	4
-1	26	27	25	10
0	27	26	26	0

10,6,ℓ				
-5*	7	2	-2	-1
-4	7	7	6	3
-3	12	11	5	10
-2	32	29	23	18
-1	12	11	-8	-7
0	28	29	-29	0

10,7,ℓ				
-5*	8	9	-8	3
-4*	8	8	-8	-1
-3*	7	4	-4	-1
-2	7	5	1	-5
-1*	11	9	7	-6
0	7	6	6	0

10,8,ℓ				
-4*	8	10	9	-2
-3	7	6	6	0
-2	13	10	10	0
-1	15	14	-14	2
0	36	33	-33	0

10,9,ℓ				
-4	13	12	11	2
-3*	10	7	7	0
-2*	7	9	9	-4
-1	7	3	3	1
0	27	26	-26	0

10,10,ℓ				
-4*	8	6	4	4
-3*	7	4	4	1
-2*	7	6	-4	-4
-1*	7	9	-6	-7
0	7	7	7	0

11,0,ℓ				
-5*	8	3	0	-3
-4*	7	2	2	0
-3	7	1	0	-1
-2*	10	9	-9	0
-1	7	2	0	-2

11,1,ℓ				
-5*	8	12	11	-3
-4*	7	2	-2	1
-3*	11	12	-11	-3
-2*	7	9	9	2
-1*	7	5	4	-3
0	7	2	0	-2

11,2,ℓ				
-5*	7	6	4	-5
-4	7	3	3	-1
-3*	18	17	-15	10
-2*	7	5	0	-5
-1*	7	9	6	7
0	7	5	0	5

11,3,ℓ				
-4	15	15	-12	9
-3*	13	10	-4	9
-2*	7	10	10	-1
-1*	7	4	3	-3
0	7	8	0	-8

11,4,ℓ				
-4*	7	3	1	-3
-3*	7	4	-3	-2
-2	7	3	2	-2
-1	11	12	12	0
0	12	12	0	12

11,5,ℓ				
-4*	8	4	-4	1
-3	15	14	12	6
-2	14	14	14	-1
-1*	16	14	-7	-13
0	7	6	0	6

11,6,ℓ				
-4*	8	7	-5	5
-3*	7	10	8	-5
-2*	7	4	-2	-3
-1*	7	6	-4	3
0	7	9	0	-9

11,7,ℓ				
-4*	8	7	5	-4
-3*	7	4	-3	-2
-2	7	6	4	-4
-1*	13	13	5	-12
0	7	2	0	-2

11,8,ℓ				
-4*	8	4	1	4
-3*	7	5	5	-1
-2	7	9	0	9
-1*	15	12	-4	12
0	7	6	0	-6

12,0,ℓ				
-4*	8	9	-9	0
-3*	8	8	0	8
-2*	7	5	-5	0
-1	7	4	0	-4
0	15	16	16	0

12,1,ℓ				
-4*	8	6	2	6
-3*	8	7	-7	1
-2*	7	3	2	-3
-1*	7	6	2	6
0	7	9	-9	0

12,2,ℓ				
-3*	8	9	-4	8
-2	10	10	-4	-10
-1	10	10	10	-3
0*	7	5	5	0

12,3,ℓ				
-3*	8	7	-4	-6
-2*	7	6	4	-4
-1*	7	8	7	-4
0	7	6	-6	0

12,4,ℓ				
-3*	8	5	4	-1
-2	8	4	0	-4
-1*	11	8	8	1
0	7	7	7	0

12,5,ℓ				
-3*	8	8	-7	-5
-2	16	17	-3	17
-1*	12	11	11	0
0	7	8	-8	0

12,6,ℓ				
-3*	8	3	-3	-1
-2*	8	6	4	-4
-1*	8	7	-6	2
0	8	3	3	0

12,7,ℓ				
-3*	8	6	6	1
-2	8	8	3	7
-1*	17	17	17	4
0	8	5	-5	0

TABLE 19

FINAL ATOMIC FRACTIONAL COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^4$) WITH ESTIMATED STANDARD DEVIATIONS

Anisotropic temperature factor = $\exp\{-(h^2\beta_{11} + k^2\beta_{22} + \ell^2\beta_{33} + 2hk\beta_{12} + 2h\ell\beta_{13} + 2k\ell\beta_{23})\}$ with

$$\beta_{11} = 2\pi^2 a^{*2} U_{11}, \quad \beta_{12} = 2\pi^2 a^* b^* U_{12}, \text{ etc.}$$

The least-squares standard errors are given in parentheses.

Isotropic temperature factors are given in the last column.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B
S(1)	1729 (4)	3003 (2)	0905 (6)	91 (4)	28 (1)	264 (10)	-9 (2)	30 (6)	8 (3)	5.83
S(2)	0079 (3)	5809 (2)	3137 (5)	73 (3)	41 (2)	138 (6)	-3 (2)	16 (4)	-24 (3)	4.93
N(1)	2181 (8)	5584 (5)	1552 (13)	45 (8)	22 (4)	145 (18)	-10 (5)	36 (10)	4 (7)	3.50
N(2)	5626 (8)	5272 (6)	2031 (13)	38 (7)	36 (5)	112 (18)	-9 (5)	-5 (9)	4 (7)	3.66
N(3)	6933 (9)	4193 (7)	3230 (15)	68 (9)	44 (5)	165 (22)	1 (6)	16 (13)	15 (9)	4.80
C(1)	1302 (12)	3823 (8)	1455 (16)	64 (11)	30 (5)	130 (24)	4 (7)	-38 (15)	-19 (9)	4.24
C(2)	1941 (10)	4380 (7)	1168 (16)	44 (9)	13 (4)	188 (25)	-14 (6)	-23 (13)	-1 (8)	2.98
C(3)	1567 (10)	4998 (7)	1689 (15)	39 (9)	26 (5)	106 (20)	-11 (6)	10 (12)	26 (8)	3.13
C(4)	0525 (12)	5030 (7)	2401 (16)	90 (13)	23 (5)	121 (23)	-11 (7)	15 (15)	10 (8)	3.79
C(5)	-0127 (14)	4449 (9)	2565 (16)	84 (14)	45 (7)	88 (20)	-5 (8)	-5 (14)	9 (9)	4.20
C(6)	0252 (13)	3837 (8)	2125 (18)	75 (14)	33 (6)	154 (26)	-6 (7)	12 (16)	-2 (10)	4.52
C(7)	0604 (11)	6354 (7)	1770 (15)	69 (11)	29 (5)	75 (18)	-1 (6)	-7 (13)	-15 (8)	3.69
C(8)	1602 (12)	6194 (7)	1106 (16)	80 (12)	25 (5)	107 (21)	9 (7)	18 (14)	3 (8)	4.13
C(9)	2024 (13)	6608 (7)	0010 (17)	91 (14)	17 (4)	163 (26)	-8 (7)	10 (16)	-9 (8)	4.10
C(10)	1440 (16)	7188 (9)	-0348 (22)	100 (17)	43 (7)	217 (34)	-8 (9)	-39 (22)	-9 (13)	6.18
C(11)	0449 (17)	7340 (9)	0313 (23)	121 (19)	36 (7)	230 (37)	-18 (10)	-17 (23)	-15 (14)	5.77
C(12)	0003 (14)	6930 (9)	1390 (21)	81 (13)	33 (6)	256 (35)	4 (8)	-65 (21)	-41 (12)	5.40
C(13)	3374 (12)	5534 (7)	1176 (19)	61 (11)	22 (5)	213 (29)	1 (6)	4 (16)	-4 (9)	3.67
C(14)	4044 (11)	6067 (7)	2007 (18)	57 (10)	29 (5)	147 (24)	-7 (6)	4 (14)	-3 (9)	4.12
C(15)	5288 (10)	5957 (7)	1690 (16)	61 (10)	23 (5)	136 (23)	-2 (6)	-11 (14)	24 (9)	3.98
C(16)	5698 (13)	5151 (8)	3652 (15)	81 (13)	36 (5)	87 (20)	8 (7)	4 (14)	9 (8)	4.84
C(17)	5934 (12)	4408 (9)	3925 (21)	65 (12)	47 (7)	223 (33)	6 (8)	46 (17)	8 (13)	5.29
C(18)	7176 (15)	3469 (9)	3484 (26)	118 (17)	38 (6)	349 (48)	25 (9)	16 (26)	77 (15)	7.66
C(19)	6923 (12)	4325 (8)	1645 (17)	79 (12)	37 (6)	130 (25)	1 (7)	-4 (15)	1 (10)	4.93
C(20)	6688 (11)	5081 (8)	1389 (15)	66 (11)	44 (6)	77 (20)	9 (7)	-1 (13)	20 (9)	3.95
C(21)	3192 (18)	3104 (9)	0453 (27)	136 (21)	33 (7)	380 (52)	9 (10)	97 (30)	21 (16)	7.71
C(22)	3673 (24)	2454 (14)	0180 (39)	207 (33)	69 (10)	559 (75)	26 (16)	210 (45)	-11 (24)	12.43

TABLE 20

BOND LENGTHS AND ANGLES AND ESTIMATED STANDARD DEVIATIONS

The e.s.d.'s in the bond lengths × 10^2 and the e.s.d.'s in the bond angles are given in parentheses.

Bond	ℓ	Angle	θ
C(1) - C(2)	1.38(2) Å	C(6) - C(1) - C(2)	124.8°(1.4°)
C(2) - C(3)	1.40(2)	C(1) - C(2) - C(3)	117.7 (1.2)
C(3) - C(4)	1.42(2)	C(2) - C(3) - C(4)	119.0 (1.2)
C(4) - C(5)	1.41(2)	C(3) - C(4) - C(5)	120.4 (1.4)
C(5) - C(6)	1.37(2)	C(4) - C(5) - C(6)	121.2 (1.4)
C(6) - C(1)	1.41(2)	C(5) - C(6) - C(1)	116.7 (1.4)
C(7) - C(8)	1.39(2)	C(12) - C(7) - C(8)	121.7 (1.5)
C(8) - C(9)	1.40(2)	C(7) - C(8) - C(9)	119.8 (1.4)
C(9) - C(10)	1.39(2$_5$)	C(8) - C(9) - C(10)	118.5 (1.6)
C(10) - C(11)	1.38(2$_5$)	C(9) - C(10) - C(11)	121.1 (1.9)
C(11) - C(12)	1.39(2$_5$)	C(10) - C(11) - C(12)	121.4 (1.9)
C(12) - C(7)	1.40(2)	C(11) - C(12) - C(7)	117.4 (1.6)
C(4) - S(2)	1.78(1$_5$)	S(2) - C(4) - C(3)	118.9 (1.1)
C(7) - S(2)	1.78(1$_5$)	C(4) - C(3) - N(1)	118.4 (1.3)
C(3) - N(1)	1.39(1$_5$)	C(3) - N(1) - C(8)	118.1 (1.0)
C(8) - N(1)	1.46(1$_5$)	N(1) - C(8) - C(7)	118.8 (1.3)
S(1) - C(1)	1.79(1$_5$)	C(8) - C(7) - S(2)	118.7 (1.2)
S(1) - C(21)	1.82(2)	C(7) - S(2) - C(4)	99.0 (0.7)
C(21) - C(22)	1.44(3)	C(6) - C(1) - S(1)	113.7 (1.2)
N(1) - C(13)	1.48(1$_5$)	C(2) - C(1) - S(1)	121.5 (1.1)
C(13) - C(14)	1.54(2)	C(1) - S(1) - C(21)	104.0 (0.8)
C(14) - C(15)	1.54(2)	S(1) - C(21) - C(22)	109.2 (1.6)
C(15) - N(2)	1.46(1$_5$)	C(3) - N(1) - C(13)	118.7 (1.1)
N(2) - C(16)	1.52(2)	C(8) - N(1) - C(13)	117.0 (1.1)
C(16) - C(17)	1.53(2)	N(1) - C(13) - C(14)	110.3 (1.2)
C(17) - N(3)	1.43(2)	C(13) - C(14) - C(15)	108.6 (1.2)
N(3) - C(19)	1.48(2)	C(14) - C(15) - N(2)	111.3 (1.1)
C(19) - C(20)	1.55(2)	C(15) - N(2) - C(16)	112.2 (1.2)
C(20) - N(2)	1.46(1$_5$)	C(15) - N(2) - C(20)	113.7 (1.1)
N(3) - C(18)	1.49(2)	C(20) - N(2) - C(16)	107.9 (1.1)
		N(2) - C(16) - C(17)	109.1 (1.3)
		C(16) - C(17) - N(3)	111.9 (1.4)
		C(17) - N(3) - C(19)	112.4 (1.3)
		N(3) - C(19) - C(20)	108.8 (1.3)
		C(19) - C(20) - N(2)	110.6 (1.2)
		C(17) - N(3) - C(18)	112.7 (1.5)
		C(19) - N(3) - C(18)	109.1 (1.5)
		C(2) - C(3) - N(1)	122.6 (1.2)
		N(1) - C(8) - C(9)	121.4 (1.4)
		C(5) - C(4) - S(2)	120.6 (1.2)
		S(2) - C(7) - C(12)	119.6 (1.3)

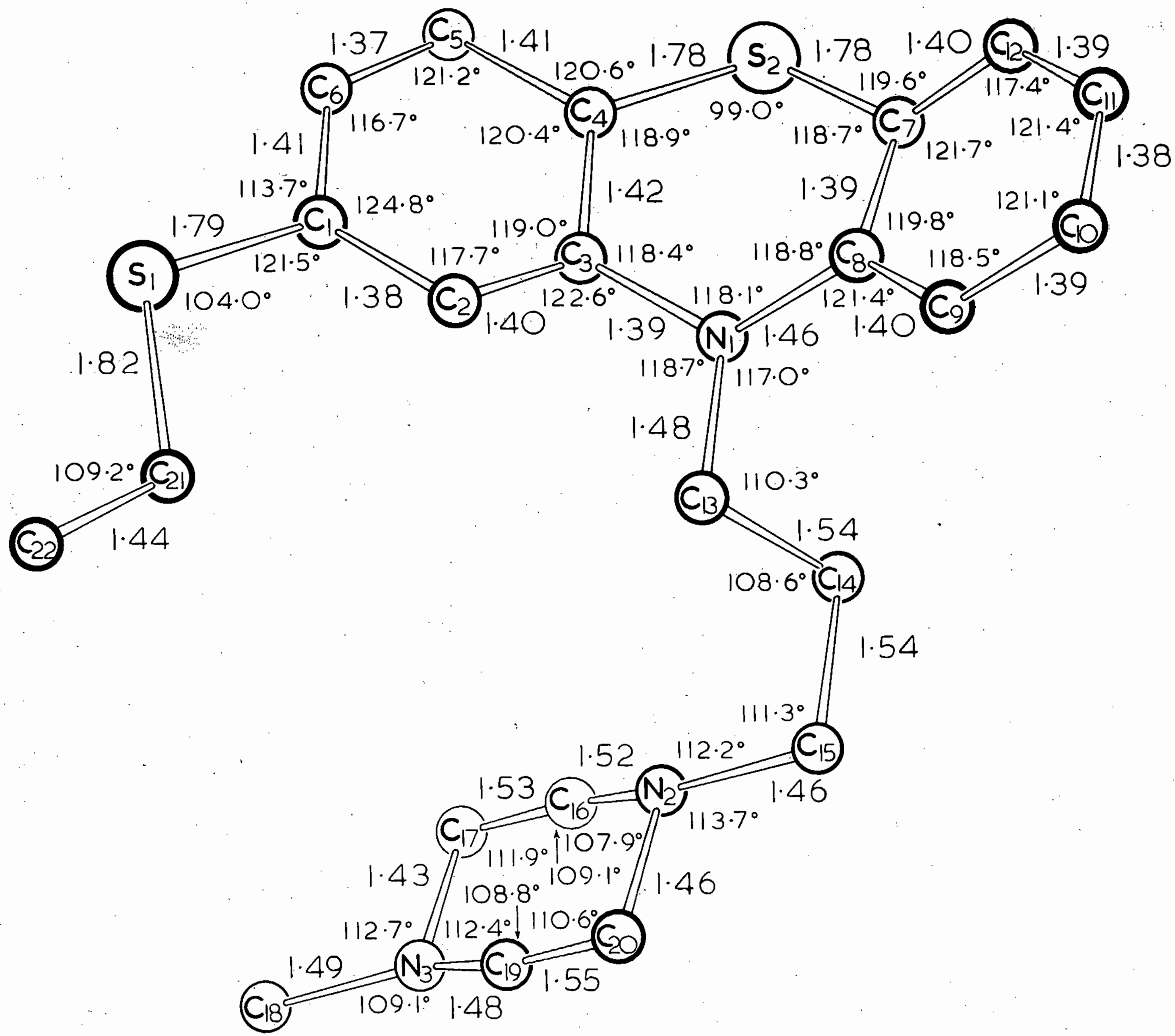


FIGURE 16

BOND LENGTHS AND ANGLES

13. Discussion

The structure of the molecule and bond lengths and angles are shown in Fig. 16. Table 20 lists the interatomic distances and angles with associated e.s.d.'s, which were calculated from the results of the last anisotropic refinement cycle using the Busing, Martin & Levy (1964) program ORFFE.

(a) The Tricyclic Group

All C-C distances are between 1.37 and 1.42 Å, and the mean length of the C-C bonds within the first benzene ring, C(1) - C(6), which is 1.396 Å, and that of the second ring, C(7) - C(12), 1.393 Å, compare favourably with accepted values for benzene (1.397 Å, Pauling, 1960; 1.394 Å, Sutton, 1965).

Applying Cruickshank's (1949) criterion to the two C-N(1) bonds of 1.39, 1.46 ± 0.015 Å which should be expected to be chemically equivalent, the value obtained for $\frac{\ell_1 - \ell_2}{(\sigma_1^2 + \sigma_2^2)^{\frac{1}{2}}}$ is 3.5, which is in the zone of probable significance. However, no explanation for a significant difference in the two bonds can be suggested, as the N(1) atom is in a symmetrical environment and secluded from short intermolecular contacts. It appears more likely that the discrepancy would be reduced if the following factors, inter alia, were taken into consideration:-

1) the bonds are not independent since a change in the position of N(1) would affect both lengths;
2) corrections for temperature librations, which could amount to as much as 0.02 Å (Cruickshank, 1960), have not been applied; and
3) as discussed above, the number of measurable reflections was unfortunately limited by the nature of the compound.

Abrahams (1956) has calculated a value of 1.82 Å for a C-S single bond distance, which is close to the sum of the covalent radii for sulphur and carbon given by Pauling (1960). Using Pauling's relation

$$R = R_S - (R_S - R_D) \frac{3x}{(2x + 1)}$$

for the resonance-interatomic distance curve, the value of x obtained for the C-S(2) bond lengths, which are both 1.78 ± 0.015 Å, is 0.07, i.e. they have 7% double bond character. (Abrahams' bond-order, bond-length curve gives a value of 25%).

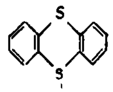
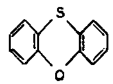
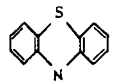
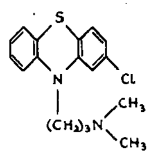
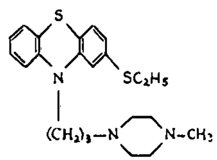
The angles of the heterocyclic ring are all approximately 118° except for the C-S-C angle which is 99.0 ± 0.7°. Table 21 lists a number of compounds of interest for comparative purposes. It can be seen that C-S-C angles are all in the range 93°-100°, and that all C-S lengths are shorter than a C-S single bond. Further, the tricyclic molecules which contain S are folded with a dihedral angle of approximately 140°.

The size of the C-S-C angles, the folding of the molecules and the contraction of the C-S bonds in substituted anthracene-type molecules may possibly be explained in terms of π-bonding molecular orbitals formed by the carbon atoms with the $3d$ orbitals of the sulphur. The suggestion that S in heterocyclic compounds can have a decet of electrons was first made by Schomaker & Pauling (1939), and calculations of the molecular orbitals in thiophene were subsequently performed by Longuet-Higgins (1949). In thiethylperazine it is possible that the $2p_z$ atomic orbitals of the C atoms conjugate with hybrid orbitals formed from linear combinations of the $3p_z$, $3d_{yz}$ and $3d_{xz}$ atomic orbitals of the S atom.

The best planes for the two benzene rings were calculated by the method of Schomaker, Waser, Marsh & Bergman (1959), with the program LSPLANE and are given in Table 22, together with the individual displacements of atoms from the planes. The maximum deviation of the C atoms is 0.03 Å so that the benzene rings may be regarded as planar, within the limits of error. The S and N atoms

TABLE 21

COMPARISON OF BOND LENGTHS AND ANGLES IN HETEROCYCLIC COMPOUNDS CONTAINING SULPHUR

Compound	Chemical Formula	C-S-C (°)	C-S (Å)	C-N (Å)	Dihedral angle(°)	Reference
Thiophene		91±4 92.16±0.10	1.74 ±0.03 1.714±0.002	- -	- -	(a) (b) (c)
Thianthrene		100±0.5	1.76 ±0.015	-	128	(d) (e) (f)
Phenoxthionine		97.7±0.03	1.75±0.04	-	138	(d) (g) (h)
Phenothiazine		99.6±1.5	1.770±0.003	1.406±0.002	153.3	(d) (g) (i)
Chlorpromazine		97.3±0.3	1.75±0.01	1.41±0.01	139.4	(j)
Thiethylperazine		99.0±0.7	1.78±0.02	1.425±0.02	139.0	(k)

a) Schomaker & Pauling (1939).
b) Longuet-Higgins (1949).
c) Bak, Christensen, Hansen-Nygaard & Rastrup-Anderson (1961).
d) Cullinane & Rees (1940).
e) Lynton & Cox (1956).
f) Rowe & Post (1958)
g) Wood, McCale & Williams (1941).
h) Hosoya (1966).
i) Bell, Blount, Briscoe & Freeman (1968).
j) McDowell (1969).
k) Present work.

TABLE 22

MEAN PLANE PARAMETERS AND DEVIATIONS OF ATOMS FROM THE PLANE

I Benzene ring, C(1) - C(6).

$$-0.4453x + 0.1523y - 0.8824z = -0.6911$$

	Deviation		Deviation
C(1)	-0.029Å	S(2)	-0.137 Å
C(2)	0.030	N(1)	-0.045
C(3)	-0.005	S(1)	-0.061
C(4)	-0.015	C(13)	-0.395
C(5)	0.025		
C(6)	-0.006		

II Benzene ring, C(7) - C(12)

$$0.4963x + 0.5202y + 0.6950z = 8.0889$$

	Deviation		Deviation
C(7)	0.001 Å	S(2)	-0.003 Å
C(8)	0.007	N(1)	0.006
C(9)	-0.013	C(13)	0.427
C(10)	0.010		
C(11)	-0.002		
C(12)	-0.004		

III Piperazine ring,

N(2) - C(16) - C(17) - N(3) - C(19) - C(20)

$$0.7107x + 0.6009y + 0.3657z = 11.9721$$

	Deviation		Deviation
N(2)	-0.145 Å	C(18)	-0.489 Å
C(16)	0.318	C(15)	0.272
C(17)	-0.279		
N(3)	0.085		
C(19)	-0.299		
C(20)	0.320		

TABLE 23

INTRAMOLECULAR AND INTERMOLECULAR DISTANCES

The e.s.d.'s × 10^2 are given in parentheses.

The superscripts^{i},^{ii},^{iii} and ^{iv} denote the equivalent positions at $(x+1,y,z)$, $(\frac{1}{2}-x,\bar{y},\frac{1}{2}+z)$, $(\frac{1}{2}+x,\frac{1}{2}-y,\bar{z})$ and $(\bar{x},\frac{1}{2}+y,\frac{1}{2}-z)$ respectively.

C(2) - C(21)	3.03(2) Å
C(13) - C(2)	2.88(1_5)
C(13) - C(9)	2.90(2)
C(13) - N(2)	2.87(2)
C(22) - C(18)	5.59(4)
S(1) - S(2)	6.29(1)
S(2) - C(21^{ii})	3.69(2)
C(1) - C(9^{ii})	3.94(2)
C(4) - C(13^{ii})	3.89(2)
C(5) - C(13^{ii})	3.94(2)
C(5) - C(15^{ii})	3.89(2)
C(7) - C(21^{ii})	3.85(3)
C(11) - C(6^{iv})	3.90(3)
C(12) - S(1^{iv})	3.89(2)
C(16) - C(3^{ii})	3.92(2)
C(16) - C(4^{ii})	3.77(2)
C(16 - C(5^{ii})	3.76(2)
C(16) - C(6^{ii})	3.95(2)
C(17) - C(4^{ii})	3.82(2)
C(17) - C(7^{ii})	3.55(2)
C(17) - C(12^{ii})	3.68(2)
C(18) - C(6^{i})	3.98(2)
C(18) - C(11^{ii})	3.93(4)
C(18) - C(12^{ii})	3.84(3)
C(19) - C(5^{i})	3.66(2)
N(3) - C(5^{i})	3.63(2)
C(22) - S(1^{iii})	3.92(3)
C(22) - C(6^{iii})	3.84(3)

however do not lie in both planes of the aromatic rings, as is also the case in phenothiazine and in chlorpromazine. The dihedral angle between the planes is 139.0°, in close agreement with chlorpromazine, but differing by 14° from phenothiazine.

(b) Aliphatic Chains and Piperazine Ring

When the C(21) - C(22) bond is compared with a C-C single bond of 1.54 Å the value obtained for $\frac{\delta \ell}{\sigma}$ is 3.3, which again is in the zone of probable significance. Double-bond character of a C-C bond in such a position would be most unusual, and it does seem more likely that the standard deviations in the positions of the two atoms with high thermal motion may have been underestimated.

The difference in the angles C(2) - C(1) - S(1), 121.5°, and C(6) - C(1) - S(1), 113.7° , is probably caused by steric hindrance between the hydrogen atoms attached to C(2) and C(21). The angles centred at N(1) are nearly trigonally symmetric, and the angles between the chain carbons are quite close to the tetrahedral value (109°28').

The average value of the six C-N bonds associated with the piperazine ring is 1.47 Å, which is close to the value given by Kennard (1962) for three-covalent nitrogen (1.472 Å for sp^2 - sp^3 bond type), but the individual bonds vary between 1.43 and 1.52 Å. It was shown by Kitajgorodskij (1965) that the effects of intermolecular interaction on molecular shape are generally small, but that the packing can affect the molecular geometry in some cases. The atoms of the piperazine ring have a number of contacts shorter than 3.85 Å, as shown in Table 23; also the distance between C(16) and benzene ring I of molecule (2) is 3.67 Å, and that between C(17) and benzene ring II is 3.73 Å. It seems possible that the slight distortions in the ring may partly be attributed to molecular close packing requirements.

The best plane for the piperazine ring and the deviation of the atoms are given in Table 22, from which it can be seen that the ring has the chair configuration.

(c) Molecular Packing

In Figs. 17 and 18 the packing in the crystals is viewed along the *c* and *a* axes respectively. Table 23 gives some intramolecular non-bonded distances and intermolecular contacts less than 4.0 Å. The molecules are arranged in parallel undulating layers perpendicular to the *y*-*z* plane.

(d) Optical activity

Unlike chlorpromazine, one enantiomorph only appears in the crystal. The molecular dissymmetry suggested the study of the optical activity of solutions of the compound. A 2½% solution of powdered thiethylperazine in absolute alcohol was tested in the polarimeter using sodium D light and, as expected, was found to be optically inactive. Further experiments are now in progress to investigate the optical activity of this material and it is hoped to establish whether the crystals exhibit enantiomorphism.

FIGURE 17

THE STRUCTURE VIEWED DOWN THE *C* - AXIS

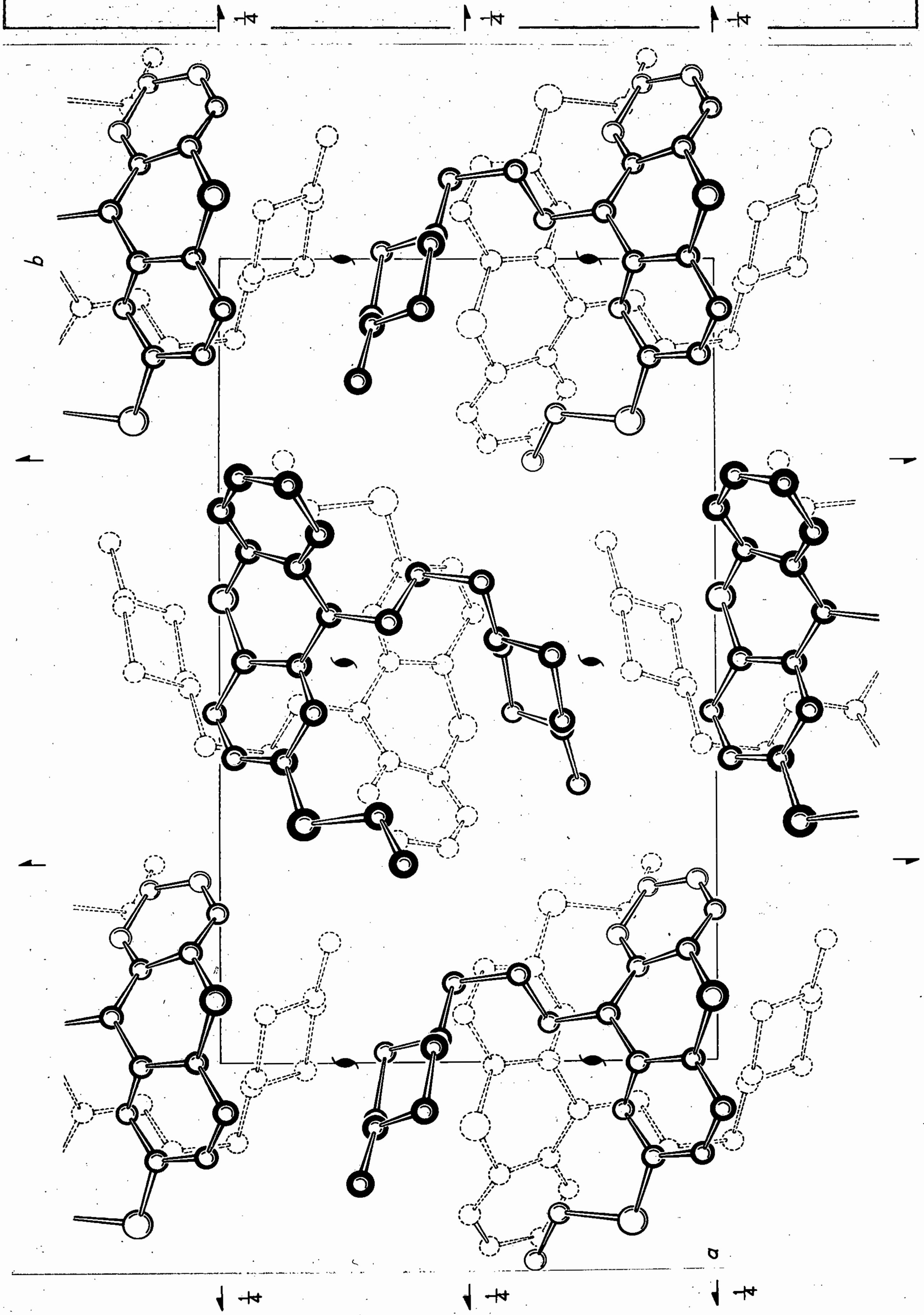
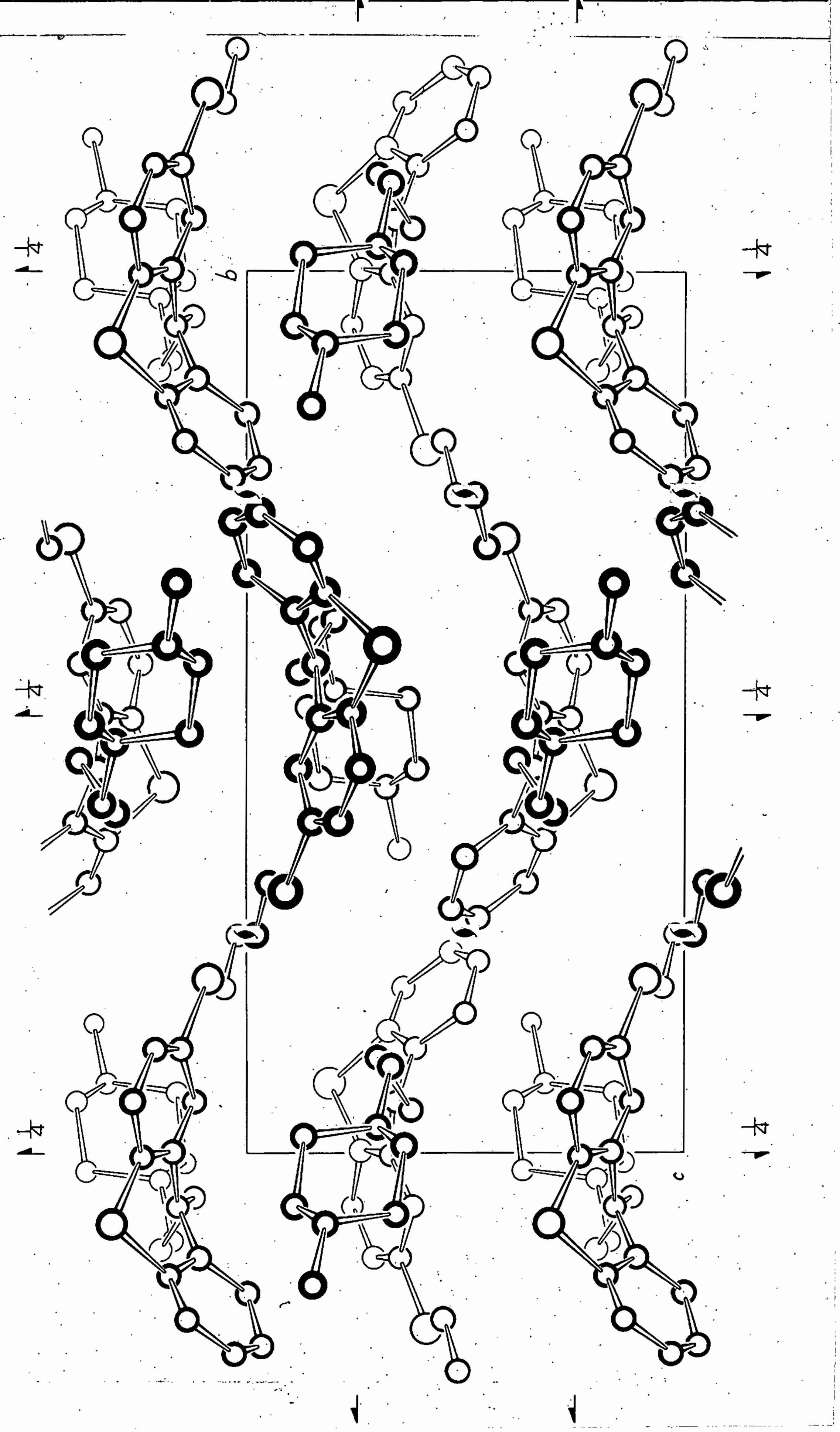


FIGURE 18

THE STRUCTURE VIEWED DOWN THE a - AXIS



SECTION D

MOLECULAR STRUCTURE AND THE MECHANISM OF ACTION OF THE PHENOTHIAZINES

1. Introduction

The crystallographic study of the phenothiazine derivatives has considerable intrinsic interest, but in addition it is hoped to discover the relation between the structural parameters and the mechanism of action of the drugs *in vivo*. Clearly this is beyond the scope of the crystallographer acting alone. All that can be attempted here is to outline certain relevant aspects and to present a fascinating theory suggested by Szent-Györgyi (1960) which is compatible with the results of the present study.

Even this ostensibly simple task is difficult. As an indication, almost 7000 references published between 1952 and 1962 are listed in *Progress in Drug Research* (1963), and over 3,500 synthetic derivatives of phenothiazine are tabulated. The difficulties are further accentuated as most of the articles are in foreign languages which, incidentally, demonstrates the world-wide interest in the subject.

2. Properties and uses of the phenothiazine derivatives

The phenothiazines are famous principally for their tranquillizing action and the consequent uses for the suppression of symptom-complexes of the major psychiatric diseases. Certain phenothiazines control abnormal and excessive psychomotor activity in schizophrenia, manic-depressive psychoses and the motor restlessness of the organic psychoses; they are effective in blocking conditioned avoidance responses, relieving anxiety and tension states and improving thought disorder. (Denham, 1964; Sainsbury, 1964).

Since the introduction of chlorpromazine "a great number of hospital beds have become empty, because among all diseases it was schizophrenia which had permanently occupied the most hospital space". (Szent-Györgyi, 1960) "States of excitement, whether schizophrenic, manic or confusional in origin, respond well and violent patients become docile and cooperative. Subjective anxiety and distress arising from mental tension or sudden emotional shock are controlled. Delusions, hallucinations and obsessional and hypochondriacal conditions no longer cause distress". (Buxton Hopkin, 1955). It is not surprising that "a passionate interest was provoked by the apparition of 4560 R.P. (chlorpromazine) into therapeutic practice". (Lespagnol, *circa* 1960)

Apart from the value in psychiatry, the phenothiazines have widespread clinical uses. They possess in varying degrees anti-cholinergic, anti-histiminic and anti-parkinsonian properties; they antagonise the peripheral action of adrenaline; extensive use is made of their anti-emetic properties (prochlorperazine and thiethylperazine). Some phenothiazines are used to alleviate intractable pain by inducing a state of indifference; some, particularly chlorpromazine and promethazine, are used as adjuvants in anaesthesia to reduce the amount of anaesthetic required and to reduce operative shock and post-operative discomfort. Certain symptoms of skin diseases, such as pruritis, are benefitted by chlorpromazine; relief is given in acute bronchospastic states such as asthma; acute alcoholism is controlled more easily by certain phenothiazines than by any other therapeutic measures.

To sum up, Professor Lespagnol may well be believed when he states: "il n'existe certainement aucun foyer où les dérivés de la phénothiazine n'aient pénétré à l'occasion d'une quelconque maladie", which may be loosely translated as "there exists certainly no hearth where the derivatives of phenothiazine have not penetrated upon the occasion of some illness or other".

3. Mode of action of the phenothiazines

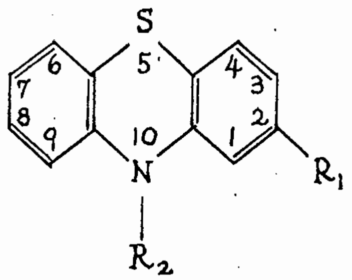
It is not easy to summarise the numerous tentative explanations of the highly complex nature of the drugs' action mechanism but the one fact certainly emerges that "the mode of action of the phenothiazines is far from being well understood". (Sexton, 1963).

The biochemical and biophysical actions of the phenothiazines may be concisely presented by quoting a summary of the article of Richter (1964):-

The phenothiazines are *in vitro* powerful metabolic blocking agents and they act in the respiratory chain at the flavoprotein level. However, it is doubtful if this is their main action *in vivo* because the brain levels of ATP and creatine phosphate are relatively high after treatment with chlorpromazine, whereas the reverse would be expected if, as has been suggested, the drug competed with flavine adenine dinucleotide. In low doses chlorpromazine has been shown to accelerate the turnover rate of phospholipids *in vivo*. This effect is specific for the phospholipids of the brain; it is of particular interest as the phenothiazines are concentrated in the mitochondrial membranes of the nerve cells which are rich in phospholipids.

Although the phenothiazines have been shown to interfere with the transport of many metabolites in the brain, this action is not specific for the brain and, as it is shown also by other surface-active substances, it is difficult to relate the effect directly to the highly specific pharmacological action on the central nervous system. The psychotropically active phenothiazines however, all have a central sympatholytic action: it has been suggested that this may be due to their interfering with the transport of biogenic amines from the point of synthesis to the storage sites or to the receptor sites in the brain.

4. Structure functional relationships within the phenothiazine class



The phenothiazine "nucleus".
($R_1 = R_2 = H$)

Although the phenothiazine derivatives form a vast class, the most useful ones have substituents at positions 2 (R_1) and 10 (R_2), and may be considered as consisting of two parts:-

(a) The R_2 substituent

Effects on the higher centres of the nervous system only appear in earnest when the side chain consists of three carbon atoms in a row. It could be surmised that a substance of this molecular size fits best into the biological binding site.

The R_2 side chains may be classified into three chemical groups:- aliphatic (dimethylaminopropyl), piperidine and piperazine. There are pharmacological differences between these groups, for instance, in the treatment of schizophrenia piperazine derivatives are more effective for apathetic and withdrawn patients, while the restless and agitated benefit from the aliphatic group. However, according to Sainsbury (1964) the differences are not sufficiently consistent and characteristic to develop even a tentative theory of neuro-pharmacological action in terms of variations in the chemical structure.

(b) The phenothiazine nucleus and R_1 substituent

The phenothiazine nucleus consists of a system of conjugated double bonds having an extensive π pool of delocalised electrons and lone pairs of electrons on the N and S atoms. As Pullman & Pullman have shown (1964), this type of structure is highly significant. All the essential biomolecules involved in the processes of life are constituted of completely, or at least partially, conjugated resonating systems, rich in delocalised π electrons. Further, the most important molecules are conjugated heterocycles containing atoms with lone pairs such as nitrogen,oxygen or sulphur, which by undergoing suitable changes in their valence states are able to bring about the most economical and spectacular transformations.

The only three solved structures, chlorpromazine, thiethylperazine and phenothiazine, have atomic parameters of the tricyclic group which are closely similar (Table 21) apart from the different dihedral angle in phenothiazine, which may be of importance.

The psychotropic potency is affected by the substituent forming all or part of R_1 in the ascending order H, S, Cℓ, F. It is significant to note that this is in parallel with the order of increasing electronegativity of the atoms.

5. Mechanism of action on a submolecular level

From all available evidence it appears probable that the key to the understanding of the subtle biological action should be sought not in the molecular dimension, but in the submolecular or subatomic dimension of electrons, governed by quantum mechanics.

In his outstanding exposition, *Introduction to a Submolecular Biology*, Szent-Gyorgyi produces much evidence to support the theory that charge transfer is involved in the biological activity of the drugs.

In charge transfer, one electron only is transferred from the highest filled orbital of a donor molecule to the lowest empty orbital of an acceptor molecule, without necessarily involving any rearrangment within the molecule; the transfer involves no change in configuration in classical chemical terms, but results in a transfer of energy. The ionization potential, IP, of the donor and the electron affinity, EA, of the acceptor become dominating factors, and the change in energy accompanying the electron transfer will be approximately equal to EA - IP.

Orbital energies

Using the LCAO approximation of the molecular orbital method, the energy levels of many molecules taking part in different biological reactions have been determined (Pullman & Pullman, 1958; Karreman, *circa* 1960). The use of quantum-mechanical methods for the investigation of the electronic structure of big molecules is generally restricted to π-electron systems, however, as discussed in Section 4(b), such systems are omnipresent in essential biomolecules.

The energy of the electron on an orbital,

$$E = \alpha + k\beta,$$

where α is the coulomb integral and β the exchange integral between two carbons. For similar chemical substances α and β are fairly constant so that the value of k gives a measure of the energy. As a rule the filled "bonding" levels have positive k, the empty "antibonding" levels have negative k. Small values of $+k$ or $-k$ mean that the substance is a good donor or acceptor of electrons respectively. In exceptional cases the k of the highest filled orbital can even be negative, which means "antibonding" character, an extremely good donor.

The $+k$ for the highest filled orbital is a linear function of the IP (Mulliken, 1948), while the $-k$ for the lowest empty orbital is related, although more indirectly, to the EA. (A strong donor has a low IP; a strong acceptor has a high EA.)

Charge transfer and drug action

If charge transfer is involved in the mechanism of drug action, then a drug having extraordinary pharmacological properties could be expected to have exceptional qualities as electron donor or acceptor. This is undoubtedly the case with chlorpromazine. A drug with a unique biological activity, it was found (Karreman, Isenberg & Szent-Györgyi, 1959) to have a most unusual antibonding highest filled orbital in its normal stable state, and is thus an exceedingly strong monovalent electron donor capable of forming stable charge transfer complexes.

Thiethylperazine has little tranquillizing action, prochlorperazine has five times and trifluperazine ten times the potency of chlorpromazine. The determination of the *k*-values of these substances would be of considerable interest as it might lead to a direct relationship between potency and electron-donating properties, and further substantiate the theory that pharmacological action is actually due to a charge transfer.

The *k*-values of phenothiazine have been determined (Karreman, *circa* 1960; Malrieu & Pullman, 1964) and are found to be quite close to those of chlorpromazine. (For chlorpromazine, $k = -0.217$ for highest filled, and -1.000 for lowest empty orbital; for phenothiazine, the corresponding values are -0.210 and -1.000.) As phenothiazine is not a psychotropically potent drug it is evident therefore that the donor-acceptor properties must be combined with a suitable molecular complement, which it appears likely is provided by the R_2 substituent.

d Orbitals

In the molecular-orbital calculations of Karreman, Isenberg & Szent-Györgyi (1959) for chlorpromazine and phenothiazine, and in those of Pullman & Pullman (1959) for a related compound, leuco-methylene blue† (for which k = -0.232), the participation of the d orbitals of sulphur in the overall electronic delocalisation was not taken into account. In 1961 Orloff & Fitts explicitly introduced these orbitals into the Hückel approximation as follows:-

$$E_i = \alpha + k_i\beta$$

α is coulomb integral for a carbon atom,
β is resonance integral for π electrons of an aromatic C-C double bond,
$(\alpha + \delta\beta)$ is the coulomb integral of a heteroatom,
$\rho\beta$ is resonance integral of a heteroatom,
where δ and ρ are dimensionless parameters characteristic of the heteroatom and its bonding in the molecule.

Assuming that the $3p$ and $3d$ orbitals of sulphur form three hybrid orbitals, the overlap parameter ρ_{ss} for two of the hybridized orbitals is taken to be 1.0, which is close to the value assigned to the S of thiophene by Longuet-Higgins (1949); the third hybrid orbital, being orthogonal to the first two and not participating in the C-S-C bonding, has vanishing resonance integrals.

The results of the calculations of Orloff & Fitts gave values of k_i for the highest filled molecular orbital which were <u>positive</u> for all three molecules, leuco-methylene blue, k_i = 0.168, phenothiazine, 0.208, chlorpromazine, 0.191; the antibonding character of the highest filled molecular orbital has disappeared.

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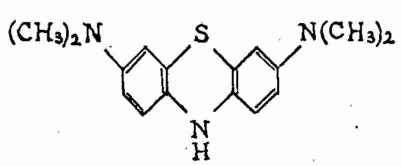
†Leuco-methylene blue has the chemical formula



The authors emphasise however that as the Hückel method is only a crude approximation to the complete quantum-mechanical problem, and the values selected for the parameters δ and ρ are somewhat arbitrary, there is no rigorous reason for giving preference to either of the two methods.

Although the k-values of Orloff & Fitts are positive, they still indicate however that the molecules studied are very good electron donors. As a basis for comparison, *d*-lysergic acid diethylamide and serotonin, drugs also having a strong action on the central nervous system, both very good donors, have k-values of 0.218 and 0.461 respectively, for the highest filled molecular orbital (Karreman, Isenberg & Szent-Györgyi, 1959).

Non-planarity

As Malrieu & Pullman have shown for phenothiazine (1964), the energy of the highest filled molecular orbital is a sensitive function of the geometrical configuration of the molecule, and therefore the non-planarity of the tricyclic group, resulting in a net decrease of electronic delocalisation, would lead to a distribution of molecular orbitals appreciably different from that calculated for the planar form.

It is hoped that the results of the present study will make a substantial contribution to the field of quantum biochemistry, because it terminates conjecture about the molecular configuration and atomic parameters of the two phenothiazine derivatives. More precise calculations of the k-values and other important quantities appertaining to the molecules should now be possible.

Experimental evidence

Summing up the quantum-mechanical results obtained by the various different methods, the general conclusion drawn by Pullman & Pullman (1963) is that irrespective of the question whether the highest filled molecular orbital is or is not antibonding in character, the phenothiazines are nevertheless exceptionally good electron donors.

This conclusion is amply supported by experimental evidence (Karreman, Isenberg & Szent-Györgyi, 1959; Szent-Györgyi, 1960; Pullman & Pullman, 1963). To mention a few examples: the phenothiazines, particularly chlorpromazine, form charge-transfer complexes with a variety of electron acceptors, such as riboflavin; free radicals are readily formed, by electron departure, during electrochemical oxidation of phenothiazine; measurement of the solid state ionization potential of phenothiazine gave the very small value of 4.36 eV, which may be considered as direct confirmation of the theory.

Schizophrenia

Szent-Györgyi (1960) brings forward some evidence in support of the fascinating suggestion that schizophrenia may be due to the presence of a strong electron acceptor in the blood. If such is the case, it seems probable that the curative influence is exerted by chlorpromazine by the donation of the desired electron, which affords additional evidence that, if the configuration of the molecule is such as to supply the right key to fit into the slot, acceptor-donor properties may underlie pharmacological action.

It is exhilarating to think that precise investigation of the nature of the electron acceptor causing the damage could open up vast fields which may lead eventually not only to permanent cure for the psychotically abnormal, but also to the prevention of this tragic disease.

APPENDIX A

MATHEMATICAL AND COMPUTING METHODS

1. Mathematical relations required for the Structure Factor, Patterson and Fourier programmes

For purposes of computation the geometrical structure factors A and B which are characteristic of the space group, and the modifications which arise in the forms of A and B for particular sets of planes are required. In order to calculate the Codewords for the Patterson and Fourier programmes for different space groups, it is necessary to know how the absolute value and the phase of the scattered wave change when h, k and/or l change sign, i.e. the relationships between $F(hkl)$, $F(\bar{h}kl)$, $F(h\bar{k}l)$ and $F(\bar{h}\bar{k}l)$ must be established for the space group concerned. For a non-centrosymmetric structure the variations in the phase angle $\alpha(hkl)$, as well as the amplitudes of the scattered wave $|F(hkl)|$, with changes in sign of h, k and/or l must be calculated.

Most of the information is given in *International Tables I* (1952). However, the author discovered an error in the space group *Pm* (*b* as unique axis):- P.377, $\alpha(\bar{h}kl) = \alpha(hk\bar{l})$ is incorrect, and it can be shown that the relation should be $\alpha(\bar{h}kl) = -\alpha(hk\bar{l})$. It was therefore considered advisable to calculate <u>all</u> the relations for the space groups of chlorpromazine, phenothiazine and thiethylperazine, *Pbca*, *Pnma* and $P2_12_12_1$, respectively.

The derivations were based entirely on the coordinates of equivalent positions and are reported in sub-sections (c), (d) and (f). To fill in the whole picture, the conditions for non-extinction and the complete terms of the electron density formula were also derived and are given in sub-sections (e) and (g) respectively.

Sub-section (h) is concerned with the derivation of the electron density expression in the form which is used for the summation in the Fourier programme; (i) describes the meaning and application of the Codewords in the Patterson and Fourier computations and, finally, sub-section (j) gives the calculations of the Codewords for the space groups *Pbca*, *Pnma* and $P2_12_12_1$.

(a) THE STRUCTURE FACTOR

$$F_{hkl} = \sum_{j \text{ over all atoms}} f_j \, e^{2\pi i (hx_j + ky_j + lz_j)}$$

| $\alpha_j = 2\pi(hx_j + ky_j + lz_j)$ 1

| x_j, y_j, z_j fract. coords.

| j = total no. of atoms.

| $f = f_0 e^{-B \sin^2\theta/\lambda^2}$

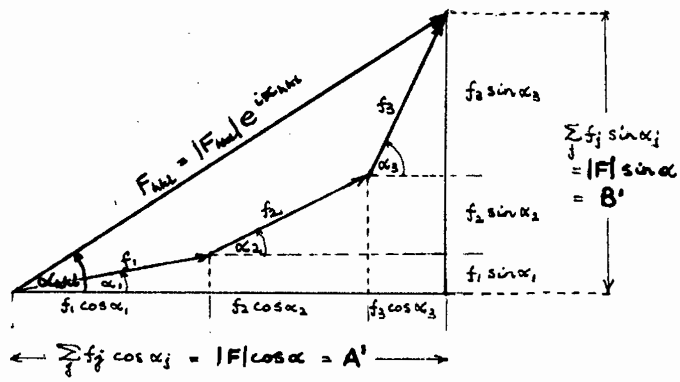
$$= \sum_j f_j e^{i\alpha_j}$$

$$= \sum_j f_j \cos\alpha_j + i \sum_j f_j \sin\alpha_j$$ 2

$$= \{f_1 \cos\alpha_1 + f_2 \cos\alpha_2 + \dots + f_j \cos\alpha_j\} + i\{f_1 \sin\alpha_1 + \dots + f_j \sin\alpha_j\}$$

$$F_{hkl} = |F_{hkl}| \cos\alpha_{hkl} + i|F_{hkl}| \sin\alpha_{hkl}$$ fr. diagram 3

$$F_{hkl} = |F_{hkl}| e^{i\alpha_{hkl}}$$ 4



$$\text{mag. of } f_1 e^{i\alpha_1} = f_1 = \sqrt{(f_1 \cos\alpha_1)^2 + (f_1 \sin\alpha_1)^2}$$

$$\text{mag. of } F_{hkl} = |F_{hkl}| = \sqrt{(\textstyle\sum_j f_j \cos\alpha_j)^2 + (\sum_j f_j \sin\alpha_j)^2}$$

$$= \sqrt{A'^2 + B'^2}$$

$$|F_{hkl}|^2 = A'^2_{hkl} + B'^2_{hkl}$$ 5

$$F_{hkl} = A'_{hkl} + iB'_{hkl} \quad \text{(fr. 2)}$$ 6 $$F_{\bar{h}\bar{k}\bar{l}} = A'_{hkl} - iB'_{hkl} \quad \text{(fr. 11)}$$ 7

The structure factor is a complex quantity, introducing both amplit. + phase of scatt. wave. A' → real part, B' → imag. $|F_{hkl}|$ = amplit. of scatt. wave.; α_{hkl} = phase angle of scatt. wave.

$$A'_{hkl} = |F_{hkl}| \cos\alpha_{hkl} \overset{\text{(fr. 3 + 6)}}{=} \sum_{j \text{ over all atoms}} f_j \cos\alpha_j \overset{\text{(fr. 2 + 6)}}{=} \sum_j f_j \cos 2\pi(hx_j + ky_j + lz_j)$$ 8

$$B'_{hkl} = |F_{hkl}| \sin\alpha_{hkl} = \sum_j f_j \sin\alpha_j = \sum_j f_j \sin 2\pi(hx_j + ky_j + lz_j)$$ 9

The phase angle, α_{hkl}

$$\tan\alpha_{hkl} = \frac{B'_{hkl}}{A'_{hkl}} = \frac{\sum_j f_j \sin\alpha_j}{\sum_j f_j \cos\alpha_j}$$ 10

Friedel's Law. $F^*_{hkl} = F_{\bar{h}\bar{k}\bar{l}}$ (for ρ real - always understood) 11

$$F_{hkl} = |F_{hkl}| e^{i\alpha_{hkl}}$$

$$F^*_{hkl} = |F_{hkl}| e^{-i\alpha_{hkl}}$$

$$F_{\bar{h}\bar{k}\bar{l}} = |F_{\bar{h}\bar{k}\bar{l}}| e^{i\alpha_{\bar{h}\bar{k}\bar{l}}}$$

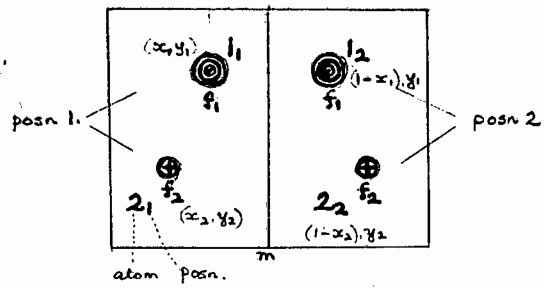
} equal, by Fried. Law. $\therefore$

$$|F_{hkl}| = |F_{\bar{h}\bar{k}\bar{l}}| \quad \text{always}$$ 12

$$\alpha_{\bar{h}\bar{k}\bar{l}} = -\alpha_{hkl} \quad \text{always.}$$ 13

$$\therefore \begin{cases} A'_{hkl} = A'_{\bar{h}\bar{k}\bar{l}} \\ A'_{\bar{h}kl} = A'_{h\bar{k}\bar{l}} \\ A'_{h\bar{k}l} = A'_{\bar{h}k\bar{l}} \\ A'_{\bar{h}\bar{k}l} = A'_{hk\bar{l}} \end{cases} \qquad \begin{cases} B'_{hkl} = -B'_{\bar{h}\bar{k}\bar{l}} \\ B'_{\bar{h}kl} = -B'_{h\bar{k}\bar{l}} \\ B'_{h\bar{k}l} = -B'_{\bar{h}k\bar{l}} \\ B'_{\bar{h}\bar{k}l} = -B'_{hk\bar{l}} \end{cases} \text{always}$$ 14

(b) EQUIVALENT POSITIONS: THE MEANING OF A AND B



$$F = A' + iB' \quad \text{(fr. 6)}$$

$$A' = \sum_{\substack{j \\ \text{over all atoms}}} f_j \cos \alpha_j \quad \text{(fr. 8)}$$

j = total no. of atoms
r = no. of independent atoms

$$A' = \sum_{\substack{\text{kinds} \\ \text{of atom}}} f_r \underbrace{\sum_{\text{posns.}} \cos 2\pi(hx_r + ky_r + lz_r)}_{A_r} \qquad 15$$

$$= \sum_{\substack{r \\ \text{kinds of atom}}} f_r A_r \qquad 16$$

$$= f_1 \underbrace{\sum_{\text{posns}} \cos 2\pi(hx_1 + ky_1 + lz_1)}_{A_1} + f_2 \underbrace{\sum_{\text{posns}} \cos 2\pi(hx_2 + ky_2 + lz_2)}_{A_2}$$

$$= \underbrace{f_1 \Big[\underbrace{\cos \underbrace{2\pi(hx_1 + ky_1)}_{\alpha_{11}}}_{A_{11}} + \underbrace{\cos \underbrace{2\pi(h(1-x_1) + ky_1)}_{\alpha_{12}}}_{A_{12}} \Big]}_{A_1}$$

first kind of atom, atom 1_1 and its sym. equiv. atom 1_2

$$+ \underbrace{f_2 \Big[\underbrace{\cos \underbrace{2\pi(hx_2 + ky_2)}_{\alpha_{21}}}_{A_{21}} + \underbrace{\cos \underbrace{2\pi(h(1-x_2) + ky_2)}_{\alpha_{22}}}_{A_{22}} \Big]}_{A_2}$$

second kind of atom, atom 2_1 and its sym. equiv., atom 2_2

$$A = \sum_{\text{posns}} \cos 2\pi(hx + ky + lz) \qquad 17$$

$$= A_1(x_1, y_1, z_1) = A_2(x_2, y_2, z_2) = A_r(x_r, y_r, z_r)$$

A is characteristic of space group, dependent entirely on the coords. of equivalent posns.
A_1 is the same fn. of (x_1, y_1, z_1) as A_2 is of (x_2, y_2, z_2) or as A_r is of (x_r, y_r, z_r), or in general, as A is of (x, y, z)

Similarly for B. $$B = \sum_{\text{posns}} \sin 2\pi(hx + ky + lz) \qquad 18$$

From Friedel's Law:

$$|F_{\bar{h}\bar{k}\bar{l}}| \cos\{2\pi(h\bar{X} + k\bar{Y} + l\bar{Z}) - \alpha_{\bar{h}\bar{k}\bar{l}}\} = |F_{\bar{h}\bar{k}\bar{l}}| \cos\{2\pi(hX + kY + lZ) + \alpha_{\bar{h}\bar{k}\bar{l}}\}$$
$$= |F_{hkl}| \cos\{2\pi(hX + kY + lZ) - \alpha_{hkl}\} \qquad 19$$

$(\cos(-\theta - \alpha) = \cos(\theta + \alpha))$

(c) GEOMETRICAL STRUCTURE FACTORS: THE GENERAL FORMS OF A AND B FOR SPACE GROUPS Pbca AND Pnma

Pbca

Coords. of equiv. posns: $\pm$ x, y, z; $\frac{1}{2}+x, \frac{1}{2}-y, \bar{z}$; $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$; $\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$

$$A = 2\left[\cos 2\pi(hx+ky+lz) + \cos 2\pi\left(-hx-ky+lz-\frac{l-h}{2}\right) + \cos 2\pi\left(hx-ky-lz-\frac{h-k}{2}\right) + \cos 2\pi\left(-hx+ky-lz-\frac{k-l}{2}\right)\right]$$

$$= 4\left[\cos 2\pi\left(lz-\frac{l-h}{4}\right)\cos 2\pi\left(hx+ky+\frac{l-h}{4}\right) + \cos 2\pi\left(-lz+\frac{l-h}{4}\right)\cos 2\pi\left(hx-ky-\frac{h-k}{4}+\frac{k-l}{4}\right)\right]$$

$$-\frac{h-k}{4}-\frac{k-l}{4} \qquad -\frac{h+k-k+l}{4}$$

$$= 8\cos 2\pi\left(lz-\frac{l-h}{4}\right)\left\{\cos 2\pi\left(hx+\frac{\frac{l-h}{4}-\frac{h-k}{4}+\frac{k-l}{4}}{2}\right)\cos 2\pi\left(ky+\frac{\frac{l-h}{4}+\frac{h-k}{4}-\frac{k-l}{4}}{2}\right)\right\}$$

$$+\frac{l-h-h+k+k-l}{8} \qquad +\frac{l-h+h-k-k+l}{8}$$

$$-\frac{h-k}{4} \qquad -\frac{k-l}{4}$$

$$A = 8\cos 2\pi\left(lz-\frac{l-h}{4}\right)\cos 2\pi\left(hx-\frac{h-k}{4}\right)\cos 2\pi\left(ky-\frac{k-l}{4}\right)$$

$$B = 0$$

Pnma

Coords. of equiv. posns: $\pm$ x, y, z; $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}-z$; $\bar{x}, \frac{1}{2}+y, \bar{z}$; $\frac{1}{2}-x, \bar{y}, \frac{1}{2}+z$

$$A = 2\left[\cos 2\pi(hx+ky+lz) + \cos 2\pi\left(-hx-ky+lz+\frac{h+l}{2}\right) + \cos 2\pi\left(hx-ky-lz-\frac{h+k+l}{2}\right) + \cos 2\pi\left(-hx+ky-lz+\frac{k}{2}\right)\right]$$

$$= 4\left[\cos 2\pi\left(lz+\frac{h+l}{4}\right)\cos 2\pi\left(hx+ky-\frac{h+l}{4}\right) + \cos 2\pi\left(-lz-\frac{h+l}{4}\right)\cos 2\pi\left(hx-ky-\frac{h+k+l}{4}-\frac{k}{4}\right)\right]$$

$$= 8\cos 2\pi\left(lz+\frac{h+l}{4}\right)\left\{\cos 2\pi\left(hx\frac{-\frac{h+l}{4}-\frac{h+k+l}{4}-\frac{k}{4}}{2}\right)\cos 2\pi\left(ky\frac{-\frac{h+l}{4}+\frac{h+k+l}{4}+\frac{k}{4}}{2}\right)\right\}$$

$$+\frac{-h-l-h-k-l-k}{8} \qquad +\frac{-h-l+h+k+l+k}{8}$$

$$-\frac{h+k+l}{4} \qquad +\frac{k}{4}$$

$$A = 8\cos 2\pi\left(hx-\frac{h+k+l}{4}\right)\cos 2\pi\left(ky+\frac{k}{4}\right)\cos 2\pi\left(lz+\frac{h+l}{4}\right)$$

$$B = 0$$

NOTES. 1) Factor of 2 in A: $A = \cos 2\pi(hx+ky+lz) + \cos 2\pi(-hx-ky-lz)$ and same for each pair of equiv. posns. opposite to each other w.r.t. centre sym.

2) $B = 0$, because each pair of oppos. equiv. posns. cancel.
e.g. $B = \sin 2\pi(hx+ky+lz) + \sin 2\pi(-hx-ky-lz) = 0$

3) $\cos 2\pi\left(\phi+\frac{h+k}{2}\right) = \cos 2\pi\left(\phi-\frac{h+k}{2}\right)$ since h and k are integers.
(This means changing the angle by $2\pi(h+k) = 0$).
Care must be taken in choosing the signs for the $\frac{h}{2}, \frac{k}{2}$ .. etc.

(d) SIMPLIFICATION OF A AND B IN SPECIAL CASES

Pbca

$$A = 8\cos 2\pi\left(hx - \frac{h-k}{4}\right)\cos 2\pi\left(ky - \frac{k-l}{4}\right)\cos 2\pi\left(lz - \frac{l-h}{4}\right)$$

$$B = 0$$

$$\left.\begin{aligned} h+k &= 2n \\ k+l &= 2n \end{aligned}\right\} \qquad \begin{aligned} h-k &= 2n-2k = 2n \\ k-l &= 2n-2l = 2n \\ l-h &= -(h-k)-(k-l) = -2n-2n = -4n \end{aligned}$$

$$A = 8\cos\Big(2\pi hx - \underbrace{2\pi\tfrac{2n}{4}}_{-n\pi}\Big)\cos\Big(2\pi ky - \underbrace{2\pi\tfrac{2n}{4}}_{-n\pi}\Big)\cos\Big(2\pi lz + \underbrace{2\pi\tfrac{4n}{4}}_{+2n\pi}\Big)$$

$$= 8(-\cos 2\pi hx)(-\cos 2\pi ky)(+\cos 2\pi lz)$$

$$\underline{A = 8\cos 2\pi hx \cdot \cos 2\pi ky \cdot \cos 2\pi lz}$$

$$\left.\begin{aligned} h+k &= 2n \\ k+l &= 2n+1 \end{aligned}\right\} \qquad \begin{aligned} h-k &= 2n-2k = 2n \\ k-l &= (2n+1)-2l = 2n+1 \\ l-h &= -(h-k)-(k-l) = -2n-(2n+1) = -4n-1 \end{aligned}$$

$$A = 8\cos\Big(2\pi hx - \underbrace{2\pi\tfrac{2n}{4}}_{-n\pi}\Big)\cos\Big(2\pi ky - \underbrace{2\pi\tfrac{2n+1}{4}}_{-(n+\frac{1}{2})\pi}\Big)\cos\Big(2\pi lz + \underbrace{2\pi\tfrac{4n+1}{4}}_{+(2n+\frac{1}{2})\pi}\Big)$$

$$= 8(-\cos 2\pi hx)(-\sin 2\pi ky)(-\sin 2\pi lz)$$

$$\underline{A = -8\cos 2\pi hx \cdot \sin 2\pi ky \cdot \sin 2\pi lz}$$

$$= 0 \text{ if } k = 0 \text{ or } l = 0$$

$$\left.\begin{aligned} h+k &= 2n+1 \\ k+l &= 2n \end{aligned}\right\} \qquad \begin{aligned} h-k &= 2n+1-2k = 2n+1 \\ k-l &= 2n-2k = 2n \\ l-h &= -(2n+1)-2n = -4n-1 \end{aligned}$$

$$A = 8\cos\Big(2\pi hx - \underbrace{2\pi\tfrac{2n+1}{4}}_{-(n+\frac{1}{2})\pi}\Big)\cos\Big(2\pi ky - \underbrace{2\pi\tfrac{2n}{4}}_{-n\pi}\Big)\cos\Big(2\pi lz + \underbrace{2\pi\tfrac{4n+1}{4}}_{+(2n+\frac{1}{2})\pi}\Big)$$

$$= 8(-\sin 2\pi hx)(-\cos 2\pi ky)(-\sin 2\pi lz)$$

$$\underline{A = -8\sin 2\pi hx \cdot \cos 2\pi ky \cdot \sin 2\pi lz}$$

$$= 0 \text{ if } h = 0 \text{ or } l = 0$$

$$\left.\begin{aligned} h+k &= 2n+1 \\ k+l &= 2n+1 \end{aligned}\right\} \qquad \begin{aligned} h-k &= 2n+1-2k = 2n+1 \\ k-l &= 2n+1-2l = 2n+1 \\ l-h &= -(2n+1)-(2n+1) = -4n-2 \end{aligned}$$

$$A = 8\cos\Big(2\pi hx - \underbrace{2\pi\tfrac{2n+1}{4}}_{-(n+\frac{1}{2})\pi}\Big)\cos\Big(2\pi ky - \underbrace{2\pi\tfrac{2n+1}{4}}_{-(n+\frac{1}{2})\pi}\Big)\cos\Big(2\pi lz + \underbrace{2\pi\tfrac{4n+2}{4}}_{+(2n+1)\pi}\Big)$$

$$= 8(-\sin 2\pi hx)(-\sin 2\pi ky)(-\cos 2\pi lz)$$

$$\underline{A = -8\sin 2\pi hx \cdot \sin 2\pi ky \cdot \cos 2\pi lz}$$

$$= 0 \text{ if } h = 0 \text{ or } k = 0$$

Pnma

$$A = 8\cos 2\pi\left(hx - \frac{h+k+l}{4}\right)\cos 2\pi\left(ky + \frac{k}{4}\right)\cos 2\pi\left(lz + \frac{h+l}{4}\right)$$

$$B = 0$$

$$\left.\begin{array}{l} h+l = 2n \\ k = 2n \end{array}\right\}$$

$$A = 8\cos\left(2\pi hx - 2\pi\frac{4n}{4}\right)\cos\left(2\pi ky + 2\pi\frac{2n}{4}\right)\cos\left(2\pi lz + 2\pi\frac{2n}{4}\right)$$

$$\qquad -2n\pi \qquad\qquad +n\pi \qquad\qquad +n\pi$$

$$= 8(+\cos 2\pi hx)(-\cos 2\pi ky)(-\cos 2\pi lz)$$

$$\underline{A = 8\cos 2\pi hx.\cos 2\pi ky.\cos 2\pi lz}$$

$$\left.\begin{array}{l} h+l = 2n \\ k = 2n+1 \end{array}\right\}$$

$$A = 8\cos\left(2\pi hx - 2\pi\frac{4n+1}{4}\right)\cos\left(2\pi ky + 2\pi\frac{2n+1}{4}\right)\cos\left(2\pi lz + 2\pi\frac{2n}{4}\right)$$

$$\qquad -(2n+\tfrac{1}{4})\pi \qquad\qquad +(n+\tfrac{1}{4})\pi \qquad\qquad +n\pi$$

$$= 8(+\sin 2\pi hx)(+\sin 2\pi ky)(-\cos 2\pi lz)$$

$$\underline{A = -8\sin 2\pi hx.\sin 2\pi ky.\cos 2\pi lz}$$

$$= 0 \text{ if } h = 0$$

$$\left.\begin{array}{l} h+l = 2n+1 \\ k = 2n \end{array}\right\}$$

$$A = 8\cos\left(2\pi hx - 2\pi\frac{4n+1}{4}\right)\cos\left(2\pi ky + 2\pi\frac{2n}{4}\right)\cos\left(2\pi lz + 2\pi\frac{2n+1}{4}\right)$$

$$\qquad -(2n+\tfrac{1}{2})\pi \qquad\qquad +n\pi \qquad\qquad +(n+\tfrac{1}{2})\pi$$

$$= 8(+\sin 2\pi hx)(-\cos 2\pi ky)(+\sin 2\pi lz)$$

$$\underline{A = -8\sin 2\pi hx.\cos 2\pi ky.\sin 2\pi lz}$$

$$= 0 \text{ if } h = 0 \text{ or } l = 0$$

$$\left.\begin{array}{l} h+l = 2n+1 \\ k = 2n+1 \end{array}\right\}$$

$$A = 8\cos\left(2\pi hx - 2\pi\frac{4n+2}{4}\right)\cos\left(2\pi ky + 2\pi\frac{2n+1}{4}\right)\cos\left(2\pi lz + 2\pi\frac{2n+1}{4}\right)$$

$$\qquad -(2n+1)\pi \qquad\qquad +(n+\tfrac{1}{4})\pi \qquad\qquad +(n+\tfrac{1}{2})\pi$$

$$= 8(-\cos 2\pi hx)(+\sin 2\pi ky)(+\sin 2\pi lz)$$

$$\underline{A = -8\cos 2\pi hx.\sin 2\pi ky.\sin 2\pi lz}$$

$$= 0 \text{ if } l = 0$$

(e) CONDITIONS FOR NON-EXTINCTION

One zero index.

Pbca

$h+k=2n$, $k+l=2n+1$	$F=0$ if $k=0$	(h0l) planes, reflect. are missing if	$h=2n$, $l=2n+1$	②
	or $l=0$	(hk0)	$h=2n+1$, $k=2n+1$	③
$h+k=2n+1$, $k+l=2n$	$F=0$ if $h=0$	(0kl)	$k=2n+1$, $l=2n+1$	①
	or $l=0$	(hk0)	$k=2n$, $h=2n+1$	③
$h+k=2n+1$, $k+l=2n+1$	$F=0$ if $h=0$	(0kl)	$k=2n+1$, $l=2n$	①
	or $k=0$	(h0l)	$h=2n+1$, $l=2n+1$	②

① (0kl) planes, reflections are missing if k odd, l even or odd : (0kl) $k=2n$
② (h0l) .. .. l .., h .. .. .. : (h0l) $l=2n$
③ (hk0) .. .. h .., k .. .. .. : (hk0) $h=2n$

These check with conditions on P. 150.

Pnma

$h+l=2n$, $k=2n+1$	$F=0$ if $h=0$	(0kl) planes, reflect. are missing if	l even, k odd	①
$h+l=2n+1$, $k=2n$	$F=0$ if $h=0$	(0kl)	l odd, k even	①
	or $l=0$	(hk0)	h odd, k even	②
$h+l=2n+1$, $k=2n+1$	$F=0$ if $l=0$	(hk0)	h odd, k odd	②

① (0kl) missing for {l even, k odd} or {l odd, k even} — (0kl) $k+l=2n$

② (hk0) .. .. h odd, k even or odd — (hk0) $h=2n$

These check with conditions on P. 151.

(International Tables I)

Two zero indices.

Pbca

(1)	$h+k=2n$, $k+l=2n$	$A = 8\cos 2\pi hx . \cos 2\pi ky \cos 2\pi lz$	e-e
(2)	$h+k=2n$, $k+l=2n+1$	$A = -8\cos 2\pi hx . \sin 2\pi ky . \sin 2\pi lz$	e-o
(3)	$h+k=2n+1$, $k+l=2n$	$A = -8\sin 2\pi hx . \cos 2\pi ky . \sin 2\pi lz$	o-e
(4)	$h+k=2n+1$, $k+l=2n+1$	$A = -8\sin 2\pi hx . \sin 2\pi ky . \cos 2\pi lz$	o-o

h00: h even: (1) → $A = 8\cos 2\pi hx (1).(1) = 8\cos 2\pi hx$
(2) → $A = -8\cos 2\pi hx (0).(0) = 0$
(3) + (4) cannot apply, for if $k=0$, $h+k$ = odd.
h odd: (1) + (2) cannot apply.
(3) → $A = -8\sin(0) \cdots = 0$ $(l=0)$
(4) → $A = -8\sin(0) \cdots = 0$ $(k=0)$
<u>So we have h00, h odd missing.</u>

0k0: k even: (1) → $A = 8\cos(0) . \cos 2\pi ky . \cos(0) = 8\cos 2\pi ky$
(2) → $A = -8 \cdots \sin(0) = 0$
(3) + (4) cannot apply, ∵ $h=0$
k odd: (3) → $A = -8\sin(0)\cos 2\pi ky . \sin(0) = 0$
(4) → $A = -8\sin(0)\sin 2\pi ky . \cos(0) = 0$
<u>Thus for 0k0, k odd missing.</u>

00l: l even: (1) → $A = 8\cos 2\pi lz$
(2) + (4) cannot apply.
(3) → $A = -8\sin(0)\cos(0)\sin 2\pi lz = 0$
l odd: (1) + (3) cannot apply
(2) + (4) → 0
<u>Thus for 00l, l odd missing.</u>

0kl: k+l even: (1) → $A = 8\cos(0)\cos 2\pi ky . \cos 2\pi lz$.
(3) → $A = 8\sin(0) \ldots = 0$, (2) + (4) cannot apply.
k+l odd: (2) → $A = -8\sin 2\pi ky . \sin 2\pi lz$
(4) → 0, (1) + (3) cannot apply.

h0l: h+l even: (1) → $A = 8\cos 2\pi hx . \cos 2\pi lz$
(4) → 0, (2) + (3) cannot apply.
h+l odd: (2) → $A = -8\cos 2\pi hx . \sin(0) . \sin 2\pi lz = 0$
(3) → $A = -8\sin 2\pi hx . \sin 2\pi lz$
(1) + (4) cannot apply.

hk0: h+k even: (1) → $A = 8\cos 2\pi hx . \cos 2\pi ky$.
(2) → 0, (3) + (4) cannot apply.
h+k odd: (3) → 0, (2) + (1) " "
(4) → $A = -8\sin 2\pi hx . \sin 2\pi ky$.

Pnma

(1) $\left.\begin{matrix} h+l = 2n \\ k = 2n \end{matrix}\right\}$ $A = 8 \cos 2\pi hx \cdot \cos 2\pi ky \cdot \cos 2\pi lz$ e-e

(2) $\left.\begin{matrix} h+l = 2n \\ k = 2n+1 \end{matrix}\right\}$ $A = -8 \sin 2\pi hx \cdot \sin 2\pi ky \cdot \cos 2\pi lz$ e-o

(3) $\left.\begin{matrix} h+l = 2n+1 \\ k = 2n \end{matrix}\right\}$ $A = -8 \sin 2\pi hx \cdot \cos 2\pi ky \cdot \sin 2\pi lz$ o-e

(4) $\left.\begin{matrix} h+l = 2n+1 \\ k = 2n+1 \end{matrix}\right\}$ $A = -8 \cos 2\pi hx \cdot \sin 2\pi ky \cdot \sin 2\pi lz$ o-o

h00: h even: (1) $A = 8 \cos 2\pi hx$ (2) $A = 0$ h odd: (3) $A = 0$ (4) $A = 0$	h odd missing. h00 : $h = 2n$
0k0: k even: (1) $A = 8 \cos 2\pi ky$ (3) $A = 0$ k odd: (2) $A = 0$ (4) $A = 0$	k odd missing 0k0 : $k = 2n$
00l: l even: (1) $A = 8 \cos 2\pi lz$ (2) $A = 0$ l odd: (3) $A = 0$ (4) $A = 0$	l odd missing 00l : $l = 2n$
0kl: k even: (1) $A = 8 \cos 2\pi ky \cdot \cos 2\pi lz$. (3) $A = 0$ k odd: (2) $A = 0$ (4) $A = -8 \sin 2\pi ky \cdot \sin 2\pi lz$	k+l even (1) $A = 8 \cos 2\pi ky \cdot \cos 2\pi lz$ (4) $A = -8 \sin 2\pi ky \cdot \sin 2\pi lz$ k+l odd (2) $A = 0$ (3) $A = 0$
h0l: h+l even: (1) $A = 8 \cos 2\pi hx \cdot \cos 2\pi lz$ (2) $A = 0$ h+l odd: (3) $A = -8 \sin 2\pi hx \cdot \sin 2\pi lz$ (4) $A = 0$	(This is ambiguous.)
hk0 k even: (1) $A = 8 \cos 2\pi hx \cdot \cos 2\pi ky$ (3) $A = 0$ k odd: (2) $A = -8 \sin 2\pi hx \cdot \sin 2\pi ky$ (4) $A = 0$	h+k even (1) $A = 8 \cos 2\pi hx \cdot \cos 2\pi ky$ (4) $A = 0$ h+k odd (2) $A = -8 \sin 2\pi hx \cdot \sin 2\pi ky$ (3) $A = 0$

(f) RELATIONSHIPS BETWEEN F's

Pbca

$$A = 8\cos 2\pi\left(hx - \frac{h-k}{4}\right)\cos 2\pi\left(ky - \frac{k-l}{4}\right)\cos 2\pi\left(lz - \frac{l-h}{4}\right)$$

e-e	$h+k=2n$, $k+l=2n$	$A = +8\cos 2\pi hx \, . \, \cos 2\pi ky \, . \, \cos 2\pi lz$ $F_{hkl} = F_{\bar h kl} = F_{h\bar k l} = F_{hk\bar l} \; (= F_{\bar h\bar k l} = F_{\bar h\bar k\bar l})$
e-o	$h+k=2n$, $k+l=2n+1$	$A = -8\cos 2\pi hx \, . \, \sin 2\pi ky \, . \, \sin 2\pi lz$ $F_{hkl} = F_{\bar h kl} = -F_{h\bar k l} = -F_{hk\bar l} \; (= -F_{\bar h\bar k l} = F_{\bar h\bar k\bar l})$
o-e	$h+k=2n+1$, $k+l=2n$	$A = -8\sin 2\pi hx \, . \, \cos 2\pi ky \, . \, \sin 2\pi lz$ $F_{hkl} = -F_{\bar h kl} = F_{h\bar k l} = -F_{hk\bar l} \; (= -F_{\bar h\bar k l} = F_{\bar h\bar k\bar l})$
o-o	$h+k=2n+1$, $k+l=2n+1$	$A = -8\sin 2\pi hx \, . \, \sin 2\pi ky \, . \, \cos 2\pi lz$ $F_{hkl} = -F_{\bar h kl} = -F_{h\bar k l} = F_{hk\bar l} \; (= F_{\bar h\bar k l} = F_{\bar h\bar k\bar l})$

The A's have been derived in Section (d)
The relationships between the F's have been obtained by substituting, for example, $-h$ for $+h$ in the relation for A (which, for a centrosym. space group, $A' = \Sigma fA = F_{hkl}$) to give $F_{\bar h kl}$. If the sign of A is not changed by this substitution, as is the case if $A = \cos 2\pi hx \ldots\ldots$, then $F_{hkl} = F_{\bar h kl}$. If the sign is changed, as is the case if $A = \sin 2\pi hx \ldots\,$, then $F_{hkl} = -F_{\bar h kl}$. etc.

Pnma

$$A = 8\cos 2\pi\left(hx - \frac{h+k+l}{4}\right)\cos 2\pi\left(ky + \frac{k}{4}\right)\cos 2\pi\left(lz + \frac{h+l}{4}\right)$$

e-e	$h+l=2n$, $k=2n$	$A = 8\cos 2\pi hx \, . \, \cos 2\pi ky \, . \, \cos 2\pi lz$ $F_{hkl} = F_{\bar h kl} = F_{h\bar k l} = F_{hk\bar l} \; (= F_{\bar h\bar k l} = F_{\bar h\bar k\bar l})$
e-o	$h+l=2n$, $k=2n+1$	$A = -8\sin 2\pi hx \, . \, \sin 2\pi ky \, . \, \cos 2\pi lz$ $F_{hkl} = -F_{\bar h kl} = -F_{h\bar k l} = F_{hk\bar l} \; (= F_{\bar h\bar k l})$
o-e	$h+l=2n+1$, $k=2n$	$A = -8\sin 2\pi hx \, . \, \cos 2\pi ky \, . \, \sin 2\pi lz$ $F_{hkl} = -F_{\bar h kl} = F_{h\bar k l} = -F_{hk\bar l} \; (= -F_{\bar h\bar k l})$
o-o	$h+l=2n+1$, $k=2n+1$	$A = -8\cos 2\pi hx \, . \, \sin 2\pi ky \, . \, \sin 2\pi lz$ $F_{hkl} = F_{\bar h kl} = -F_{h\bar k l} = -F_{hk\bar l} \; (= -F_{\bar h\bar k l})$

These results check with P.407 (Pbca) + P.408 (Pnma)

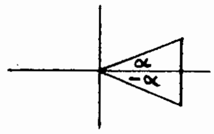
$P2_12_12_1$

The calculations performed up to this stage for $P2_12_12_1$ were so closely similar to the calculations for Pbca that they have been excluded, although available. (The A's are identical except for a factor of 2; the B's are readily obtained.) However, the relations between the phase angles in $P2_12_12_1$, which do not occur in Pbca, must be dealt with separately as follows:–

In general,
$$A_{hkl} = |F_{hkl}| \cos\alpha_{hkl}$$
$$B_{hkl} = |F_{hkl}| \sin\alpha_{hkl}$$
$$\alpha_{\bar{h}\bar{k}\bar{l}} = -\alpha_{hkl}$$
} from Section (a)

For $P2_12_12_1$, $|F_{hkl}| = |F_{\bar{h}kl}| = |F_{h\bar{k}l}| = |F_{hk\bar{l}}| = |F_{\bar{h}\bar{k}l}|$

e-e $h+k=2n$, $k+l=2n$ | $A = 4\cos 2\pi hx.\cos 2\pi ky.\cos 2\pi lz$; $B = -4\sin 2\pi hx.\sin 2\pi ky.\sin 2\pi lz$

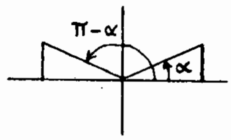


$$A_{hkl} = A_{\bar{h}kl} = |F_{\bar{h}kl}|\cos\alpha_{\bar{h}kl}$$
$$B_{hkl} = -B_{\bar{h}kl} = -|F_{\bar{h}kl}|\sin\alpha_{\bar{h}kl}$$
$$\therefore \cos\alpha_{hkl} = \cos\alpha_{\bar{h}kl}, \quad \sin\alpha_{hkl} = -\sin\alpha_{\bar{h}kl} \quad \therefore \underline{\alpha_{hkl} = -\alpha_{\bar{h}kl}}$$

$$A_{hkl} = A_{h\bar{k}l} = |F_{h\bar{k}l}|\cos\alpha_{h\bar{k}l}$$
$$B_{hkl} = -B_{h\bar{k}l} = -|F_{h\bar{k}l}|\sin\alpha_{h\bar{k}l} \quad \therefore \underline{\alpha_{hkl} = -\alpha_{h\bar{k}l}}$$

$$A_{hkl} = A_{hk\bar{l}} = A_{\bar{h}\bar{k}l} \quad (\text{fr. Sect.(a)})$$
$$B_{hkl} = -B_{hk\bar{l}} = B_{\bar{h}\bar{k}l} \quad " \quad " \quad " \quad \therefore \underline{\alpha_{hkl} = -\alpha_{hk\bar{l}} = \alpha_{\bar{h}\bar{k}l}}$$

e-o $h+k=2n$, $k+l=2n+1$ | $A = -4\cos 2\pi hx.\sin 2\pi ky.\sin 2\pi lz$; $B = 4\sin 2\pi hx.\cos 2\pi ky.\cos 2\pi lz$



$$A_{hkl} = A_{\bar{h}kl}, \quad B_{hkl} = -B_{\bar{h}kl} \quad \therefore \underline{\alpha_{hkl} = -\alpha_{\bar{h}kl}}$$

$$A_{hkl} = -A_{h\bar{k}l}, \quad B_{hkl} = B_{h\bar{k}l} \quad \therefore \cos\alpha_{hkl} = -\cos\alpha_{h\bar{k}l}, \quad \sin\alpha_{hkl} = \sin\alpha_{h\bar{k}l} \quad \therefore \underline{\alpha_{hkl} = \pi - \alpha_{h\bar{k}l}}$$

$$A_{hkl} = -A_{hk\bar{l}}, \quad B_{hkl} = B_{hk\bar{l}} \quad \therefore \underline{\alpha_{hkl} = \pi - \alpha_{hk\bar{l}} = \pi + \alpha_{\bar{h}\bar{k}l}}$$

o-e $h+k=2n+1$, $k+l=2n$ | $A = -4\sin 2\pi hx.\cos 2\pi ky.\sin 2\pi lz$; $B = 4\cos 2\pi hx.\sin 2\pi ky.\cos 2\pi lz$

The relations between α's are similarly obtained.

$$\underline{\alpha_{hkl} = \pi - \alpha_{\bar{h}kl}}$$
$$\underline{\alpha_{hkl} = -\alpha_{h\bar{k}l}}$$
$$\underline{\alpha_{hkl} = \pi - \alpha_{hk\bar{l}} = \pi + \alpha_{\bar{h}\bar{k}l}}$$

o-o $h+k=2n+1$, $k+l=2n+1$ | $A = -4\sin 2\pi hx.\sin 2\pi ky.\cos 2\pi lz$; $B = 4\cos 2\pi hx.\cos 2\pi ky.\sin 2\pi lz$

$$\underline{\alpha_{hkl} = \pi - \alpha_{\bar{h}kl}}$$
$$\underline{\alpha_{hkl} = \pi - \alpha_{h\bar{k}l}}$$
$$\underline{\alpha_{hkl} = -\alpha_{hk\bar{l}} = \alpha_{\bar{h}\bar{k}l}}$$

(g) COMPLETE TERMS OF ELECTRON DENSITY FORMULA

Pbca

The "general term" of the electron density formula can be written down direct from the results obtained in Section (d):-

$$\rho(XYZ) = \frac{8}{V}\sum_0^\infty{}^h \sum_0^\infty{}^k \sum_0^\infty{}^l \overset{\substack{h+k=2n\\k+l=2n}}{F_{hkl}} \cos 2\pi hX . \cos 2\pi kY . \cos 2\pi lZ$$

$$- \frac{8}{V}\sum_0^\infty \sum_0^\infty \sum_0^\infty \overset{\substack{h+k=2n\\k+l=2n+1}}{F_{hkl}} \cos 2\pi hX . \sin 2\pi kY . \sin 2\pi lZ$$

$$- \frac{8}{V}\sum_0^\infty \sum_0^\infty \sum_0^\infty \overset{\substack{h+k=2n+1\\k+l=2n}}{F_{hkl}} \sin 2\pi hX . \cos 2\pi kY . \sin 2\pi lZ$$

$$- \frac{8}{V}\sum_0^\infty \sum_0^\infty \sum_0^\infty \overset{\substack{h+k=2n+1\\k+l=2n+1}}{F_{hkl}} \sin 2\pi hX . \sin 2\pi kY . \cos 2\pi lZ$$

Alternatively, it may be calculated for the different terms using the relationships between F's obtained in Section (f):-

$$\rho(XYZ) = \frac{2}{V}\sum_0^\infty{}^h \sum_0^\infty{}^k \sum_0^\infty{}^l \Big[F_{hkl} \cos 2\pi(hX+kY+lZ) + F_{\bar{h}kl} \cos 2\pi(-hX+kY+lZ)$$
$$+ F_{h\bar{k}l} \cos 2\pi(hX-kY+lZ) + F_{hk\bar{l}} \cos 2\pi(hX+kY-lZ)\Big]$$

$\left.\begin{matrix} h+k=2n \\ k+l=2n \end{matrix}\right\}$
$$\rho = \frac{2}{V}\sum\sum\sum F_{hkl}\{\cos 2\pi(hX+kY+lZ) + \cos 2\pi(-hX+kY+lZ) + \cos 2\pi(hX-kY+lZ) + \cos 2\pi(hX+kY-lZ)\}$$
$$= \frac{4}{V}\sum\sum\sum F_{hkl}\{\cos 2\pi(kY+lZ) \cos 2\pi hX + \cos 2\pi hX . \cos 2\pi(-kY+lZ)\}$$
$$\underline{\rho = \frac{8}{V}\sum\sum\sum F_{hkl} \cos 2\pi hX \{\cos 2\pi lZ . \cos 2\pi kY\}}$$

$\left.\begin{matrix} h+k=2n \\ k+l=2n+1 \end{matrix}\right\}$
$$\rho = \frac{2}{V}\sum\sum\sum F_{hkl}\{\cos 2\pi(hX+kY+lZ) + \cos 2\pi(-hX+kY+lZ) - \cos 2\pi(hX-kY+lZ) - \cos 2\pi(hX+kY-lZ)\}$$
$$= \frac{4}{V}\sum\sum\sum F_{hkl}\{\cos 2\pi(kY+lZ) . \cos 2\pi hX - \cos 2\pi hX . \cos 2\pi(-kY+lZ)\}$$
$$= \frac{4}{V}\sum\sum\sum F_{hkl}\{\cos 2\pi hX [\cos 2\pi(kY+lZ) - \cos 2\pi(-kY+lZ)]\}$$
$$[-2 \sin 2\pi lZ . \sin 2\pi kY]$$
$$\underline{\rho = -\frac{8}{V}\sum\sum\sum F_{hkl} \cos 2\pi hX . \sin 2\pi kY . \sin 2\pi lZ}$$

$\left.\begin{matrix} h+k=2n+1 \\ k+l=2n \end{matrix}\right\}$
$$\rho = \frac{2}{V}\sum\sum\sum F_{hkl}\{\cos 2\pi(hX+kY+lZ) - \cos 2\pi(-hX+kY+lZ) + \cos 2\pi(hX-kY+lZ) - \cos 2\pi(hX+kY-lZ)\}$$
$$= \frac{2}{V}\sum\sum\sum F_{hkl}\{-2 \sin 2\pi(kY+lZ) \sin 2\pi hX - 2 \sin 2\pi hX . \sin 2\pi(-kY+lZ)\}$$
$$= -\frac{4}{V}\sum\sum\sum F_{hkl} \sin 2\pi hX . \{2 \sin 2\pi lZ . \cos 2\pi kY\}$$
$$\underline{\rho = -\frac{8}{V}\sum\sum\sum F_{hkl} \sin 2\pi hX . \cos 2\pi kY . \sin 2\pi lZ .}$$

$\left.\begin{matrix} h+k=2n+1 \\ k+l=2n+1 \end{matrix}\right\}$
$$\rho = \frac{2}{V}\sum\sum\sum F_{hkl}\{\cos 2\pi(hX+kY+lZ) - \cos 2\pi(-hX+kY+lZ) - \cos 2\pi(hX-kY+lZ) + \cos 2\pi(hX+kY-lZ)\}$$
$$= \frac{4}{V} \cdots \{-\sin 2\pi hX . \sin 2\pi(kY+lZ)\} - \{-\sin 2\pi hX . \sin 2\pi(-kY+lZ)\}$$
$$\underline{\rho = -\frac{8}{V}\sum\sum\sum F_{hkl} . \sin 2\pi hX . \sin 2\pi kY . \cos 2\pi lZ}$$

Pbca

Thus, from Section (e), and collecting the terms from the previous page, the complete electron density formula is :-

$$\rho(XYZ) = \frac{1}{V}\Big\{ F_{000} + 2\sum_{h=2}^{\infty}{}^{h\ even} F_{h00}\cos 2\pi hX + 2\sum_{k=2}^{\infty}{}^{k\ even} F_{0k0}\cos 2\pi kY + 2\sum_{l=2}^{\infty}{}^{l\ even} F_{00l}\cos 2\pi lZ$$

$$+ 4\sum_{k=1}^{\infty}\sum_{l=1}^{\infty}{}^{k+l\ even} F_{0kl}\cos 2\pi kY.\cos 2\pi lZ - 4\sum_{k=1}^{\infty}\sum_{l=1}^{\infty}{}^{k+l\ odd} F_{0kl}\sin 2\pi kY.\sin 2\pi lZ$$

$$+ 4\sum_{h=1}^{\infty}\sum_{l=1}^{\infty}{}^{h+l\ even} F_{h0l}\cos 2\pi hX.\cos 2\pi lZ - 4\sum_{h=1}\sum_{l=1}{}^{h+l\ odd} F_{h0l}\sin 2\pi hX.\sin 2\pi lZ$$

$$+ 4\sum_{h=1}^{\infty}\sum_{k=1}^{\infty}{}^{h+k\ even} F_{hk0}\cos 2\pi hX.\cos 2\pi kY - 4\sum\sum{}^{h+k\ odd} F_{hk0}\sin 2\pi hX.\sin 2\pi kY$$

$$+ 8\sum_{h=1}^{\infty}\sum_{k=1}^{\infty}\sum_{l=1}^{\infty}{}^{h+k=2n,\ k+l=2n} F_{hkl}\cos 2\pi hX.\cos 2\pi kY.\cos 2\pi lZ$$

$$- 8\sum_{h=1}^{\infty}\sum_{k=1}^{\infty}\sum_{l=1}^{\infty}{}^{h+k=2n,\ k+l=2n+1} F_{hkl}\cos 2\pi hX.\sin 2\pi kY.\sin 2\pi lZ$$

$$- 8\sum_{h=1}^{\infty}\sum_{k=1}^{\infty}\sum_{l=1}^{\infty}{}^{h+k=2n+1,\ k+l=2n} F_{hkl}\sin 2\pi hX.\cos 2\pi kY.\sin 2\pi lZ$$

$$- 8\sum_{h=1}^{\infty}\sum_{k=1}^{\infty}\sum_{l=1}^{\infty}{}^{h+k=2n+1,\ k+l=2n+1} F_{hkl}\sin 2\pi hX.\sin 2\pi kY.\cos 2\pi lZ \Big\}$$

Pnma

The complete form of the electron density formula is:-

$$\rho(XYZ) = \frac{1}{V}\Big\{ F_{000} + 2\sum_{h=2}^{\infty}{}^{h\ even} F_{h00}\cos 2\pi hX + 2\sum_{k=2}^{\infty}{}^{k\ even} F_{0k0}\cos 2\pi kY + 2\sum_{l=2}^{\infty}{}^{l\ even} F_{00l}\cos 2\pi lZ$$

$$+ 4\sum_{k=2}^{\infty}\sum_{l=1}^{\infty}{}^{k\ even} F_{0kl}\cos 2\pi kY.\cos 2\pi lZ - 4\sum_{k=1}^{\infty}\sum_{l=1}^{\infty}{}^{k\ odd} F_{0kl}\sin 2\pi kY.\sin 2\pi lZ$$

$$+ 4\sum_{h=1}^{\infty}\sum_{l=1}^{\infty}{}^{h+l\ even} F_{h0l}\cos 2\pi hX.\cos 2\pi lZ - 4\sum_{h=1}^{\infty}\sum_{l=1}^{\infty}{}^{h+l\ odd} F_{h0l}\sin 2\pi hX.\sin 2\pi lZ$$

$$+ 4\sum_{h=1}^{\infty}\sum_{k=2}^{\infty}{}^{k\ even} F_{hk0}\cos 2\pi hX.\cos 2\pi kY - 4\sum_{h=1}^{\infty}\sum_{k=1}^{\infty}{}^{k\ odd} F_{hk0}\sin 2\pi hX.\sin 2\pi kY$$

$$+ 8\sum_{h=1}^{\infty}\sum_{k=2}^{\infty}\sum_{l=1}^{\infty}{}^{h+l\ even,\ k\ even} F_{hkl}\cos 2\pi hX.\cos 2\pi kY.\cos 2\pi lZ$$

$$- 8\sum_{h=1}^{\infty}\sum_{k=1}^{\infty}\sum_{l=1}^{\infty}{}^{h+l\ even,\ k\ odd} F_{hkl}\sin 2\pi hX.\sin 2\pi kY.\cos 2\pi lZ$$

$$- 8\sum_{h=1}^{\infty}\sum_{k=2}^{\infty}\sum_{l=1}^{\infty}{}^{h+l\ odd,\ k\ even} F_{hkl}\sin 2\pi hX.\cos 2\pi kY.\sin 2\pi lZ$$

$$- 8\sum_{h=1}^{\infty}\sum_{k=1}^{\infty}\sum_{l=1}^{\infty}{}^{h+l\ odd,\ k\ odd} F_{hkl}\cos 2\pi hX.\sin 2\pi kY.\sin 2\pi lZ \Big\}$$

(h) EXPRESSIONS FOR THE ELECTRON DENSITY

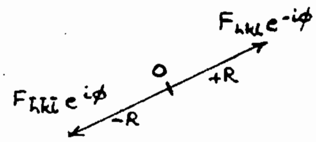
The electron density at any point X, Y, Z in the unit cell is given by

$$\rho(XYZ) = \frac{1}{V} \sum_h \sum_{k=-\infty}^{\infty} \sum_l F_{hkl}\, e^{-2\pi i(hX+kY+lZ)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ \mathrm{I}$$

where X, Y and Z are fractions of the crystallographic axes,
V is the volume of the unit cell

$$= \frac{1}{V} \sum \sum_{-\infty}^{\infty} \sum F_{hkl}\, e^{-i\phi}$$

where $\phi = 2\pi(hX + kY + lZ)$



$$= \frac{1}{2V} \sum\sum\sum \left[F_{hkl}\, e^{-i\phi} + F_{\bar{h}\bar{k}\bar{l}}\, e^{+i\phi}\right]$$

summing terms in pairs, +R and −R

$$= \frac{1}{2V} \sum\sum\sum \left[(A' + iB')e^{-i\phi} + (A' - iB')e^{i\phi}\right] \quad \text{(cf. Section (a))}$$

$$= \frac{1}{V} \sum\sum\sum \left[A' \frac{e^{i\phi} + e^{-i\phi}}{2} - i^2 B' \frac{e^{i\phi} - e^{-i\phi}}{2i}\right]$$

$$= \frac{1}{V} \sum\sum\sum \left[A' \cos\phi + B' \sin\phi\right] \quad \ldots\ldots\ldots\ldots\ \mathrm{II}$$

or, written out in full,

$$\rho(XYZ) = \frac{1}{V} \sum_h \sum_{k=-\infty}^{\infty} \sum_l \left[A'_{hkl} \cos 2\pi(hX + kY + lZ) + B'_{hkl} \sin 2\pi(hX + kY + lZ)\right]$$

$$= \frac{1}{V} \sum\sum\sum \left[|F_{hkl}| \cos\alpha_{hkl} \cos\phi + |F_{hkl}| \sin\alpha_{hkl} \sin\phi\right]$$

$$= \frac{1}{V} \sum\sum\sum |F_{hkl}| \cos(\phi - \alpha_{hkl}) \quad \text{(cf. Section (a))}$$

or, written out in full,

$$\rho(XYZ) = \frac{1}{V} \sum_h \sum_{k=-\infty}^{\infty} \sum_l |F_{hkl}| \cos\left[2\pi(hX + kY + lZ) - \alpha_{hkl}\right] \quad \ldots\ldots\ldots\ \mathrm{III}$$

For a centrosymmetric crystal, phase angle, $\alpha = 0$ or π

If $\alpha = 0$, $|F_{hkl}| \cos(\phi - \alpha_{hkl}) \rightarrow + F_{hkl} \cos\phi$

If $\alpha = \pi$, $|F_{hkl}| \cos(\phi - \alpha_{hkl}) \rightarrow + F_{hkl} \cos(\phi - \pi) = - F_{hkl} \cos\phi$

$$\rho(XYZ) = \frac{1}{V} \sum_h \sum_{k=-\infty}^{\infty} \sum_l \pm F_{hkl} \cos 2\pi(hX + kY + lZ) \quad \ldots\ldots\ldots\ldots\ \mathrm{IV}$$

The electron density expressed in the form required for the Fourier programme is derived from eqn. II as follows:–

$$\rho(XYZ) = \frac{1}{V} \sum_h \sum_{k=-\infty}^{\infty} \sum_l \left[A_{hkl} \cos(X+Y+Z) + B_{hkl} \sin(X+Y+Z)\right],$$

dropping the dashes, and writing $X = 2\pi hX$, etc.

$$= \frac{1}{V} \sum_h \sum_{k=0}^{\infty} \sum_l \big[A_{hkl} \cos(X+Y+Z) + A_{\bar{h}kl} \cos(-X+Y+Z) + A_{h\bar{k}l} \cos(X-Y+Z) + A_{\bar{h}\bar{k}l} \cos(-X-Y+Z)$$
$$+ A_{\bar{h}\bar{k}\bar{l}} \cos(-X-Y-Z) + A_{h\bar{k}\bar{l}} \cos(X-Y-Z) + A_{\bar{h}k\bar{l}} \cos(-X+Y-Z) + A_{hk\bar{l}} \cos(X+Y-Z)$$
$$+ B_{hkl} \sin(X+Y+Z) + B_{\bar{h}kl} \sin(-X+Y+Z) + B_{h\bar{k}l} \sin(X-Y+Z) + B_{\bar{h}\bar{k}l} \sin(-X-Y+Z)$$
$$+ B_{\bar{h}\bar{k}\bar{l}} \sin(-X-Y-Z) + B_{h\bar{k}\bar{l}} \sin(X-Y-Z) + B_{\bar{h}k\bar{l}} \sin(-X+Y-Z) + B_{hk\bar{l}} \sin(X+Y-Z)\big]$$

Now, as $A_{\bar{h}\bar{k}\bar{l}} \cos(-X-Y-Z) = A_{hkl}\cos(X+Y+Z)$, from Section (a), and $B_{\bar{h}\bar{k}\bar{l}} \sin(-X-Y-Z) = (-B_{hkl})(-\sin(X+Y+Z)) = B_{hkl}\sin(X+Y+Z)$, the eqn. for the electron density on the previous page can be written

$$\rho(XYZ) = \frac{2}{V}\sum_{h'}\sum_{k}^{\infty}\sum_{l}\Big[A_{hkl}\cos(X+Y+Z) + A_{\bar{h}kl}\cos(-X+Y+Z) + A_{h\bar{k}l}\cos(X-Y+Z) + A_{\bar{h}\bar{k}l}\cos(-X-Y+Z)$$
$$+ B_{hkl}\sin(X+Y+Z) + B_{\bar{h}kl}\sin(-X+Y+Z) + B_{h\bar{k}l}\sin(X-Y+Z) + B_{\bar{h}\bar{k}l}\sin(-X-Y+Z)\Big]$$

A

$$A_{hkl}[\cos X.\cos(Y+Z) - \sin X.\sin(Y+Z)] + A_{\bar{h}kl}[\cos(-X)\cos(Y+Z) - \sin(-X)\sin(Y+Z)]$$
$$+ A_{h\bar{k}l}[\cos X.\cos(-Y+Z) - \sin X.\sin(-Y+Z)] + A_{\bar{h}\bar{k}l}[\cos(-X)\cos(-Y+Z) - \sin(-X)\sin(-Y+Z)]$$

$$= (A_{hkl} + A_{\bar{h}kl})[\cos X.\cos(Y+Z)] + (-A_{hkl} + A_{\bar{h}kl})[\sin X.\sin(Y+Z)]$$
$$+ (A_{h\bar{k}l} + A_{\bar{h}\bar{k}l})[\cos X.\cos(-Y+Z)] + (-A_{h\bar{k}l} + A_{\bar{h}\bar{k}l})[\sin X.\sin(-Y+Z)]$$

$$= (A_{hkl} + A_{\bar{h}kl})[\cos X.\cos Y\cos Z - \cos X.\sin Y\sin Z]$$
$$+ (A_{h\bar{k}l} + A_{\bar{h}\bar{k}l})[\cos X.\cos(-Y)\cos Z - \cos X.\sin(-Y)\sin Z]$$
$$+ (-A_{hkl} + A_{\bar{h}kl})[\sin X.\sin Y\cos Z + \sin X.\cos Y\sin Z]$$
$$+ (-A_{h\bar{k}l} + A_{\bar{h}\bar{k}l})[\sin X.\sin(-Y)\cos Z + \sin X.\cos(-Y)\sin Z]$$

$$= (A_{hkl} + A_{\bar{h}kl} + A_{h\bar{k}l} + A_{\bar{h}\bar{k}l})\cos X.\cos Y.\cos Z$$
$$+ (-A_{hkl} - A_{\bar{h}kl} + A_{h\bar{k}l} + A_{\bar{h}\bar{k}l})\cos X.\sin Y.\sin Z$$
$$+ (-A_{hkl} + A_{\bar{h}kl} - A_{h\bar{k}l} + A_{\bar{h}\bar{k}l})\sin X.\cos Y.\sin Z$$
$$+ (-A_{hkl} + A_{\bar{h}kl} + A_{h\bar{k}l} - A_{\bar{h}\bar{k}l})\sin X.\sin Y.\cos Z$$

B

$$B_{hkl}[\sin X.\cos(Y+Z) + \cos X.\sin(Y+Z)] + B_{\bar{h}kl}[\sin(-X)\cos(Y+Z) + \cos(-X)\sin(Y+Z)]$$
$$+ B_{h\bar{k}l}[\sin X.\cos(-Y+Z) + \cos X.\sin(-Y+Z)] + B_{\bar{h}\bar{k}l}[\sin(-X)\cos(-Y+Z) + \cos(-X)\sin(-Y+Z)]$$

$$= (B_{hkl} - B_{\bar{h}kl})[\sin X.\cos(Y+Z)] + (B_{hkl} + B_{\bar{h}kl})[\cos X.\sin(Y+Z)]$$
$$+ (B_{h\bar{k}l} - B_{\bar{h}\bar{k}l})[\sin X.\cos(-Y+Z)] + (B_{h\bar{k}l} + B_{\bar{h}\bar{k}l})[\cos X.\sin(-Y+Z)]$$

$$= (B_{hkl} - B_{\bar{h}kl})[\sin X.\cos Y\cos Z - \sin X.\sin Y\sin Z]$$
$$+ (B_{hkl} + B_{\bar{h}kl})[\cos X.\sin Y\cos Z + \cos X.\cos Y\sin Z]$$
$$+ (B_{h\bar{k}l} - B_{\bar{h}\bar{k}l})[\sin X.\cos(-Y)\cos Z - \sin X.\sin(-Y)\sin Z]$$
$$+ (B_{h\bar{k}l} + B_{\bar{h}\bar{k}l})[\cos X.\sin(-Y)\cos Z + \cos X.\cos(-Y)\sin Z]$$

$$= (-B_{hkl} + B_{\bar{h}kl} + B_{h\bar{k}l} - B_{\bar{h}\bar{k}l})\sin X.\sin Y.\sin Z$$
$$+ (B_{hkl} - B_{\bar{h}kl} + B_{h\bar{k}l} - B_{\bar{h}\bar{k}l})\sin X.\cos Y.\cos Z$$
$$+ (B_{hkl} + B_{\bar{h}kl} - B_{h\bar{k}l} - B_{\bar{h}\bar{k}l})\cos X.\sin Y.\cos Z$$
$$+ (B_{hkl} + B_{\bar{h}kl} + B_{h\bar{k}l} + B_{\bar{h}\bar{k}l})\cos X.\cos Y.\sin Z$$

Thus, the expression for the electron density becomes

$$\rho(XYZ) = \frac{2}{V}\sum_{h=0}^{\infty}\sum_{k=0}^{\infty}\sum_{l=0}^{\infty}\Big[(+A_{hkl} + A_{\bar{h}kl} + A_{h\bar{k}l} + A_{\bar{h}\bar{k}l})\cos X\cos Y\cos Z$$
$$+ (-A_{hkl} - A_{\bar{h}kl} + A_{h\bar{k}l} + A_{\bar{h}\bar{k}l})\cos X\sin Y\sin Z$$
$$+ (-A_{hkl} + A_{\bar{h}kl} - A_{h\bar{k}l} + A_{\bar{h}\bar{k}l})\sin X\cos Y\sin Z$$
$$+ (-A_{hkl} + A_{\bar{h}kl} + A_{h\bar{k}l} - A_{\bar{h}\bar{k}l})\sin X\sin Y\cos Z \qquad \ldots\ldots \underline{V}$$
$$+ (-B_{hkl} + B_{\bar{h}kl} + B_{h\bar{k}l} - B_{\bar{h}\bar{k}l})\sin X\sin Y\sin Z$$
$$+ (+B_{hkl} - B_{\bar{h}kl} + B_{h\bar{k}l} - B_{\bar{h}\bar{k}l})\sin X\cos Y\cos Z$$
$$+ (+B_{hkl} + B_{\bar{h}kl} - B_{h\bar{k}l} - B_{\bar{h}\bar{k}l})\cos X\sin Y\cos Z$$
$$+ (+B_{hkl} + B_{\bar{h}kl} + B_{h\bar{k}l} + B_{\bar{h}\bar{k}l})\cos X\cos Y\sin Z\Big]$$

(i) THE MEANING AND APPLICATION OF THE FOURIER AND PATTERSON CODEWORDS

(i) The Fourier Codeword

From equation V, sub-section (h),

$$\left.\begin{array}{llrlrlrlrl}
A^1 & = & + & A(hkl) & + & A(\bar{h}kl) & + & A(h\bar{k}l) & + & A(\bar{h}\bar{k}l) \\
A^2 & = & - & & - & & + & & + & \\
A^3 & = & - & & + & & - & & + & \\
A^4 & = & - & & + & & + & & - & \\
 & & & & & & & & & \\
B^1 & = & - & B(hkl) & + & B(\bar{h}kl) & + & B(h\bar{k}l) & - & B(\bar{h}\bar{k}l) \\
B^2 & = & + & & - & & + & & - & \\
B^3 & = & + & & + & & - & & - & \\
B^4 & = & + & & + & & + & & + &
\end{array}\right\} \quad \text{VI}$$

In the operation of the Fourier programme all reflections with the same values of $|h|$, $|k|$ and $|l|$ are collected and the coefficients A^1 ...... B^4 are computed. Due to the relations between the structure factors which are specific to each space group (e.g. sub-section 1(f)), certain of the coefficients will be zero. In general, because of symmetry elements, the reflections (hkl), $(\bar{h}kl)$, $(h\bar{k}l)$ and $(\bar{h}\bar{k}l)$ are not <u>all</u> measured, and therefore the full set of structure factors is not read into the computer. The result is that the coefficients will be computed, using only the available structure factors, and some of the coefficients which should equal 0 will have non-zero values.

To rectify the situation, the coefficients A^1...... B^4 are thus subsequently multiplied in the computer by a set of constants s_1 ...... s_8 respectively. The constants have the values either 1, if the corresponding coefficient should be non-zero, or 0, if the corresponding coefficient should be zero. The set of constants s_1 ...... s_8 is called the Codeword of the space group; it must be calculated for the space group concerned, and an input card with the Codeword punched on it must be fed into the computer.

(ii) Calculation of the Codeword for special values of *h*, *k* and *l* .

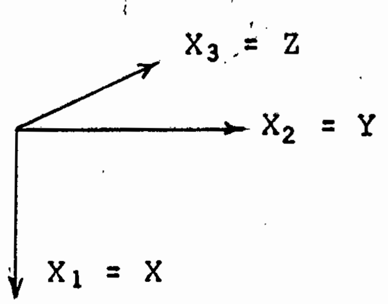
Although one set of constants only is required for those space groups which have no limiting conditions, (e.g. *P*1, *P*2, *Pm*), it is generally necessary to use more than one set. Reference to sub-section 1(f) shows that the relationships between F's, and consequently the values of the coefficients A^1 ...... B^4, depend upon the values of *h*, *k* and *l*. It follows that for each set of special values of the indices, leading to a specific set of F relationships, the corresponding Codeword must be calculated. The Fourier programme has the facility to test whether one index, two indices, or two pairs of indices are even or odd, and then to apply the correct Codeword. A maximum of four Codewords and four indices are catered for; if more are required the programme must be suitably modified.

The index tests and Codewords are punched in Card 3 of the Fourier input as follows:-

CONSTANTS I

Card no.	Description	Position on card	Punch
3	Tests on indices,	9	$h_1 = 1$ number of index } 1st test
		11	$h_2 = 2$ number of index } 1st test
		13	$h_3 = 3$ number of index } 2nd test
		15	number of index } 2nd test
			If no test is to be applied all four columns contain zeros. If only one test is necessary, cols. 13 & 15 are made zero. If the tests involve only one index the second number must be zero (i.e. cols. 11 & 15). No blanks must be left where there should be zeros.
	Codewords $s_1 \ldots . s_8$	17-24	Codewords 1, containing the constants $s_1 \ldots . s_8$ to be used for the case that the result of the test is even-even (e-e). It will also be used for the case that no test will be applied.
		26-33	Codeword 2, for the case o-e
		35-42	" 3, " " " e-o
		44-51	" 4, " " " o-o
			Note that there are no blanks between the constants s_1 and s_2 etc. The only blanks are between the Codewords.

(iii) Calculation of the Codeword for a changed summation order

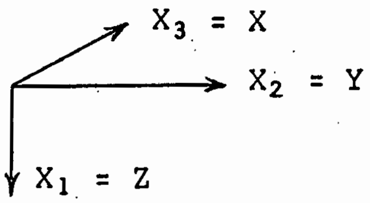


Normal order of axes.

The Fourier programme uses indices h_1, h_2, h_3 and a coordinate system X_1, X_2, X_3 , which may be called the "internal" indices and coordinates. The result of the electron density computations is printed in sections with a constant value of X_3. Input data must be provided to establish the relation between the "external" or crystal structure indices and coordinates h, k, l and X, Y, Z, and the internal or computer indices and coordinates.

If it is desired to alter the normal order of the axes such that $X_1 \neq X$, $X_2 \neq Y$ and/or $X_3 \neq Z$, then the order of the summation will also necessarily be altered. The Code-words may be different and must be freshly calculated for the new order.

The method is best illustrated by an example. Suppose the order of axes required is



then the summation order will be ZYX. The equation for the electron density is

$$\rho(XYZ) = \frac{1}{V} \sum_{h} \sum_{k=-\infty}^{\infty} \sum_{l} F_{hkl}\, e^{-2\pi i(hX+kY+lZ)}, \quad \text{or}$$

$$\rho(ZYX) = \frac{1}{V} \sum_{l} \sum_{k} \sum_{h} F_{lkh}\, e^{-2\pi i(lZ+kY+hX)}$$

The expansion of the second equation gives:-

$$\begin{aligned}\rho(ZYX) = \frac{2}{V} \sum_{l} \sum_{k=0}^{\infty} \sum_{h} \big[& A^1 \cos 2\pi lZ \cos 2\pi kY \cos 2\pi hX \\ & + A^2 \cos 2\pi lZ \sin 2\pi kY \sin 2\pi hX \\ & + A^3 \sin 2\pi lZ \cos 2\pi kY \sin 2\pi hX \\ & + A^4 \sin 2\pi lZ \sin 2\pi kY \cos 2\pi hX \\ & + B^1 \sin 2\pi lZ \sin 2\pi kY \sin 2\pi hX \\ & + B^2 \sin 2\pi lZ \cos 2\pi kY \cos 2\pi hX \\ & + B^3 \cos 2\pi lZ \sin 2\pi kY \cos 2\pi hX \\ & + B^4 \cos 2\pi lZ \cos 2\pi kY \sin 2\pi hX \big].\end{aligned}$$

and the coefficients have the values

$A^1 =$	$+A_{lkh}$	$+A_{\bar{l}kh}$	$+A_{l\bar{k}h}$	$+A_{\bar{l}\bar{k}h}$	$B^1 =$	$-B_{lkh}$	$+B_{\bar{l}kh}$	$+B_{l\bar{k}h}$	$-B_{\bar{l}\bar{k}h}$
$A^2 =$	$-$	$-$	$+$	$+$	$B^2 =$	$+$	$-$	$+$	$-$
$A^3 =$	$-$	$+$	$-$	$+$	$B^3 =$	$+$	$+$	$-$	$-$
$A^4 =$	$-$	$+$	$+$	$-$	$B^4 =$	$+$	$+$	$+$	$+$

By rearranging the indices and applying Friedel's Law, the coefficients may be written

$A^1 =$	$+A_{hkl}$	$+A_{\bar{h}\bar{k}l}$	$+A_{h\bar{k}l}$	$+A_{\bar{h}kl}$	$B^1 =$	$-B_{hkl}$	$+B_{\bar{h}\bar{k}l}$	$+B_{h\bar{k}l}$	$-B_{\bar{h}kl}$
$A^2 =$	$-$	$-$	$+$	$+$	$B^2 =$	$+$	$-$	$+$	$-$
$A^3 =$	$-$	$+$	$-$	$+$	$B^3 =$	$+$	$+$	$-$	$-$
$A^4 =$	$-$	$+$	$+$	$-$	$B^4 =$	$+$	$+$	$+$	$+$

The final set of coefficients may now be used in the same manner as before to calculate the new Codewords for the space group concerned; it is plain that in general the Codewords will not be the same for different orders of the axes.

(iv) <u>The Patterson Codeword</u>

Commencing with the equation for the Patterson function,

$$P(XYZ) = \frac{1}{V} \sum_{h} \sum_{k=-\infty}^{\infty} \sum_{l} |F_{hkl}|^2 \cos 2\pi\,(hX+kY+lZ) \; ,$$

the form of the expression which is used for the summation in the Patterson programme, derived by the method shown in sub-section (h), is

$$\left.\begin{aligned} P(XYZ) = \frac{2}{V} \sum_{h} \sum_{k=0}^{\infty} \sum_{l} \big[& A^1 \cos 2\pi hX \cos 2\pi kY \cos 2\pi lZ \\ & + A^2 \cos 2\pi hX \sin 2\pi kY \sin 2\pi lZ \\ & + A^3 \sin 2\pi hX \cos 2\pi kY \sin 2\pi lZ \\ & + A^4 \sin 2\pi hX \sin 2\pi kY \cos 2\pi lZ \,\big] \end{aligned}\right\} \text{VII}$$

$$\left.\begin{array}{lllllll} \text{where } A^1 = + & |F_{hkl}|^2 & + & |F_{\bar{h}kl}|^2 & + & |F_{h\bar{k}l}|^2 & + \; |F_{\bar{h}\bar{k}l}|^2 \\ \quad\quad A^2 = - & & - & & + & & + \\ \quad\quad A^3 = - & & + & & - & & + \\ \quad\quad A^4 = - & & + & & + & & - \end{array}\right\} \text{VIII}$$

The Codeword calculated as for the Fourier comprises four constants instead of eight, and it is easily shown that as $|F|^2$'s and not F's are involved, one Codeword suffices for a space group.

The Patterson Codeword must also be re-calculated if the order of the axes is changed.

(j) CODEWORDS FOR Pbca, Pnma, $P2_12_12_1$ (NORMAL ORDER OF AXES)

Pbca

$A^1 = +A_1 + A_2 + A_3 + A_4$
$A^2 = -A_1 - A_2 + A_3 + A_4$
$A^3 = -A_1 + A_2 - A_3 + A_4$
$A^4 = -A_1 + A_2 + A_3 - A_4$

(e − e): $h+k = 2n$, $k+l = 2n$

$F_{hkl} = F_{\bar{h}kl} = F_{h\bar{k}l} = F_{\bar{h}\bar{k}l}$
$A^1 = 4A_{hkl}$
$A^2 = 0$
$A^3 = 0$
$A^4 = 0$

$S_1 - S_8 = 1000,0000$

(e − o): $h+k = 2n$, $k+l = 2n+1$

$F_{hkl} = F_{\bar{h}kl} = -F_{h\bar{k}l} = -F_{\bar{h}\bar{k}l}$
$A^1 = 0$
$A^2 = -A-A-A-A = -4A_{hkl}$
$A^3 = -A+A+A-A = 0$
$A^4 = -A+A-A+A = 0$

$A_1 = A_{hkl} = +A$
$A_2 = A_{\bar{h}kl} = +A$
$A_3 = A_{h\bar{k}l} = -A$
$A_4 = A_{\bar{h}\bar{k}l} = -A$

$S_1 - S_8 = 0100,0000$

(o − e): $h+k = 2n+1$, $k+l = 2n$

$F_{hkl} = -F_{\bar{h}kl} = F_{h\bar{k}l} = -F_{\bar{h}\bar{k}l}$
$A^1 = 0$
$A^2 = -A+A+A-A = 0$
$A^3 = -A-A-A-A = -4A_{hkl}$
$A^4 = -A-A+A+A = 0$

$A_{hkl} = +A$
$A_{\bar{h}kl} = -A$
$A_{h\bar{k}l} = +A$
$A_{\bar{h}\bar{k}l} = -A$

$S_1 - S_8 = 0010,0000$

(o − o): $h+k = 2n+1$, $k+l = 2n+1$

$F_{hkl} = -F_{\bar{h}kl} = -F_{h\bar{k}l} = F_{\bar{h}\bar{k}l}$
$A^1 = 0$
$A^2 = -A+A-A+A = 0$
$A^3 = -A-A+A+A = 0$
$A^4 = -A-A-A-A = -4A_{hkl}$

$A_{hkl} = +A$
$A_{\bar{h}kl} = -A$
$A_{h\bar{k}l} = -A$
$A_{\bar{h}\bar{k}l} = +A$

$S_1 - S_8 = 0001,0000$

Constants I. card no. 3.

9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51
1 2 2 3 1 0 0 0 0 0 0 0 0 0 1 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 0 1 0 0 0 0
h+k (1st test), k+l (2nd test), e−e, o−e, e−o, o−o

Pnma

(e − e): $h+l = 2n$, $k = 2n$

$F_{hkl} = F_{\bar{h}kl} = F_{h\bar{k}l} = F_{\bar{h}\bar{k}l}$
$A^1 = 4A_{hkl}$
$A^2 = A^3 = A^4 = 0$

$S_1 - S_8 = 1000,0000$

(e − o): $h+l = 2n$, $k = 2n+1$

$F_{hkl} = -F_{\bar{h}kl} = -F_{h\bar{k}l} = F_{\bar{h}\bar{k}l}$
$A^1 = A^2 = A^3 = 0$
$A^4 = -4A_{hkl}$

$S_1 - S_8 = 0001,0000$

(o − e): $h+l = 2n+1$, $k = 2n$

$F_{hkl} = -F_{\bar{h}kl} = F_{h\bar{k}l} = -F_{\bar{h}\bar{k}l}$
$A^1 = A^2 = A^4 = 0$
$A^3 = -4A_{hkl}$

$S_1 - S_8 = 0010,0000$

(o − o): $h+l = 2n+1$, $k = 2n+1$

$F_{hkl} = F_{\bar{h}kl} = -F_{h\bar{k}l} = -F_{\bar{h}\bar{k}l}$
$A^1 = A^3 = A^4 = 0$
$A^2 = -4A_{hkl}$

$S_1 - S_8 = 0100,0000$

9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51
1 3 2 0 1 0 0 0 0 0 0 0 0 0 1 0 0 0 0 0 0 0 0 1 0 0 0 0 1 0 0 0 0 0 0
h+l (1st test), k (2nd test), e−e, o−e, e−o, o−o

$P2_12_12_1$

(e-e) $h+k=2n$, $k+l=2n$ $\quad\Big|\quad \alpha_{hkl} = -\alpha_{\bar{h}kl} = -\alpha_{h\bar{k}l} = \alpha_{\bar{h}\bar{k}l}$

$$A_{\bar{h}kl} = |F_{\bar{h}kl}|\cos\alpha_{\bar{h}kl} = |F_{hkl}|\cos(-\alpha_{hkl}) = |F_{hkl}|\cos\alpha_{hkl} = A_{hkl}$$

$$A_{h\bar{k}l} = A_{hkl} \quad \text{(similarly)}$$

$$A_{\bar{h}\bar{k}l} = |F_{\bar{h}\bar{k}l}|\cos\alpha_{\bar{h}\bar{k}l} = |F_{hkl}|\cos\alpha_{hkl} = A_{hkl}$$

$$\begin{aligned}
A' &= A_{hkl} + A_{hkl} + A_{hkl} + A_{hkl} = 4A_{hkl}\\
A^2 &= -A_{hkl} - A_{hkl} + A_{hkl} + A_{hkl} = 0\\
A^3 &= -A_{hkl} + A_{hkl} - A_{hkl} + A_{hkl} = 0\\
A^4 &= -A_{hkl} + A_{hkl} + A_{hkl} - A_{hkl} = 0
\end{aligned}$$

$$B_{\bar{h}kl} = |F_{\bar{h}kl}|\sin\alpha_{\bar{h}kl} = |F_{hkl}|\sin(-\alpha_{hkl}) = -|F_{hkl}|\sin\alpha_{hkl} = -B_{hkl}$$

$$B_{h\bar{k}l} = -B_{hkl} \quad \text{(similarly)}$$

$$B_{\bar{h}\bar{k}l} = |F_{\bar{h}\bar{k}l}|\sin\alpha_{\bar{h}\bar{k}l} = |F_{hkl}|\sin\alpha_{hkl} = B_{hkl}$$

$$\begin{aligned}
B' &= -B_{hkl} + (-B_{hkl}) + (-B_{hkl}) - (+B_{hkl}) = -4B_{hkl}\\
B^2 &= +B_{hkl} - (-B_{hkl}) + (-B_{hkl}) - (+B_{hkl}) = 0\\
B^3 &= +B_{hkl} + (-B_{hkl}) - (-B_{hkl}) - (+B_{hkl}) = 0\\
B^4 &= +B_{hkl} + (-B_{hkl}) + (-B_{hkl}) + (+B_{hkl}) = 0
\end{aligned}$$

<u>$S_1 \cdots S_8$ is 10001000 for (e-e)</u>

(e-o) $h+k=2n$, $k+l=2n+1$ $\quad\Big|\quad \alpha_{hkl} = -\alpha_{\bar{h}kl} = \pi - \alpha_{h\bar{k}l} = \pi + \alpha_{\bar{h}\bar{k}l}$

$$\alpha_{\bar{h}kl} = -\alpha_{hkl}: \quad \left.\begin{aligned}\cos\alpha_{\bar{h}kl} &= \cos\alpha_{hkl}\\ \sin\alpha_{\bar{h}kl} &= -\sin\alpha_{hkl}\end{aligned}\right\}$$

$$\alpha_{h\bar{k}l} = \pi - \alpha_{hkl}: \quad \left.\begin{aligned}\cos\alpha_{h\bar{k}l} &= -\cos\alpha_{hkl}\\ \sin\alpha_{h\bar{k}l} &= \sin\alpha_{hkl}\end{aligned}\right\}$$

$$\alpha_{\bar{h}\bar{k}l} = \pi + \alpha_{hkl}: \quad \left.\begin{aligned}\cos\alpha_{\bar{h}\bar{k}l} &= -\cos\alpha_{hkl}\\ \sin\alpha_{\bar{h}\bar{k}l} &= -\sin\alpha_{hkl}\end{aligned}\right\}$$

$$\begin{aligned}
A_{\bar{h}kl} &= |F_{\bar{h}kl}|\cos\alpha_{\bar{h}kl} = A_{hkl} & B_{\bar{h}kl} &= |F_{\bar{h}kl}|\sin\alpha_{\bar{h}kl} = -B_{hkl}\\
A_{h\bar{k}l} &= |F_{h\bar{k}l}|\cos\alpha_{h\bar{k}l} = -A_{hkl} & B_{h\bar{k}l} &= |F_{h\bar{k}l}|\sin\alpha_{h\bar{k}l} = +B_{hkl}\\
A_{\bar{h}\bar{k}l} &= |F_{\bar{h}\bar{k}l}|\cos\alpha_{\bar{h}\bar{k}l} = -A_{hkl} & B_{\bar{h}\bar{k}l} &= |F_{\bar{h}\bar{k}l}|\sin\alpha_{\bar{h}\bar{k}l} = -B_{hkl}
\end{aligned}$$

$$\begin{aligned}
A' &= +A_{hkl} + (+A_{hkl}) + (-A_{hkl}) + (-A_{hkl}) = 0\\
A^2 &= -A_{hkl} - (+A_{hkl}) + (-A_{hkl}) + (-A_{hkl}) = -4A_{hkl}\\
A^3 &= -A_{hkl} + (+A_{hkl}) + (-A_{hkl}) + (-A_{hkl}) = 0\\
A^4 &= -A_{hkl} + (+A_{hkl}) - (-A_{hkl}) - (-A_{hkl}) = 0
\end{aligned}$$

$$\begin{aligned}
B' &= -B_{hkl} + (-B_{hkl}) + (+B_{hkl}) - (-B_{hkl}) = 0\\
B^2 &= +B_{hkl} - (-B_{hkl}) + (+B_{hkl}) - (-B_{hkl}) = 4B_{hkl}\\
B^3 &= +B_{hkl} + (-B_{hkl}) - (+B_{hkl}) - (-B_{hkl}) = 0\\
B^4 &= +B_{hkl} + (-B_{hkl}) + (+B_{hkl}) + (-B_{hkl}) = 0
\end{aligned}$$

<u>$S_1 \cdots S_8$ is 01000100 for (e-o)</u>

$(o-e)\quad h+k=2n+1,\quad k+l=2n \quad\Big|\quad \alpha_{hkl} = \pi - \alpha_{\bar{h}kl} = -\alpha_{h\bar{k}l} = \pi + \alpha_{\bar{h}\bar{k}l}$

$$\alpha_{\bar{h}kl} = \pi - \alpha_{hkl} \;:\; \left.\begin{array}{l}\cos\alpha_{\bar{h}kl} = -\cos\alpha_{hkl}\\ \sin\alpha_{\bar{h}kl} = \sin\alpha_{hkl}\end{array}\right\}$$

$$\alpha_{h\bar{k}l} = -\alpha_{hkl} \;:\; \left.\begin{array}{l}\cos\alpha_{h\bar{k}l} = \cos\alpha_{hkl}\\ \sin\alpha_{h\bar{k}l} = -\sin\alpha_{hkl}\end{array}\right\}$$

$$\alpha_{\bar{h}\bar{k}l} = \pi + \alpha_{hkl} \;:\; \left.\begin{array}{l}\cos\alpha_{\bar{h}\bar{k}l} = -\cos\alpha_{hkl}\\ \sin\alpha_{\bar{h}\bar{k}l} = -\sin\alpha_{hkl}\end{array}\right\}$$

$$\begin{array}{l|l} A_{\bar{h}kl} = |F_{\bar{h}kl}|\cos\alpha_{\bar{h}kl} = -A_{hkl} & B_{\bar{h}kl} = |F_{\bar{h}kl}|\sin\alpha_{\bar{h}kl} = +B_{hkl}\\ A_{h\bar{k}l} = |F_{h\bar{k}l}|\cos\alpha_{h\bar{k}l} = +A_{hkl} & B_{h\bar{k}l} = |F_{h\bar{k}l}|\sin\alpha_{h\bar{k}l} = -B_{hkl}\\ A_{\bar{h}\bar{k}l} = |F_{\bar{h}\bar{k}l}|\cos\alpha_{\bar{h}\bar{k}l} = -A_{hkl} & B_{\bar{h}\bar{k}l} = |F_{\bar{h}\bar{k}l}|\sin\alpha_{\bar{h}\bar{k}l} = -B_{hkl}\end{array}$$

$$\begin{array}{l} A^1 = +A_{hkl} + (-A_{hkl}) + (+A_{hkl}) + (-A_{hkl}) = 0\\ A^2 = - \;\;{\cdot\cdot}\;\; -(- \;{\cdot\cdot}\;) + (+ \;{\cdot\cdot}\;) + (- \;{\cdot\cdot}\;) = 0\\ A^3 = - \;\;{\cdot\cdot}\;\; +(- \;{\cdot\cdot}\;) - (+ \;{\cdot\cdot}\;) + (- \;{\cdot\cdot}\;) = -4A_{hkl}\\ A^4 = - \;\;{\cdot\cdot}\;\; +(- \;{\cdot\cdot}\;) + (+ \;{\cdot\cdot}\;) - (- \;{\cdot\cdot}\;) = 0\end{array}$$

$$\begin{array}{l} B^1 = -B_{hkl} + (+B_{hkl}) + (-B_{hkl}) - (-B_{hkl}) = 0\\ B^2 = + \;\;{\cdot\cdot}\;\; -(+ \;{\cdot\cdot}\;) + (- \;{\cdot\cdot}\;) - (- \;{\cdot\cdot}\;) = 0\\ B^3 = + \;\;{\cdot\cdot}\;\; +(+ \;{\cdot\cdot}\;) - (- \;{\cdot\cdot}\;) - (- \;{\cdot\cdot}\;) = +4B_{hkl}\\ B^4 = + \;\;{\cdot\cdot}\;\; +(+ \;{\cdot\cdot}\;) + (- \;{\cdot\cdot}\;) + (- \;{\cdot\cdot}\;) = 0\end{array}$$

$s_1 \cdots\cdots s_8$ is 0010 0010 for $(o-e)$

$(o-o)\quad h+k=2n+1,\quad k+l=2n+1 \quad\Big|\quad \alpha_{hkl} = \pi - \alpha_{\bar{h}kl} = \pi - \alpha_{h\bar{k}l} = \alpha_{\bar{h}\bar{k}l}$

$$\left.\begin{array}{l}\cos\alpha_{\bar{h}kl} = -\cos\alpha_{hkl}\\ \sin\alpha_{\bar{h}kl} = \sin\alpha_{hkl}\end{array}\right\}$$

$$\left.\begin{array}{l}\cos\alpha_{h\bar{k}l} = -\cos\alpha_{hkl}\\ \sin\alpha_{h\bar{k}l} = \sin\alpha_{hkl}\end{array}\right\}$$

$$\left.\begin{array}{l}\cos\alpha_{\bar{h}\bar{k}l} = \cos\alpha_{hkl}\\ \sin\alpha_{\bar{h}\bar{k}l} = \sin\alpha_{hkl}\end{array}\right\}$$

$$\begin{array}{l|l} A_{\bar{h}kl} = -A_{hkl} & B_{\bar{h}kl} = B_{hkl}\\ A_{h\bar{k}l} = -A_{hkl} & B_{h\bar{k}l} = B_{hkl}\\ A_{\bar{h}\bar{k}l} = +A_{hkl} & B_{\bar{h}\bar{k}l} = B_{hkl}\end{array}$$

$$\begin{array}{l|l} A^1 = + \;\; +(-)\;\; +(-)\;\; +(+) = 0 & B^1 = 0\\ A^2 = - \;\; -(-)\;\; +(-)\;\; +(+) = 0 & B^2 = 0\\ A^3 = - \;\; +(-)\;\; -(-)\;\; +(+) = 0 & B^3 = 0\\ A^4 = - \;\; +(-)\;\; +(-)\;\; -(+) = -4A_{hkl} & B^4 = 4B_{hkl}\end{array}$$

$s_1 \cdots\cdots s_8$ is 0001 0001 for $(o-o)$

Constants I, card no. 3

9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51
1		2		2			3	1	0	0	0	1	0	0	0		0	0	1	0	0	0	1	0		0	1	0	0	0	1	0	0		0	0	0	1	0	0	0	1
h + k				k + l				e − e									o − e									e − o									o − o							
1st test				2nd test																																						

2. Computing methods, formulae and programmes

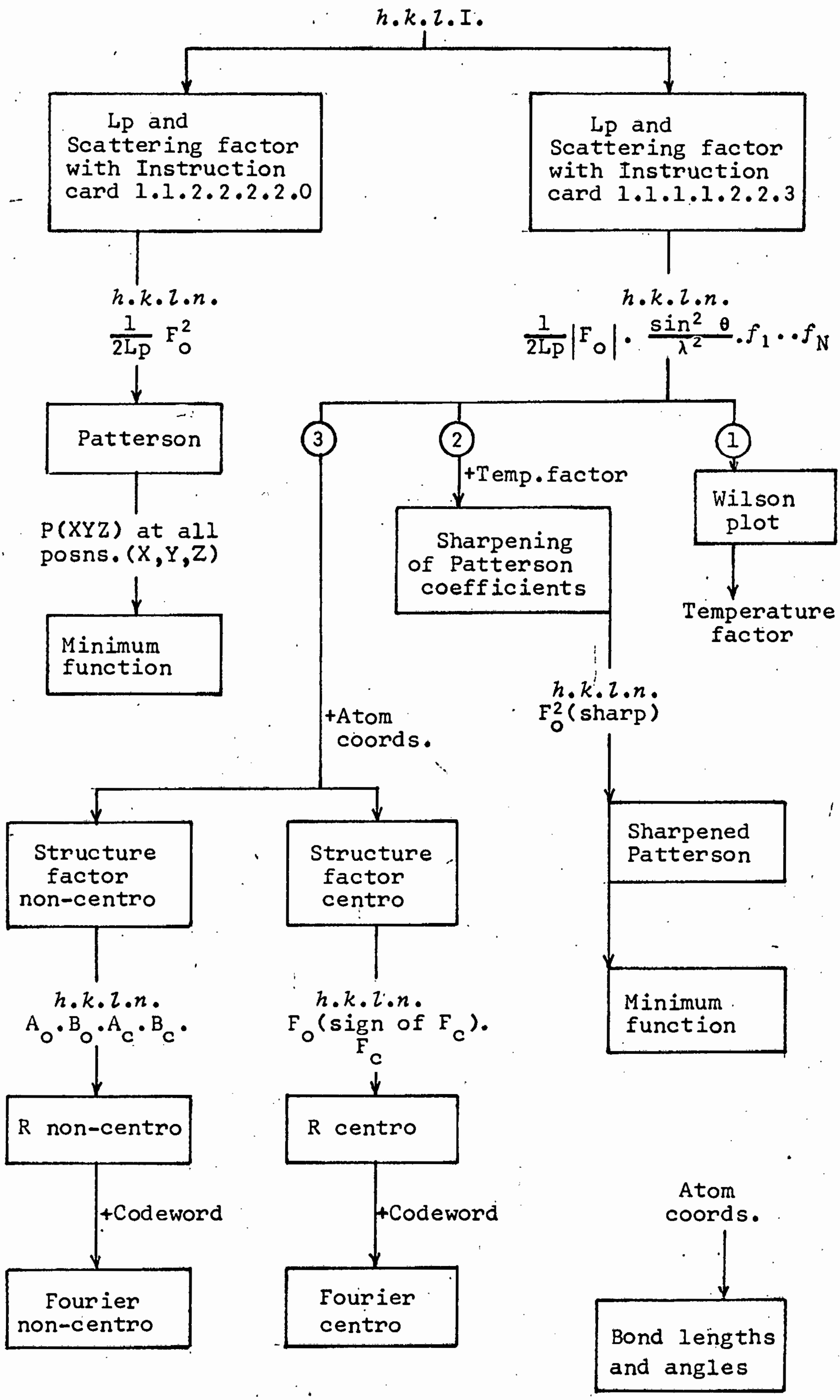
The computations involved in the structure determinations were carried out on an ICT 1301 computer in Cape Town. As the storage capacity of the ICT computer was quite inadequate to carry out the least-squares refinements, the author was required to commute between the U.C.T., Cape Town, and the C.S.I.R., Pretoria, in order to utilise an IBM 360/40 computer for chlorpromazine and an IBM 360/65 computer for thiethylperazine. In addition to the ORFLS programme certain of the data correction programmes used for thiethylperazine were available only in Pretoria. It was therefore necessary to be acquainted with the basic Fortran IV language, as well as being thoroughly conversant with the MAC programming and operation of the ICT computer.

Although the crystallographic programmes listed in sub-sections (a) and (b) were available at the different centres, it was essential to:-

(1) write ancillary programmes required for specific purposes;
(2) adapt certain existing programmes (e.g. Patterson and Fourier) to provide for the greater drum storage requirements of the structures which had a larger number of reflections and more atoms than were catered for in the original programmes;
(3) insert sections into some of the programmes (e.g. Structure Factor, Minimum Function) relevant to the particular space groups of the structures under investigation;
(4) understand the method of performing the summations involved in the Patterson and Fourier programmes in order to calculate the Codewords for the space groups and, in general, to understand all programmes so that the input and output data could be worked out correctly.
(5) convert the input data cards from MAC to Fortran codes.

(a) THE ICT PROGRAMMES

(Written by D. Feil & M.H. Linck.)



(b) THE IBM PROGRAMMES

1.	BACKGROUND	
2.	STREACOR	
3.	CORRECT	E.G. Boonstra.
4.	CENTROSY	P. Gantzel, H. Hope.
5.	ORFLS	W.R. Busing, K.O. Martin, H.A. Levy (1962)
6.	ORFFE	" " " (1964)
7.	LSPLANE	V. Schomaker, J. Waser, R.E. Marsh, G. Bergman. (1959)

(c) Lp AND SCATTERING FACTOR PROGRAMME

The programme calculates $\frac{\sin^2\theta}{\lambda^2}$ for each reflection, using the formula

$$\frac{\sin^2\theta}{\lambda^2} = \tfrac{1}{4}\left[h^2a^{*2} + k^2b^{*2} + l^2c^{*2} + 2hka^*b^*\cos\gamma^* + 2klb^*c^*\cos\alpha^* + 2lhc^*a^*\cos\beta^*\right]$$

The corrections for the Lorentz and polarisation factors are applied using the relation

$$\frac{1}{2Lp} = \frac{\sqrt{\cos^4\mu - (1 - 2\sin^2\theta + \sin^2\mu)^2}}{2 - 4\sin^2\theta + 4\sin^4\theta}$$

for equi-inclination; the derivation of the formula is given on the succeeding two pages (equations I and III combined).† In the case of thiethylperazine the data

†The author has endeavoured to exclude as far as possible derivations of formulae which can be found in standard test-books. However, there are several exceptions such as the Lorentz factor, which it is hoped is a concise representation, and is included for easy reference.

was measured on the diffractometer and therefore the inclination angle $\mu = 0$. The substitution of $\mu = 0$ reduces the equation above to

$$\frac{1}{2Lp} = \frac{\sin^2\theta}{1 + \cos^2 2\theta}$$

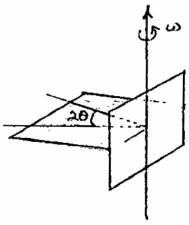
Optional calculations and punch output are then performed according to the punching of the input Instruction card. If input for the Patterson programme is required, no further calculations are done and the output cards are punched with the values for each reflection of $h.k.l.n.\ \frac{1}{2Lp}\ F_o^2$, where n denotes the signs of h, k and l (e.g. $n = 1$ for h, k, l; $n = 2$ for $\bar{h}, k, l$, ... $n = 8$ for $\bar{h}, \bar{k}, \bar{l}$). If input is required for the Wilson plot, Sharpening of Patterson coefficients or Structure factor programmes, the atomic scattering factors, f, as functions of $\frac{\sin^2\theta}{\lambda^2}$ are calculated for each type of atom in the structure. Cards containing the selected scattering factor tables must of course be included in the input data. Absorption correction tables may also be included if required. The format of the Instruction card and of the output cards is shown in sub-section 2(a).

Geometrical Factors affecting Intensities

1. Lorentz factor.

Case A. Specialised form for the case where

1. Reflection is from a plane parallel to rotn. axis.
2. X-ray beam is ⊥ar to axis.

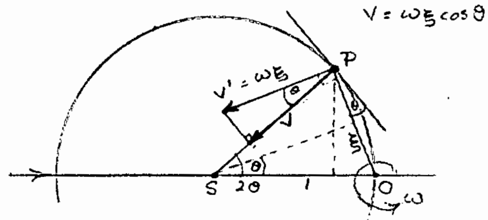


Then

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

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

$$L = \frac{1}{\xi\cos\theta} \qquad (14)$$



$\xi/2 = \sin\theta$

Let crystal + its recip. lattice rotate with ang. vel. ω.

The velocity of pt. P at distance ξ fr. rotn. axis is $\omega\xi$

This vel. vector (V') makes an angle θ with normal to sphere.

∴ Compt. of vel. of P normal to sphere is

$$V = \omega\xi\cos\theta$$

$$\therefore \frac{\omega}{V} = \frac{1}{\xi\cos\theta} = L \qquad (21)$$

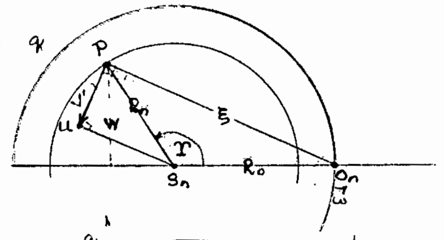
$t = \frac{c}{V}$ ∴ $t \propto L$

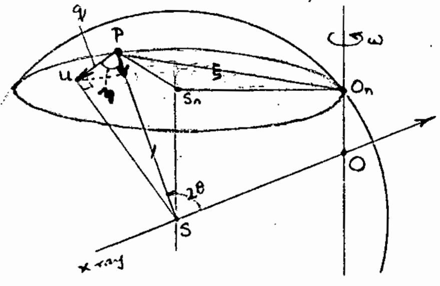
So L is the relative time opportunity for the various planes of the crystal to reflect.

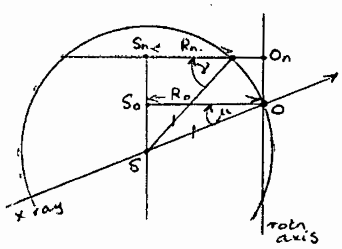
The $\cos\theta$ factor represents the ratio of the velocity of the pt. P to its normal compt. thro' the sphere of reflec.

(i.e. $\frac{1}{\cos\theta} = \frac{\omega\xi}{V} = \frac{V'}{V}$ — veloc. of pt. / normal compt.)

Case B. Generalisation of ratio V'/V.

5a


5b


5c


Recip. lattice is rotating with vel. ω.
Recip. lattice pt. P, on n^{th} level, has just reached n-layer reflecting circle + is in process of reflecting.
P is moving in dirn PU, has linear vel. $V' = \omega\xi$
But the vel. with which it passes thro' sphere, V, is its compt. on PS.

$$V = \omega\xi\cos\eta \qquad (22)$$

$$= \omega\xi . q \qquad (\because P\hat{U}S \text{ is a rt.} \angle)$$

$$= \omega . 2A \qquad (\cos\eta = \tfrac{q}{1})$$

$$\therefore \frac{V}{\omega} = 2A = \frac{1}{L} = \xi\cos\eta \qquad (27)$$

A is area of shaded Δ, $O_n P S_n$, of sides ξ, $R_o = \cos\mu$, $R_n = \cos\nu$

Using $\frac{1}{L} = 2A$, $A = \sqrt{s(s-a)(s-b)(s-c)}$, $s = \frac{1}{2}(a+b+c)$

$$\frac{1}{L} = \frac{1}{4}\sqrt{(\xi + \cos\mu + \cos\nu)(-\xi + \cos\mu + \cos\nu)(\xi - \cos\mu + \cos\nu)(\xi + \cos\mu - \cos\nu)} \quad (32)$$

$$\frac{1}{L} = \frac{\xi}{2}\sqrt{4\cos^2\mu - \xi^2} \quad (34) \qquad (\text{for } \mu = -\nu \text{ or } \mu = \nu)$$

To express L in terms of the film coord. Υ

$$\frac{1}{L} = 2A = 2\left(\tfrac{1}{2} W R_o\right) \qquad (\text{Fig 5a})$$

$$= W\cos\mu \qquad (R_o = \cos\mu)$$

$$= R_n \sin\Upsilon \cos\mu \qquad \left(\sin\Upsilon = \frac{W}{R_n}\right)$$

$$\frac{1}{L} = \cos\mu\cos\nu\sin\Upsilon \quad (38) \qquad (R_n = \cos\nu)$$

$\frac{1}{L} = \cos^2\mu \sin\Upsilon$ for equi-inclin: $\mu = -\nu$
and anti-equi: $\mu = \nu$

$\frac{1}{L} = \cos\nu\sin\Upsilon$ for normal-beam: $\mu = 0$

(Υ is a film coord: for camera diam. 57.3 mm. Υ in degrees = $2x$ = 2 × distance of spot fr. centre line of film, measured in mms.)

To express L in terms of θ and μ.

$$\cos 2\theta = \sin\mu.\sin\nu + \cos\mu\cos\nu\cos\Upsilon \quad (81) \qquad (\text{P. 175 Buer})$$

$$\cos 2\theta = 1 - \sin^2\theta \qquad (\text{Trig. identity})$$

Equi-inclination: $\mu = -\nu$

$$1 - 2\sin^2\theta = -\sin^2\mu + \cos^2\mu\cos\Upsilon \qquad (\sin\mu = \sin(-\nu) = -\sin\nu)$$

$$\therefore \cos\Upsilon = \frac{1 - 2\sin^2\theta + \sin^2\mu}{\cos^2\mu}$$

$$\therefore \sin\Upsilon = \sqrt{1 - \left(\frac{1 - 2\sin^2\theta + \sin^2\mu}{\cos^2\mu}\right)^2}$$

$$= \sqrt{\frac{\cos^4\mu - (1 - 2\sin^2\theta + \sin^2\mu)^2}{\cos^4\mu}}$$

$$\frac{1}{L} = \cos^2\mu\sin\Upsilon$$

$$\frac{1}{L} = \sqrt{\cos^4\mu - (1 - 2\sin^2\theta + \sin^2\mu)^2}_{\text{equi}} \qquad \text{I}$$

Anti-equi-inclination: $\mu = \nu$

$$1 - 2\sin^2\theta = \sin^2\mu + \cos^2\mu\cos\Upsilon$$

$$\therefore \cos\Upsilon = \frac{1 - 2\sin^2\theta - \sin^2\mu}{\cos^2\mu}$$

$$\frac{1}{L} = \sqrt{\cos^4\mu - (1 - 2\sin^2\theta - \sin^2\mu)^2}_{\text{anti-equi}} \qquad \text{II}$$

2. Polarisation Factor.

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

$$= \tfrac{1}{2}\left[1 + (1 - 2\sin^2\theta)^2\right]$$

$$p = 1 - 2\sin^2\theta + 2\sin^4\theta \qquad \text{III}$$

$(\cos 2\theta = 1 - 2\sin^2\theta)$

$$|F_{hkl}|^2 = \frac{1}{K}\,\frac{1}{L_{hkl}P_{hkl}}\,E_{hkl}$$

(K: scale factor; E: measured)

measure E's
multiply by $\frac{1}{Lp} \rightarrow |F|^2$

(d) WILSON PLOT PROGRAMME

Using Wilson's (1942) statistical method the programme calculates the first approximate temperature factor for use in the structure analysis. The normal $\frac{\sin^2\theta}{\lambda^2}$ zones into which the reflections are sorted have the values 0 - 0.10, 0.10 - 0.18, 0.18 - 0.24, 0.24 - 0.30, 0.30 - 0.35, 0.35 - 0.42, although other zones can be selected by suitable modification of the programme. For each zone the value of

$$\log_e \left(\frac{\sum f_j^2}{F_o^2} \right)$$

is computed and printed, together with the number of reflections in the zone.

(e) PATTERSON PROGRAMME

For the normal order of axes (P.128), the Patterson summation is performed in the order l, k, h. Equation VII, P. 130, can be rearranged as follows:-

$$\begin{aligned} P(XYZ) = \frac{2}{V} \Big[& \sum_k \sum_h \sum_l A^1 \cos 2\pi lZ . \cos 2\pi hX \cos 2\pi kY \\ & + \sum_k \sum_h \sum_l A^2 \sin 2\pi lZ \quad \cos 2\pi hX \sin 2\pi kY \\ & + \sum_k \sum_h \sum_l A^3 \sin 2\pi lZ \quad \sin 2\pi hX \cos 2\pi kY \\ & + \sum_k \sum_h \sum_l A^4 \cos 2\pi lZ \quad \sin 2\pi hX \sin 2\pi kY \Big] \end{aligned}$$

where the coefficients A^1 .... A^4 , having the values given in equation VIII, P.131, are computed first and stored on the drum. Approximately 11,000 positions are available, which permits a maximum number of reflections of 2,200.

The first summation over l calculates the quantities

$$\Xi^1_{hk} = \sum_{l=0}^{l(max)} A^1_{hkl} \cos 2\pi lZ$$

$$\Xi^2_{hk} = \sum_{l} A^2_{hkl} \sin 2\pi lZ$$

$$\Xi^3_{hk} = \sum_{l} A^3_{hkl} \sin 2\pi lZ$$

$$\Xi^4_{hk} = \sum_{l} A^4_{hkl} \cos 2\pi lZ \quad .$$

The Patterson function becomes

$$P(XYZ) = \frac{2}{V} \Big[\sum_k \sum_h \Xi^1_{hk} \cos 2\pi hX \cos 2\pi kY$$

$$+ \sum_k \sum_h \Xi^2_{hk} \cos 2\pi hX \sin 2\pi kY$$

$$+ \sum_k \sum_h \Xi^3_{hk} \sin 2\pi hX \cos 2\pi kY$$

$$+ \sum \sum \Xi^4_{hk} \sin 2\pi hX \sin 2\pi kY \Big]$$

The second summation over h calculates

$$\Omega^1_k = \sum_{h=0}^{h(max)} \Xi^1_{hk} \cos 2\pi hX$$

$$\Omega^2_k = \sum_h \Xi^2_{hk} \cos 2\pi hX$$

$$\Omega^3_k = \sum_h \Xi^3_{hk} \sin 2\pi hX$$

$$\Omega^4_k = \sum_h \Xi^4_{hk} \sin 2\pi hX$$

The Patterson function becomes

$$P(XYZ) = \frac{2}{V} \Big[\sum_k \Omega^1_k \cos 2\pi kY + \sum_k \Omega^2_k \sin 2\pi kY$$

$$+ \sum_k \Omega^3_k \cos 2\pi kY + \sum_k \Omega^4_k \sin 2\pi kY \Big]$$

$$= \frac{2}{V} \Big[\sum_k (\Omega^1_k + \Omega^3_k) \cos 2\pi kY + \sum (\Omega^2_k + \Omega^4_k) \sin 2\pi kY \Big]$$

The third summation over k calculates

$$\rho^{13} = \sum_{k=0}^{k(max)} (\Omega_k^1 + \Omega_k^3) \cos 2\pi kY$$

$$\rho^{24} = \sum_k (\Omega_k^2 + \Omega_k^4) \sin 2\pi kY$$

The final Patterson function can now be written

$$P(XYZ) = \text{Scale factor } (\rho^{13} + \rho^{24})$$

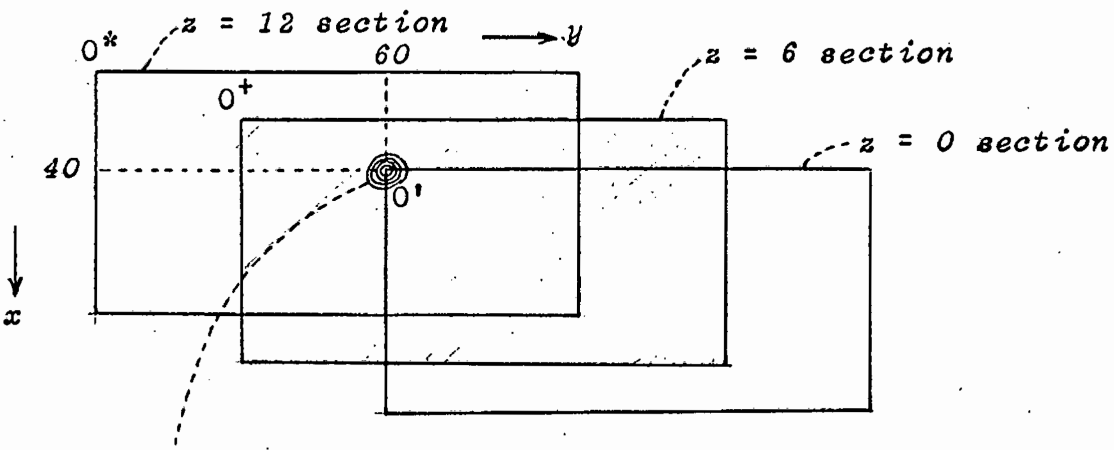
The input data cards must be sorted in the correct sequence $n.X_3.X_2.X_1$, which is n.Z.Y.X. for the normal arrangement of axes. If it is desired to alter the normal order or to calculate Patterson sections X = 50 or Y = 50, etc., as was the case with both chlorpromazine and thiethylperazine, the input data cards must be re-sorted, and the corresponding Patterson Codeword calculated, as described in sub-section 1(i). An input Instruction card is always included to specify the required order of axes.

It is possible, by making minor alterations to the programme, to obtain a print output of the Patterson values in sections which are approximately proportional to the corresponding sections of the unit cell; this is quite useful when searching the Patterson for special features such as a benzene ring.

The author encountered practical problems when attempting to use the programme and therefore subjected it to a complete analysis (available on request). The main cause of trouble was traced to insufficient drum capacity and consequent over-writing of data already stored. By omitting the unobserved reflections, which reduced the number of coefficients to be stored, and modifying the drum storage arrangements to accommodate $h_{max} = 30$, $k_{max} = 19$, the programme was eventually put into working order for chlorpromazine.

(f) MINIMUM FUNCTION PROGRAMME

This ingenious programme was devised by Mr. M.H. Linck of the University of Cape Town. The meaning of the terms employed may be best understood by an illustrated example. Suppose that in a three-dimensional Patterson function (computed over the normal order of axes), a shift is to be made to a peak at x = 40, y = 60, z = 12. The situation can be represented as follows:-



For the first round,

0^* is the z = 12 section, i.e. the section containing the peak,

0' " " z = 0 " " " " containing the origin,

0^+ " " z = 6 " " the first section of the corresponding minimum function,

0^{*+} is a re-arrangement of the z= 12 section to occupy the position of 0^+,

0'+ is a re-arrangement of the z= 0 section to occupy the position of 0^+.

For the first round, Patterson values in corresponding (x,y) positions of 0^* and 0' are compared; the minimum of each pair of values is taken and printed on to a section, 0^+, which is the first section of the minimum function (i.e. $z = 6$). The origin of 0^{+} is midway between the origins of 0^{*} and $0'$.

For the second round, Patterson values of 0^{*} (now the $z = 14$ section) and $0'$ (now the $z = 2$ section) are compared, and the minima printed on to a section of 0^{+}, which is the second z-section of the minimum function ($z = 8$).

In subsequent rounds, Patterson sections are compared in pairs and the corresponding sections of the minimum function are similarly computed, until the entire three-dimensional minimum function has been generated.

Each round is performed by the computer in the following stages:-

(1) The Patterson values of the section of 0^{*} are read in, rearranged to a normal block and stored on the drum in the correct sequence, e.g. Patterson values at (x,y) = (0,0) (0,2) (0,4) ..... (0,50); (2,0) (2,2) .... (2,50); ..... ; (50,0) (50,2) .... (50,50) are stored in 676 consecutive spaces on the drum.

(2) The symmetry elements of the Patterson space group concerned¶ are applied in order to generate the complete section of 0^{*}, and the Patterson values are stored on the drum in sequence, e.g. values at (x,y) = (0,0) (0,2) .... (0,100); (2,0) .... (2,100); .... ; (100,0) ... (100,100) are stored in 2601 consecutive spaces on the drum.

(3) 0^{*+} is calculated by bringing down from the drum the values of 0^{*} and re-arranging the data to the sequential order required for the computation of 0^{+},

---

¶ Chapter 2 of the programme, which applies the symmetry elements of the Patterson space group under investigation, must be specially written for each structure.

e.g. if, as in the illustration above, the origin of 0^{+} is at (20,30,6), then the Patterson values of 0^{*+} will be re-arranged to the sequence (x,y) = (20,30) (20,32) .... (20,130); (22,30) .... (120,130). The Patterson values of 0^{*+} are now stored on the drum in the new order.

(4) Stages (1), (2) and (3) are carried out for the data of 0'.

(5) The section of the minimum function 0^{+} is computed by comparing corresponding values of 0^{*+} and $0'^{+}$, and the minimum of each pair is stored on the drum.

(6) The Patterson values on the z-section of 0^{+} are printed and cards are punched if specified. The punch output permits the subsequent computation of minimum functions of higher rank.

(g) STRUCTURE FACTOR AND R PROGRAMMES

The centrosymmetric Structure factor programme computes the value of

$$F_{cal}(hkl) = \sum_j f_j(hkl) \cos 2\pi (hx_j + ky_j + lz_j) e^{-B_j \sin^2\theta/\lambda^2}$$

for each reflection, where

f_j is the scattering factor of the atom j,
x_j, y_j, z_j are fractional coordinates of the atom j,
B_j is temperature factor of the atom j.

For each reflection, the values of h, k, l,

$$F_{obs}, \; F_{cal}, \; \frac{||F_{obs}| - |F_{cal}||}{|F_{obs}|} \quad \text{and} \quad \frac{\sin^2\theta}{\lambda^2} \quad \text{are}$$

printed out. When the calculations have been performed for all reflections, the values of

$$z = \frac{\sum |F_{cal}|}{\sum |F_{obs}|} \quad \text{and}$$

$$R = \frac{\sum ||F_{obs}|-|F_{cal}||}{\sum |F_{obs}|} \times 100$$

are printed out. Suitable punched card output (sub-section 2(a)) provides input for the R centro. or Fourier centro. programmes.

The above formula for F_{cal} is general and can be used for any space group, but necessitates putting in each atom at all equivalent positions which, for a structure such as chlorpromazine possessing 8 equivalent positions and 21 atoms, would involve punching coordinates and temperature factors for 168 atoms. The preparation and computation times are considerably shortened if the value for F_{cal} specific to the space group concerned is substituted in the structure factor formula, so that only the coordinates and temperature factors of the atoms in the asymmetric unit need be supplied to the computer.

The programme must therefore be modified to calculate the value of

$$F_{cal}(hkl) = \sum_r f_r(hkl)\, A\, e^{-B_r \sin^2\theta/\lambda^2} \text{ for each}$$

reflection,

where r is the number of independent atoms, and A is the geometrical structure factor for the space group concerned. The general forms of A to be used for space groups *Pbca* and *Pnma* were derived in sub-section 1(c).

The programme modification for *Pbca* is as follows:-

$B_2 = F_oC_K - .25\ F_o + .25\ F_1$	$B_2 = hx - \frac{h}{4} + \frac{k}{4}$
$B_2 = \phi\ \mathrm{COS}\ (2\pi B_2)$	$B_2 = \cos 2\pi(hx - \frac{h}{4} + \frac{k}{4})$
$B_3 = F_1C_{K+1} - .25\ F_1 + .25\ F_2$	$B_3 = ky - \frac{k}{4} + \frac{l}{4}$
$B_3 = \phi\ \mathrm{COS}\ (2\pi B_3)$	$B_3 = \cos 2\pi(ky - \frac{k}{4} + \frac{l}{4})$
$B_4 = F_2C_{K+2} - .25\ F_2 + .25\ F_o$	$B_4 = lz - \frac{l}{4} + \frac{h}{4}$
$B_4 = \phi\ \mathrm{COS}\ (2\pi B_4)$	$B_4 = \cos 2\pi(lz - \frac{l}{4} + \frac{h}{4})$
$B_o = 8\ B_2B_3B_4$	$B_o = A$

The R centrosymmetric programme applies the scale factor z, where

$$\frac{\sum|F_{cal}|}{\sum z|F_{obs}|} = 1.0,$$ to the output of the

Structure factor programme and then calculates the value of

$$R = \frac{\sum\left|z|F_{obs}|-|F_{cal}|\right|}{\sum z|F_{obs}|} \times 100$$

The non-centrosymmetric Structure factor programme computes the values of

$$|F_{cal}(hkl)| = \sqrt{A'(hkl)^2 + B'(hkl)^2} \quad \text{and}$$

$$\alpha(hkl) = \arc\tan \frac{B'(hkl)}{A'(hkl)}, \text{ where}$$

$$A'(hkl) = A_{cal} = \sum_j f_j(hkl) \cos 2\pi(hx_j + ky_j + lz_j)e^{-B_j \sin^2\theta/\lambda^2}$$

$$B'(hkl) = B_{cal} = \sum_j f_j(hkl) \sin 2\pi(hx_j + ky_j + lz_j)e^{-B_j \sin^2\theta/\lambda^2}$$

The values of A_{obs} and B_{obs} are then calculated as

$$A_{obs} = |F_{obs}| \cos \alpha(hkl)$$

$$B_{obs} = |F_{obs}| \sin \alpha(hkl)$$

For each reflection, the values of h, k, l, $|F_{obs}|$, $|F_{cal}|$, A_{obs}, B_{obs}, A_{cal}, B_{cal} and

$\frac{||F_{obs}|-|F_{cal}||}{|F_{obs}|}$ are printed out, and z and R calculated as for the centro. Structure factor programme.

Modifications must also be applied to the non-centro. programme for the space group concerned. For $P2_12_12_1$ the appropriate section was written as follows:-

$B_0 = 2\pi F_0 C_K - 0.5\ \pi F_0 + 0.5\ \pi F_1$	$B_0 = 2\pi(hx - \frac{h}{4} + \frac{k}{4})$
$B_2 = 2\pi F_1 C_{K+1} - 0.5\ \pi F_1 + 0.5 \pi F_2$	$B_2 = 2\pi(ky - \frac{k}{4} + \frac{l}{4})$
$B_3 = 2\pi F_2 C_{K+2} - 0.5\ \pi F_2 + 0.5 \pi F_0$	$B_3 = 2\pi(lz - \frac{l}{4} + \frac{h}{4})$

$B_4 = \phi \text{ COS } (B_0)$

$B_5 = \phi \text{ COS } (B_2)$

$B_6 = \phi \text{ COS } (B_3)$

$B_{11} = \phi \text{ SIN } (B_0)$

$B_{12} = \phi \text{ SIN } (B_2)$

$B_{13} = \phi \text{ SIN } (B_3)$

$B_9 = 4\ B_4 B_5 B_6$

$B_{10} = -4\ B_{11} B_{12} B_{13}$

$$B_9 = 4 \cos 2\pi(hx - \frac{h}{4} + \frac{k}{4}) \cos 2\pi(ky - \frac{k}{4} + \frac{l}{4}) \cos 2\pi(lz - \frac{l}{4} + \frac{h}{4}) = A$$

$$B_{10} = -4 \sin 2\pi(hx - \frac{h}{4} + \frac{k}{4}) \sin 2\pi(ky - \frac{k}{4} + \frac{l}{4}) \sin 2\pi(lz - \frac{l}{4} + \frac{h}{4}) = B$$

On insertion of the above instructions into Chapter 2 of the programme, further modifications became necessary as the permitted chapter length was exceeded.

The R non-centrosymmetric programme operates similarly to the R centro. programme but differs in that it accepts the non-centro. input and produces output suitable for the non-centro. Fourier programme.

(h) THE FOURIER PROGRAMMES

The form of the electron density expression used in the programmes was derived in sub-section 1(h), (equation V); the meaning of the coefficients and the Codewords was discussed in sub-sections 1(i) and (j). The method of performing the triple summation, which is similar to that described in sub-section 2(e), is illustrated for the centrosymmetric Fourier on the next page. The input specifications and the sorting of cards in sequential order, etc. resemble the Patterson programme. Modifications to drum storage required in the Patterson programme had also to be made in both Fourier programmes.

The time consumed on the ICT 1301 computer to perform one set of structure factor calculations with 27 atoms and one three-dimensional Fourier of $\frac{1}{4}$ unit cell was $14\frac{1}{2}$ hours. (All operations on the ICT computer were carried out solely by the author.)

THE FOURIER PROGRAM. CALCULATION OF ELECTRON DENSITY

THE SUMMATION - CENTRO SYMMETRIC

$$\rho(x,y,z) = \sum_h \sum_k \sum_l A^1 \cos 2\pi hx \cos 2\pi ky \cos 2\pi lz + A^2 \cos 2\pi hx \sin 2\pi ky \sin 2\pi lz + A^3 \sin 2\pi hx \cos 2\pi ky \sin 2\pi lz + A^4 \sin 2\pi hx \sin 2\pi ky \cos 2\pi lz$$

$$= \sum_k \sum_h \sum_l A^1 \cos 2\pi lz \cos 2\pi hx \cos 2\pi ky + A^2 \sin 2\pi lz \cos 2\pi hx \sin 2\pi ky + A^3 \sin 2\pi lz \sin 2\pi hx \cos 2\pi ky + A^4 \cos 2\pi lz \sin 2\pi hx \sin 2\pi ky$$

First Summation - over l

$$\Xi'_{kh} = \sum_l A'_{khl} \cos 2\pi lz = A'_{kh0} \cos 2\pi 0z + A'_{kh1} \cos 2\pi 1z + A'_{kh2} \cos 2\pi 2z + \dots + A'_{khl} \cos 2\pi lz$$

(keep k & h constant)

l terms ← k × h of these

Second Summation - over h

$${}^{x_m}\Omega'_k = \sum_h \Xi'_{kh} \cos 2\pi h x_{min} = \Xi'_{k0} \cos 2\pi 0 x_m + \Xi'_{k1} \cos 2\pi 1 x_m + \Xi'_{k2} \cos 2\pi 2 x_m + \dots + \Xi'_{kh} \cos 2\pi h x_m$$

(keep k constant)

$$= (A'_{k00} \cos 2\pi 0z + A'_{k01} \cos 2\pi 1z + A'_{k02} \cos 2\pi 2z + \dots + A'_{k0l} \cos 2\pi lz) \cos 2\pi 0 x_{min}$$
$$+ (A'_{k10} \cos 2\pi 0z + A'_{k11} \cos 2\pi 1z + A'_{k12} \cos 2\pi 2z + \dots + A'_{k1l} \cos 2\pi lz) \cos 2\pi 1 x_{min}$$
$$+ (A'_{k20} \cos 2\pi 0z + A'_{k21} \cos 2\pi 1z + A'_{k22} \dots + A'_{k2l} \cos 2\pi lz) \cos 2\pi 2 x_{min}$$
$$+ (A'_{kh0} \cos 2\pi 0z + A'_{kh1} \cos 2\pi 1z + \dots + A'_{khl} \cos 2\pi lz) \cos 2\pi h x_{min}$$

h terms ← k of these for each x

$${}^{x_m+\Delta x}\Omega'_k = \sum_h \Xi'_{kh} \cos 2\pi h (x_m+\Delta x) = \Xi'_{k0} \cos 2\pi 0 (x_m+\Delta x) + \Xi'_{k1} \cos 2\pi 1 (x_m+\Delta x) + \Xi'_{k2} \cos 2\pi 2 (x_m+\Delta x) + \dots + \Xi'_{kh} \cos 2\pi h (x_m+\Delta x)$$

" ....

$${}^{x_m+25\Delta x}\Omega'_k = \sum_h \Xi'_{kh} \cos 2\pi h (x_m+25\Delta x) = \Xi'_{k0} \cos 2\pi 0 (x_m+25\Delta x) + \Xi'_{k1} \cos 2\pi 1 (x_m+25\Delta x) + \Xi'_{k2} \cos 2\pi 2 (x_m+25\Delta x) + \dots + \Xi'_{kh} \cos 2\pi h (x_m+25\Delta x)$$

Third Summation - over k

$$\rho'(y_m, x_m, z) = \sum_k {}^{x_m}\Omega'_k \cos 2\pi k y_{min} = {}^{x_m}\Omega'_0 \cos 2\pi 0 y_m + {}^{x_m}\Omega'_1 \cos 2\pi 1 y_m + {}^{x_m}\Omega'_2 \cos 2\pi 2 y_m + \dots + {}^{x_m}\Omega'_k \cos 2\pi k y_m$$

k terms ← 1 of these for each x, y

$\rho'(y_m+\Delta y, x_m, z)$ .... $\rho'(y_m+25\Delta y, x_m, z)$

$$= [\Xi'_{00} \cos 2\pi 0 x_m + \Xi'_{01} \cos 2\pi 1 x_m + \Xi'_{02} \cos 2\pi 2 x_m + \dots + \Xi'_{0h} \cos 2\pi h x_m] \cos 2\pi 0 y_m$$
$$+ [\Xi'_{10} \cos 2\pi 0 x_m + \Xi'_{11} \cos 2\pi 1 x_m + \Xi'_{12} \cos 2\pi 2 x_m + \dots + \Xi'_{1h} \cos 2\pi h x_m] \cos 2\pi 1 y_m$$
$$+ [\Xi'_{20} \cos 2\pi 0 x_m + \Xi'_{21} \cos 2\pi 1 x_m + \Xi'_{22} \cos 2\pi 2 x_m + \dots + \Xi'_{2h} \cos 2\pi h x_m] \cos 2\pi 2 y_m$$
$$+ [\Xi'_{k0} \cos 2\pi 0 x_m + \Xi'_{k1} \cos 2\pi 1 x_m + \dots + \Xi'_{kh} \cos 2\pi h x_m] \cos 2\pi k y_m$$

$$= [(A'_{000} \cos 2\pi 0z + A'_{001} \cos 2\pi 1z + \dots + A'_{00l} \cos 2\pi lz) \cos 2\pi 0 x_m + (A'_{010} \cos 2\pi 0z + \dots + A'_{01l} \cos 2\pi lz) \cos 2\pi 1 x_m + \dots + (A'_{0h0} \cos 2\pi 0z + A'_{0h1} \cos 2\pi 1z + \dots + A'_{0hl} \cos 2\pi lz) \cos 2\pi h x_m] \cos 2\pi 0 y_m$$
$$+ [(A'_{100} \cos 2\pi 0z + A'_{101} \cos 2\pi 1z + \dots + A'_{10l} \cos 2\pi lz) \cos 2\pi 0 x_m + (A'_{110} \cos 2\pi 0z + \dots + A'_{11l} \cos 2\pi lz) \cos 2\pi 1 x_m + \dots + (A'_{1h0} \cos 2\pi 0z + A'_{1h1} \cos 2\pi 1z + \dots + A'_{1hl} \cos 2\pi lz) \cos 2\pi h x_m] \cos 2\pi 1 y_m$$
$$\vdots$$
$$+ [(A'_{k00} \cos 2\pi 0z + A'_{k01} \dots + A'_{k0l} \cos 2\pi lz) \cos 2\pi 0 x_m + (A'_{k10} \cos 2\pi 0z + \dots + A'_{k1l} \cos 2\pi lz) \cos 2\pi 1 x_m + \dots + (A'_{kh0} \cos 2\pi 0z + A'_{kh1} \cos 2\pi 1z + \dots + A'_{khl} \cos 2\pi lz) \cos 2\pi h x_m] \cos 2\pi k y_m$$

$\rho'(y_m, x+\Delta x, z)$ ---------- $\rho'(y_m+25\Delta y, x_m+25\Delta x, z)$

(i) BOND LENGTHS AND ANGLES PROGRAMME.

1. TRANSFORMATION OF AXES

In a triclinic crystal, $a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$
To find distance betw. 2 points we use Pythagoras' Thm, provided that the system of axes is orthogonal.
If we have fractional coords. $[x^i]$ measured in triclinic system, converted to Cartesian coords. $[X^i]$, ie.

triclinic fract: $[x^i] = [x^1, x^2, x^3] = [x/a, y/b, z/c]$
cartesian: $[X^i] = [X^1, X^2, X^3] = [X, Y, Z]$

Then $[X^i] = [x^j][\beta_j^{\ i}]$ .... (row matrices) .... ①

$$\text{where } [\beta_j^{\ i}] = \begin{bmatrix} a & 0 & 0 \\ b\cos\gamma & b\sin\gamma & 0 \\ c\cos\beta & -c\left(\frac{\cos\beta\cos\gamma - \cos\alpha}{\sin\gamma}\right) & \frac{1}{c^*} \end{bmatrix} \quad \text{.......} ②$$

Proof. Int. Tables II. P. 54-61 Tensor Analysis.

54 Covariant quantities - transform in same way as base vectors - use subscripts. ie. $\underline{a}_i$. $\underline{a}_j$
Contravariant quantities - transform in same way as reciprocal base vectors - use superscripts. $\underline{a}^i$. $\underline{a}^j$

56 Second order symmetric tensor, g. whose components are defined by the relations:-

$g_{ij} = (\underline{a}_i\, \underline{a}_j)$ $\qquad |\underline{g}| = |g_{ij}| = |g^{ij}|^{-1} = g$
$g^{ij} = (\underline{a}^i\, \underline{a}^j)$ $\qquad g_i^{\ j} = g^i_{\ j} = (\underline{a}^i \underline{a}_j) = \delta^i_{\ j}$

57 **Properties of Base + Reciprocal Vectors**

A. Scalar Products.

(1) $(\underline{a}_i\, \underline{a}_j) = g_{ij}$
(2) $(\underline{a}^i\, \underline{a}^j) = g^{ij}$
(3) $(\underline{a}^i\, \underline{a}_j) = g^i_{\ j}$

B. Transformations betw. Base + Recipr. Vectors.

(4) $\underline{a}_i = g_{ij}\, \underline{a}^j$
(5) $\underline{a}^i = g^{ij}\, \underline{a}_j$

No summations implied

C. Transformations betw. Base + Recip. Metric Tensors.

(6) $g g^{ij} = g_{ik} g_{kj} - g_{ij} g_{kk}$ → $g g^{12} = g_{13} g_{32} - g_{12} g_{33}$
(7) $g g^{ii} = g_{jj} g_{kk} - (g_{jk})^2$ → $g g^{33} = g_{11} g_{22} - (g_{12})^2$
(8) $\frac{g_{ij}}{g} = g^{ik} g^{kj} - g^{ij} g^{kk}$ → $\frac{g_{12}}{g} = g^{13} g^{32} - g^{12} g^{33}$
(9) $\frac{g_{ii}}{g} = g^{jj} g^{kk} - (g^{jk})^2$ → $\frac{g_{11}}{g} = g^{22} g^{33} - (g^{23})^2$

D. Vector Products in Base + Recip. Systems. i, j, k in cyclic order.

(10) $[\underline{a}_i\, \underline{a}_j] = \sqrt{g}\, \underline{a}^k$ → $[\underline{a}\, \underline{b}] = ab\sin\gamma$
$\doteq Vc^*$ fr. P.106.
(11) $[\underline{a}^i\, \underline{a}^j] = \frac{1}{\sqrt{g}}\, \underline{a}_k$ $\qquad [\underline{a}_1 \underline{a}_2] = \sqrt{g}\, \underline{a}^3 = \sqrt{g}\, c^*$
$\therefore \sqrt{g} = V$

(11a) $\begin{cases} \sqrt{g} = V \\ \frac{1}{\sqrt{g}} = V^* \end{cases}$

106 Triclinic System. Reciprocal Lattice.

$$a^* = \frac{bc \sin\alpha}{V} \qquad V = \frac{bc \sin\alpha}{a^*}$$

$$b^* = \frac{ca \sin\beta}{V} \qquad = \frac{ca \sin\beta}{b^*} \quad \ldots\ldots (16)$$

$$c^* = \frac{ab \sin\gamma}{V} \qquad = \frac{ab \sin\gamma}{c^*}$$

$$\cos\alpha^* = \frac{\cos\beta \cos\gamma - \cos\alpha}{\sin\beta \sin\gamma} \quad \ldots\ldots (17)$$

$$\cos\beta^* = \frac{\cos\gamma \cos\alpha - \cos\beta}{\sin\gamma \sin\alpha}$$

$$\cos\gamma^* = \frac{\cos\alpha \cos\beta - \cos\gamma}{\sin\alpha \sin\beta}$$

60 Metric Tensors for Crystal Lattices.

	g_{ii}	g_{ij}	g^{ii}	g^{ij}
Triclinic	a_i^2 (12)	$a_i a_j \cos\alpha_k$ (13)	$(a^i)^2$ (14)	$a^i a^j \cos\alpha^k$ (15)

61 Transformations for Contravariant Components.

Triclinic compts: x^i
Orthogonal ": X^i $\Big\}$ $[X^i] = [x^j][\beta_j{}^i]$

$$X^1 = \sqrt{g_{11}}\, x^1 + \frac{g_{12}}{\sqrt{g_{11}}}\, x^2 + \frac{g_{31}}{\sqrt{g_{11}}}\, x^3$$

$$X^2 = 0 + \sqrt{\frac{g g^{33}}{g_{11}}}\, x^2 - \frac{\sqrt{g}\, g^{32}}{\sqrt{g_{11}\, g^{33}}}\, x^3$$

$$X^3 = 0 + 0 + \frac{1}{\sqrt{g^{33}}}\, x^3$$

$$\beta_{11} = \sqrt{g_{11}} = a \rightarrow \qquad \text{fr.(12)}$$

$$\beta_{12} = \frac{g_{12}}{\sqrt{g_{11}}} = \frac{ab\cos\gamma}{a} \qquad \text{fr.(13)}, \text{fr.(12)}$$

$$= b\cos\gamma \rightarrow$$

$$\beta_{13} = \frac{g_{31}}{\sqrt{g_{11}}} = \frac{ca\cos\beta}{a} \qquad \text{fr.(13)}, \text{fr.(12)}$$

$$= c\cos\beta \rightarrow$$

$$\beta_{21} = 0$$

$$\beta_{22} = \sqrt{\frac{g g^{33}}{g_{11}}}$$

$$= \sqrt{\frac{g_{11} g_{22} - (g_{12})^2}{g_{11}}} \qquad i=3,\ j=1,\ k=2 \quad \text{fr.(7)}$$

$$= \sqrt{\frac{a^2 b^2 - (ab\cos\gamma)^2}{a^2}} \qquad \text{fr.(12)+(13)}$$

$$= \sqrt{b^2 - b^2\cos^2\gamma}$$

$$= b\sin\gamma \rightarrow$$

$$\beta_{23} = -\frac{\sqrt{g}\, g^{32}}{\sqrt{g_{11}\, g^{33}}}$$

$$= -\frac{V c^* b^* \cos\alpha^*}{\sqrt{a^2 c^{*2}}} \qquad \text{fr.(11a), (15)}, \text{fr.(12), (14)}$$

$$= -\frac{V b^* \cos\alpha^*}{a}$$

$$= -\frac{ca\sin\beta}{a}\left(\frac{\cos\beta\cos\gamma - \cos\alpha}{\sin\beta\sin\gamma}\right) \qquad \text{fr.(16),(17)}$$

$$= -c\left(\frac{\cos\beta\cos\gamma - \cos\alpha}{\sin\gamma}\right) \rightarrow$$

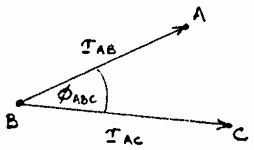
$$\beta_{31} = \beta_{32} = 0$$

$$\beta_{33} = \frac{1}{\sqrt{g^{33}}} = \frac{1}{c^*} \rightarrow \qquad \text{fr.(14)}$$

2. INTERATOMIC DISTANCES

$$|r_{AB}| = \left[(X_B - X_A)^2 + (Y_B - Y_A)^2 + (Z_B - Z_A)^2\right]^{1/2} \quad \text{------------} \quad (3)$$

3. INTERATOMIC ANGLES



$$r_{AB} \cdot r_{BC} = |r_{AB}|\,|r_{BC}| \cos\phi_{ABC}$$

$$\therefore \cos\phi_{ABC} = \frac{r_{AB} \cdot r_{BC}}{|r_{AB}|\,|r_{BC}|}$$

$$(\because \underline{a} \cdot \underline{b} = a_x b_x + a_y b_y + a_z b_z)$$

$$r_{AB} \cdot r_{BC} = X_{AB} X_{BC} + Y_{AB} Y_{BC} + Z_{AB} Z_{BC}$$

$$\cos\phi_{ABC} = \frac{|(X_A - X_B)(X_B - X_C) + (Y_A - Y_B)(Y_B - Y_C) + (Z_A - Z_B)(Z_B - Z_C)|}{|r_{AB}|\,|r_{BC}|} \quad \text{------} \quad (4)$$

4. BEST PLANES THROUGH ATOMS

Let the eqn. of the plane be $Y = m'X + n'Z + c$

If (X_i, Y_i, Z_i) lies off the plane, then $m'X_i + n'Z_i + c \neq Y_i$, but $= Y$

$$Y - Y_i = m'X_i + n'Z_i + c - Y_i$$

Principle of least squares: The sum of the squares of these ⊥ar distances = minimum for the best plane.

Let N = total no. of atoms in the plane.

Define u by $u = \sum_{i=1}^{N} (m'X_i + n'Z_i + c - Y_i)^2$

For u to be a minimum, $\frac{\partial u}{\partial m'}, \frac{\partial u}{\partial n'}, \frac{\partial u}{\partial c} = 0$

$$u = (m'X_1 + n'Z_1 + c - Y_1)^2 + (m'X_2 + n'Z_2 + c - Y_2)^2 + \cdots$$

$$\frac{\partial u}{\partial m'} = 2(m'X_1 + n'Z_1 + c - Y_1).X_1 + 2(m'X_2 + n'Z_2 + c - Y_2).X_2 + \cdots + 2(m'X_N + n'Z_N + c - Y_N)X_N = 0$$

$$\frac{\partial u}{\partial m'} = \sum_{i=1}^{N} (m'X_i + n'Z_i + c - Y_i)X_i = 0 \quad (2)$$

$$\frac{\partial u}{\partial n'} = \sum_{i=1}^{N} (m'X_i + n'Z_i + c - Y_i)Z_i = 0 \quad (3)$$

$$\frac{\partial u}{\partial c} = \sum_{i=1}^{N} (m'X_i + n'Z_i + c - Y_i) = 0 \quad (1)$$

These may be written:

$$\Sigma Y = m\Sigma X + n\Sigma Z + Nc \quad (1)$$

$$\Sigma XY = m\Sigma X^2 + n\Sigma XZ + c\Sigma X \quad (2)$$

$$\Sigma ZY = m\Sigma XZ + n\Sigma Z^2 + c\Sigma Z \quad (3)$$

Put $\Sigma X = A$, $\Sigma XY = D$, $\Sigma X^2 = G$

$\Sigma Y = B$, $\Sigma YZ = E$, $\Sigma Z^2 = H$

$\Sigma Z = K$, $\Sigma ZX = F$

$$B = mA + nK + cN \quad (1)$$

$$D = mG + nF + cA \quad (2)$$

$$E = mF + nH + cK \quad (3)$$

$$B = mA + nK + cN \qquad (1)$$
$$D = mG + nF + cA \qquad (2)$$
$$E = mF + nH + cK \qquad (3)$$

$(1) \times A - (2) \times N$: $\quad (BA - ND) = m(AA - NG) + n(AK - NF) \qquad (4)$

$(1) \times K - (3) \times N$: $\quad (BK - NE) = m(AK - NF) + n(KK - NH) \qquad (5)$

$(4) \times (AK - NF) - (5) \times (AA - NG)$:

$$(BA - ND)(AK - NF) - (BK - NE)(AA - NG) = n\left[(AK - NF)(AK - NF) - (KK - NH)(AA - NG)\right]$$

$$\therefore n = \frac{(BA - ND)(AK - NF) - (BK - NE)(AA - NG)}{(AK - NF)(AK - NF) - (KK - NH)(AA - NG)}$$

$$n' = \frac{(\Sigma X \Sigma Y - N\Sigma XY)(\Sigma X \Sigma Z - N \Sigma XZ) - (\Sigma Y \Sigma Z - N\Sigma YZ)(\Sigma X \Sigma X - N\Sigma X^2)}{(\Sigma X \Sigma Z - N\Sigma XZ)(\Sigma X \Sigma Z - N\Sigma XZ) - (\Sigma Z \Sigma Z - N\Sigma Z^2)(\Sigma X \Sigma X - N\Sigma X^2)} \qquad ⑤$$

$(4) \times (KK - NH) - (5) \times (AK - NF)$:

$$(BA - ND)(KK - NH) - (BK - NE)(AK - NF) = m\left[(AA - NG)(KK - NH) - (AK - NF)(AK - NF)\right]$$

$$\therefore m = \frac{(BA - ND)(KK - NH) - (BK - NE)(AK - NF)}{(AA - NG)(KK - NH) - (AK - NF)(AK - NF)}$$

$$m' = \frac{(\Sigma X \Sigma Y - N\Sigma XY)(\Sigma Z \Sigma Z - N\Sigma Z^2) - (\Sigma Y \Sigma Z - N\Sigma YZ)(\Sigma X \Sigma Z - N\Sigma XZ)}{(\Sigma X \Sigma X - N\Sigma X^2)(\Sigma Z \Sigma Z - N\Sigma Z^2) - (\Sigma X \Sigma Z - N\Sigma XZ)(\Sigma X \Sigma Z - N\Sigma XZ)} \qquad ⑥$$

From (1): $\quad c = \dfrac{B - m'A - n'K}{N}$

$$c = \frac{\Sigma Y - m'\Sigma X - n'\Sigma Z}{N} \qquad ⑦$$

In Intern. Tables, the eqns. of a plane are:

$$\left.\begin{aligned} LX + mY + nZ - p &= 0 \\ L^2 + m^2 + n^2 &= 1 \end{aligned}\right\}$$

c.f. $\quad m'X - Y + n'Z + c = 0$

equate coeffts: $\quad \therefore L = Am' \qquad (Am')^2 + (A)^2 + (An')^2 = 1$

$m = A(-1) \qquad \therefore A^2 = \dfrac{1}{(m')^2 + (1) + (n')^2}$

$n = An'$

$p = A(-c) \qquad A = \pm \dfrac{1}{\sqrt{1 + (m')^2 + (n')^2}}$

Thus the relations betw. L, m, n, p, and m', n', c are :-

$$\left.\begin{aligned} L &= -m' / \sqrt{1 + (m')^2 + (n')^2} \\ m &= 1 / \sqrt{1 + (m')^2 + (n')^2} \\ n &= -n' / \sqrt{1 + (m')^2 + (n')^2} \\ p &= c / \sqrt{1 + (m')^2 + (n')^2} \end{aligned}\right\} \qquad ⑧$$

5. ANGLE BETWEEN TWO PLANES.

Int. Tables II P.43.

Let the eqns. of the two planes be:

$l_1X + m_1Y + n_1Z - p_1 = 0$ and $l_1^2 + m_1^2 + n_1^2 = 1$

$l_2X + m_2Y + n_2Z - p_2 = 0$ .. $l_2^2 + m_2^2 + n_2^2 = 1$

Then the angle betw. the planes, θ, which is the angle betw. their outward normals, is given by:

$$\cos\theta = l_1l_2 + m_1m_2 + n_1n_2 \quad (9)$$

The planes are parallel if $l_1l_2 + m_1m_2 + n_1n_2 = \pm 1$
and they intersect at rt. ∠s. if $l_1l_2 + m_1m_2 + n_1n_2 = 0$

6. PERPENDICULAR DISTANCE BETWEEN A POINT AND A PLANE. P.43

Let coords. of the point be X_1, Y_1, Z_1

Let the eqn. of the plane concerned be

$lX + mY + nZ - p = 0$ and $l^2 + m^2 + n^2 = 1$

Then perpen. distance D from point to plane is

$$D = lX_1 + mY_1 + nZ_1 - p \quad (10)$$

D is +ve if point (X_1, Y_1, Z_1) is on the side of the plane opposite to that containing the origin.

APPENDIX B

DEVICE FOR RAPIDLY DETERMINING THE LOCATIONS IN THE PATTERSON AT WHICH POSSIBLE A-B PEAKS CAN BE SOUGHT

"Master" card

	X	Y	Z		
(1)	1	1	1	+ + +	First quarter
First	1	1	2	+ + -	
equivalent	1	2	1	+ - +	
position	1	2	2	+ - -	
x	2	1	1	- + +	
y	2	1	2	- + -	
z	2	2	1	- - +	
	2	2	2	- - -	
(2)	3	2	4		Second quarter
Second	3	2	3		
equivalent	3	1	4		
position	3	1	3		
$\frac{1}{2} - x$	4	2	4		
$\bar{y}$	4	2	3		
$\frac{1}{2} + z$	4	1	4		
	4	1	3		
(3)	4	3	2	1=A-B	Third quarter
Third	4	3	1		
equivalent	4	4	2	2=A+B	
position	4	4	1		
$\frac{1}{2} + x$	3	3	2	3=50+A+B	
$\frac{1}{2} - y$	3	3	1		
$\bar{z}$	3	4	2	4=50+A-B	
	3	4	1		
(4)	2	4	3		Fourth quarter
Fourth	2	4	4		
equivalent	2	3	3		
position	2	3	4		
$\bar{x}$	1	4	3		
$\frac{1}{2} + y$	1	4	4		
$\frac{1}{2} - z$	1	3	3		
	1	3	4		

If atom A(1), i.e. atom A in its first equivalent position, is combined with the eight permutations of signs of atom B in the order printed on the right hand side of the "master" card, the values of the x, y and z coordinates of the corresponding A(1) - B Patterson peaks are represented by the numbers in the first quarter of the x-, y-, z-columns, where the number 1 in the x-column stands for $A_x - B_x$, 1 in the y-column stands for $A_y - B_y$, 1 in the z-column stands for $A_z - B_z$; the number 2 in the x-column stands for $A_x + B_x$, etc.

If atom A(2), i.e. atom A in its second equivalent position, is combined with the eight permutations of signs of atom B <u>in the same order</u>, the values of the coordinates of the A(2) - B Patterson peaks are represented by the numbers in the second quarter, where 1 and 2 have the same meaning as before, while the number 3 in the x-column stands for 50 + A_x + B_x and 4 in the x-column stands for 50 + A_x - B_x, etc.

The third quarter on the master card gives values for A(3) - B and the fourth quarter for A(4) - B Patterson peaks.

An example will clarify the procedure:-

Atom A at (18,20,10),

Atom B at (1, 8,18),

and the signs of the coordinates of B are to be determined by the device.

Number 1 in x-column	$= A_x - B_x$	= 18 - 1	= 17
" 2 " " "	$= A_x + B_x$	= 18 + 1	= 19
" 3 " " "	$= 50 + A_x + B_x$	= 50 + 19	= 69 (= 31)
" 4 " " "	$= 50 + A_x - B_x$	= 50 + 17	= 67 (= 33)
Number 1 in y-column	$= A_y - B_y$	= 20 - 8	= 12
" 2 " " "	$= A_y + B_y$	= 20 + 8	= 28
" 3 " " "	$= 50 + A_y + B_y$	= 50 + 28	= 78 (= 22)
" 4 " " "	$= 50 + A_y - B_y$	= 50 + 12	= 62 (= 38)
Number 1 in z-column	$= A_z - B_z$	= 10 - 18	= -8 (= 8)
" 2 " " "	$= A_z + B_z$	= 10 + 18	= 28
" 3 " " "	$= 50 + A_z + B_z$	= 50 + 28	= 78 (= 22)
" 4 " " "	$= 50 + A_z - B_z$	= 50 - 8	= 42

Due to the symmetry of the Patterson, a peak at (69,78,-8) is the same as a peak at (31,22, 8), hence the "master" card can be filled in as follows:-

	X	Y	Z	
(1)	17	12	8	+ + +
	17	12	28	+ + -
	17	28	8	+ - +
	17	28	28	+ - -
	19	12	8	- + +
	19	12	28	- + -
	19	28	8	- - +
	19	28	28	- - -
(2)	31	28	42	
	31	28	22	
	31	12	42	
	31	12	22	
	33	28	42	
	33	28	22	
	33	12	42	
	33	12	22	
(3)	33	22	28	
	33	22	8	
	33	38	28	
	33	38	8	
	31	22	28	
	31	22	8	
	31	38	28	
	31	38	8	
(4)	19	38	22	
	19	38	42	
	19	22	22	
	19	22	42	
	17	38	22	
	17	38	42	
	17	22	22	
	17	22	42	

The card now lists the 32 locations in the Patterson at which A-B peaks must be sought. If A and B are true atoms, four A-B peaks will be found at the Patterson coordinates occupying the same position on the card in each of the four quarters, and the signs of the coordinates of atom B will be given by this position: e.g. if Patterson peaks are found at (17,12,28), (31,28,22), (33,22, 8) and (19,38,42), then atoms A and B are true atoms and the signs of the coordinates of B are (++-).

"Coordinate difference" cards

X = 18	1	2	3	4
0	18	18	32	32
2	16	20	30	34
4	14	22	28	36
6	12	24	26	38
8	10	26	24	40
10	8	28	22	42
12	6	30	20	44
14	4	32	18	46
16	2	34	16	48
18	0	36	14	50
20	2	38	12	48
22	4	40	10	46
24 25	6 7	42 43	8 7	44 43

Y = 20	1	2	3	4
0	20	20	30	30
2	18	22	28	32
4	16	24	26	34
6	14	26	24	36
8	12	28	22	38
10	10	30	20	40
12	8	32	18	42
14	6	34	16	44
16	4	36	14	46
18	2	38	12	48
20	0	40	10	50
22	2	42	8	48
24 25	4 5	44 45	6 5	46 45

Z = 10	1	2	3	4
0	10	10	40	40
2	8	12	38	42
4	6	14	36	44
6	4	16	34	46
8	2	18	32	48
10	0	20	30	50
12	2	22	28	48
14	4	24	26	46
16	6	26	24	44
18	8	28	22	42
20	10	30	20	40
22	12	32	18	38
24 25	14 15	34 35	16 15	36 35

In order to further expedite the process "coordinate difference" cards are prepared which automatically assign values to the numbers 1, 2, 3 and 4, so that the twelve calculations for $A_x - B_x$, etc. need not be done.

The x "coordinate difference" card shown above gives the values to be assigned to the numbers 1, 2, 3, 4 in the x-column of the master card for two atoms, one of which is situated at $x = 18$: e.g. if the second atom is at $x = 6$, the numbers 1-4 must be given the values 12, 24, 26, 38; if the second atom is at $x = 22$, the numbers 1-4 have the values 4, 40, 10, 46; etc. If the second atom were at $x = 21$, the corresponding values can be readily interpolated as 3, 39, 11, 47. Similarly the y card shown above is used to obtain the y coordinate differences of two atoms, one of which is situated at $y = 20$, etc.

Illustrated above are three "coordinate difference" cards which were actually made out for an atom at (18,20,10), but it soon became plain that a set of 14 cards would give <u>all</u> the Patterson values required for insertion in the "master card" for <u>any</u> pair of atoms.

The application of this device is thus extremely simple:- firstly, the equations represented by the numbers 1-4 must be calculated from the coordinates of equivalent positions of the particular space group concerned and the master card is then made out; secondly, the values to be assigned to the numbers must be calculated for the preparation of the 14 coordinate difference cards, but in practice, once one card has been calculated, the remaining cards can be filled in virtually by inspection.

The comparison of any pair of possible atoms then becomes an error-free process occupying a few minutes.

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ADDENDA

3rd October, 1969.

When the paper on thiethylperazine was accepted for publication by Acta Crystallographica on 22nd September, 1969, the referee requested further information on two points:-

1. The method of correcting the diffractometer data for peak spread;
2. The sharpened Patterson function.

Further details were therefore written for inclusion in the publication, and as a consequence it was considered advisable to include the additional information in the thesis.

1. Method of correcting the diffractometer data for peak spread

(Section C7, p.66)

From the shape of the peak profile (Figure 11) it is clear that the (5,2,0) peak may overlap certain other peaks with θ values between approximately 2° and 12°, thus altering the peak intensities. This overlap is subtracted by the following procedure. A generalised peak profile common to any selected peak must be obtained by calculating normalised values of I as a function of λ, and not θ. The direct readings obtained from the graph are values of I and θ. The interplanar spacing of the (5,2,0) planes, d, is calculated from

$$2d = \frac{\lambda_{Mo(at\ \theta\ max)}}{\sin\theta_{max}} = 5.4\ \text{Å}\ ,$$

and this value of d is re-substituted into Bragg's equation to give $\lambda = 5.4 \sin\theta$, from which the λ values corresponding to each reading of θ may be calculated. Normalised values of I are calculated from

$$I_{norm.} = \frac{I_L}{I_{L(max.)}} ,$$

where $I_{L(max)}$ is the Lp-corrected value of the peak intensity. The graph of the (5,2,0) peak if plotted for values of $I_{norm.}$ against λ would now be the same as the graph of any other peak, because at the maximum point the ordinate has the value 1 and the abscissa has the value

$$\lambda = .70926 \ (= \lambda_{Mo})$$

i.e. a generalised peak profile has been obtained.

2. The sharpened Patterson function
(Sections B10(d), p. 33; C10, p.70)

The Patterson function,

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

$$= \frac{1}{V} \sum_h \sum_k \sum_l \ |F_{hkl}|^2 \cos 2\pi\ (hu+kv+lw) \qquad (1)$$

may be sharpened by the use of the exponential function, $e^{B \sin^2\theta/\lambda^2}$, but false minima are likely to be introduced. Jacobson, Wunderlich & Lipscomb (1959,1961) investigated a procedure which would reduce the false minima and yet leave the peaks highly sharpened. Functions of *r* which change more rapidly with *r* than ρ(*r*) were sought, and the gradient Patterson function, Q(*u*,*v*,*w*) was chosen, where

$$Q(u,v,w) = V \int_0^1 \int_0^1 \int_0^1 \nabla\ \rho(x,y,z).\nabla\rho(x+u,\ y+v,\ z+w)\ dx\ dy\ dz$$

where the gradient operator† is

†Condon & Odishaw, 1958

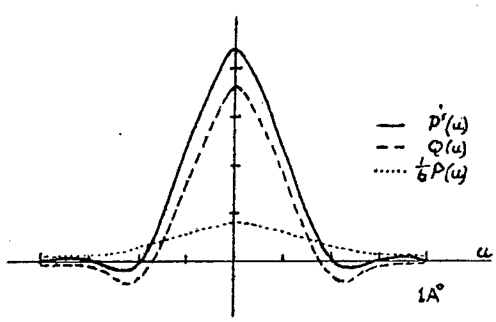
$$V = a^* \frac{\partial}{\partial x} + b^* \frac{\partial}{\partial y} + c^* \frac{\partial}{\partial z}$$

The usual expression for $\rho(x,y,z)$ in terms of F_{hkl} reduces Q to

$$Q(u,v,w) = \frac{16\pi^2}{V} \sum_h \sum_k \sum_l \frac{\sin^2\theta}{\lambda^2} |F_{hkl}|^2 \cos 2\pi(hu+kv+lw) \tag{2}$$

The gradient Patterson function in itself is only slightly better than a highly sharpened Patterson function; it is in fact a familiar sharpening function, which has negative regions.

However, a weighted combination of $Q(u,v,w)$ with a normal sharpened Patterson function can be chosen in which positive regions of $P(u,v,w)$ of approximately the right magnitude correspond with the negative regions of $Q(u,v,w)$, resulting in very sharp peaks surrounded by comparatively small residual regions. This is illustrated by the following one-dimensional diagram:-



The new combination function $P'(u,v,w)$ may thus be expressed as

$$P'(u,v,w) = A\,Q(u,v,w) + B\,P(u,v,w) \tag{3}$$

where P is the usual sharpened Patterson function, Q is the gradient sharpened Patterson function, and A and B may be chosen empirically to give the best sharpening while decreasing the negative regions around the peaks.

Values for A and B of 1 and $\frac{1}{6}$ $(16\pi^2)$, respectively, were selected. The $|F_{hkl}|^2$ were the usual sharpened coefficients (Spencer & Lipscomb, 1961):-

$$|F_{hkl}|^2 = \frac{F_o^2 \, e^{B \sin^2\theta/\lambda^2}}{(\hat{f})^2} \qquad (4)$$

where $\hat{f}$ is the unitary scattering factor (Lipson & Cochran, 1953, P. 64, P. 153),
and is given by

$$\hat{f} = \frac{\sum_i f_i}{\sum_i Z_i}$$

Combining equations 1,2,3,4 and the chosen values for A and B leads to the equation

$$P'(u,v,w) = \frac{16\pi^2}{V} \sum_h \sum_k \sum_l \left(\frac{\sin^2\theta}{\lambda^2} + \frac{1}{6} \right) \frac{F_o^2 \, e^{B \sin^2\theta/\lambda^2}}{(\hat{f})^2} \cos 2\pi(hu+kv+lw)$$

in which the sharpened coefficients closely resemble those given in the text of this thesis on p.33.

According to Jacobson, Wunderlich & Lipscomb (1959,1961), and Spencer & Lipscomb (1961), the new procedure which emphasizes the gradient of the electron density function is of considerable importance in resolving closely neighbouring peaks. The sharpened Patterson functions calculated for chlorpromazine and thiethylperazine certainly support this conclusion.

Further advantages claimed for the modified Patterson function, P', by Jacobson *et al.* are that low order reflections susceptible to extinction and absorption are given low weight, and interactions between heavy atoms are relatively enhanced due to the fact that as sin θ increases, the decrease in the atomic scattering factors for heavy atoms is less than for light atoms.

Note. In the main text of this thesis (pp.70,71), the unsharpened and sharpened Patterson functions have been designated P(u) and P(s) respectively; P(s) is the combination function referred to in the addendum as P'.

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