THE DETERMINATION OF TWO ORGANIC CRYSTAL STRUCTURES
BY
X-RAY DIFFRACTION

by.

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The work described in this thesis was carried out in the Department of Physics between February 1960 and August 1963; except where stated otherwise it is the personal work of the author.

No material contained in this thesis has been submitted for the award of another degree or diploma in this or any other university.

B.W. Matthews.

August, 1963.

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Summary

This thesis describes, in the main, the determination and refinement of two crystal structures.

The first structure, phenyl thiazolidine dione, was solved via a partial interpretation of the three dimensional Patterson function. The intensities of the diffracted spectra were measured more accurately than is usual, and the structure has been refined to give calculated structure amplitudes in close agreement with those observed. All the bond lengths are within normal limits and are interpreted in terms of a resonance structure.

The second crystal structure described is that of a bromo-benzimidazole derivative, and has two independent molecules in the asymmetric unit. The two heavy atoms were located by a combination of Harker and line sections through the three dimensional Patterson function; their successful location led to the determination of the remainder of the structure. Refinement of this structure has revealed that the two independent molecules are generally very similar, and that all bond lengths are normal.

Computer programs were written to facilitate the many numerical calculations; brief descriptions of selected programs are included.

Programs written for the purpose of structural refinement were based on the method of "Differential Difference" Fourier syntheses. An outline is given of the theory underlying this method of refinement which is also compared with the more commonly used "Least Squares" technique.

A brief description is given of an X-ray power supply which was modified for the purposes of X-ray diffraction.

Acknowledgments

I would like to thank my supervisors, Dr. S.G. Tomlin and Dr. E.H. Medlin, for their guidance and practical help.

During the formative stages of this work Mr. (now Dr.) G.E. Gurr gave considerable practical help for which I am most grateful. I would also like to thank Dr. C.J.E. Kempster, Dr. B. Dawson, Dr. J.W. Clark-Lewis and Mr. J. Edgar for helpful discussions.

The facilities of the Department of Physics were generously provided firstly by Professor L.G.H. Huxley, and later by Professor J.H. Carver.

Several people helped indirectly with the numerical calculations, in particular I would like to thank the staff of the University Computing Centre for their friendly cooperation. Dr. F.M. Lovell kindly supervised several computations on "SILLIAC" in Sydney.

Misses H. Barrow and M. Chapman helped with several of the diagrams; Mr. G. Tomlinson took the photographs.

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CHAPTER 1.

EQUIPMENT AND EXPERIMENTAL TECHNIQUES

1.1 X-ray generators.

Two power supplies were used for the investigations described in this thesis; the first had been built in this laboratory and will be called the "Medlin" supply, the second was a modified "Solus" medical X-ray set.

1.1.1 Medlin power supply.

The power supply used for the work described in Chapter 2 was constructed by Dr. E.H. Medlin and used in conjunction with a Philips type 25293/62 self rectifying X-ray tube. A complete description is given by Medlin (1955) and Gurr (1961).

The supply, which was used for the work described in Chapter 2, was largely trouble free, but as time passed it became difficult to suppress discharges between the high tension tube lead and the surrounding earthed casing. This fault was later traced to a malfunction in the "Stabilac" voltage regulator which gave a very distorted wave form.

1.1.2 Solus power supply.

Before the investigation described in Chapter 3 had commenced, the Broken Hill Mining Managers Association donated to the Physics Department a Solus medical X-ray set originally purchased in 1935. This supply, in addition to having six times the power rating of the Medlin unit, had rectification of the H.T. voltage and was modified for the purposes of X-ray diffraction.

Additions included meters to measure the tube current and H.T. voltage directly, and relays to guard against excessive tube currents or failure of the flow of cooling water. Initially the supply was run without the H.T. condenser, however the maximum H.T. voltage available fell off under load from 45 K.V. to 27 K.V. for a tube current of 20 m.a.; with the condenser the voltage exceeded 40 K.V. for the same load.

Since the original diagram of the supply had been lost and a copy could not be obtained, that part of the circuitry revelant to the supply's present operation is shown in fig. 1.

Although the supply was run without voltage or current stabilisation, short term tube current fluctuations generally did not exceed ± 2% and were not thought serious while using photographic measuring techniques. Overnight mains voltage variation caused the tube current to increase by up to 25% and some form of regulation to suppress this would be a worthwhile addition to the supply.

The modified unit is shown in Plate 1. : after settling in it has given little trouble and has, on occasion, been run continuously for more than a fortnight. Operation of the generator is described in Appendix 1.

PLATE 1 - SOLUS POWER SUPPLY

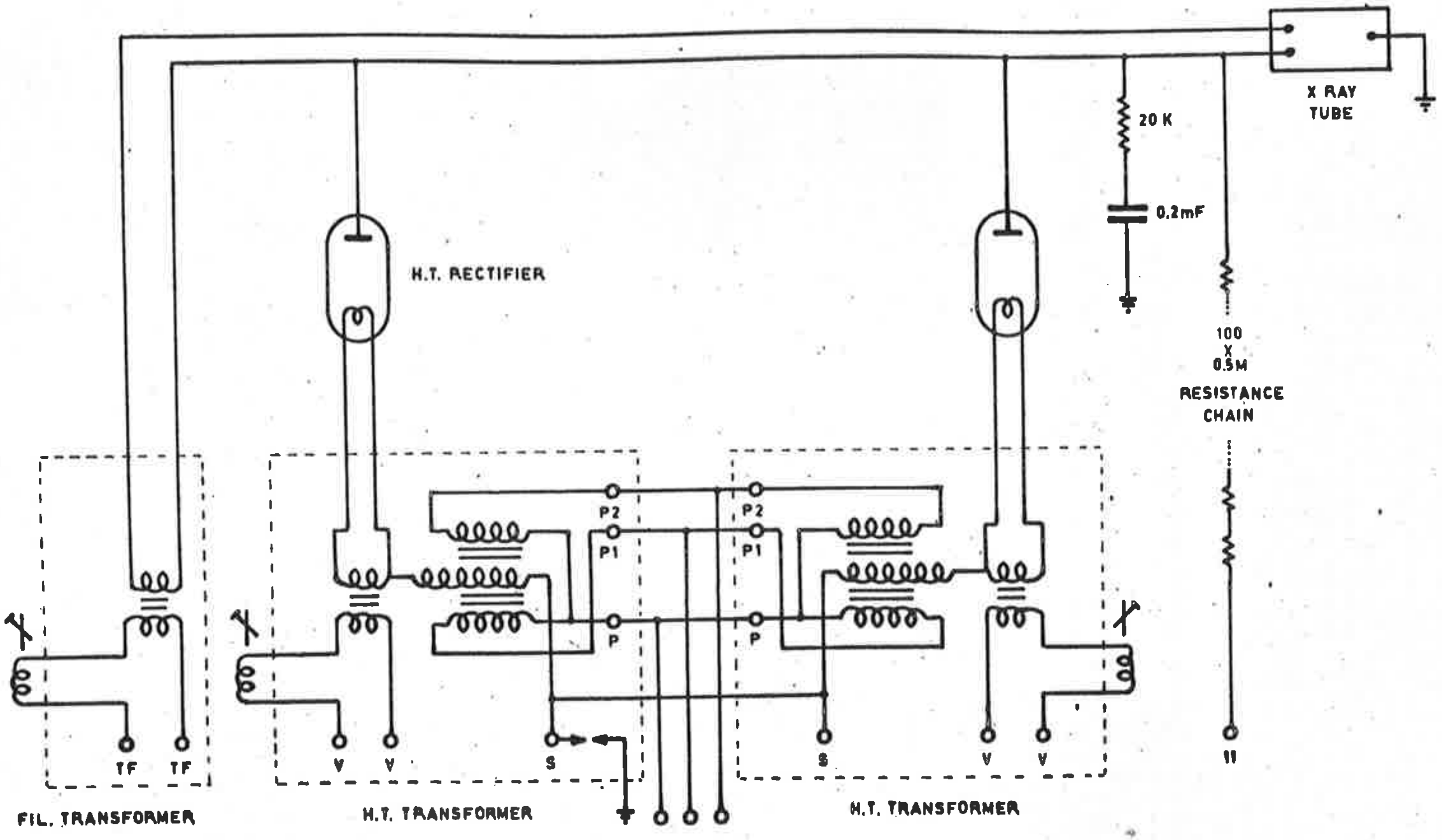

Fig. 1a. High tension circuit.

Fig. 1. Solus power supply.

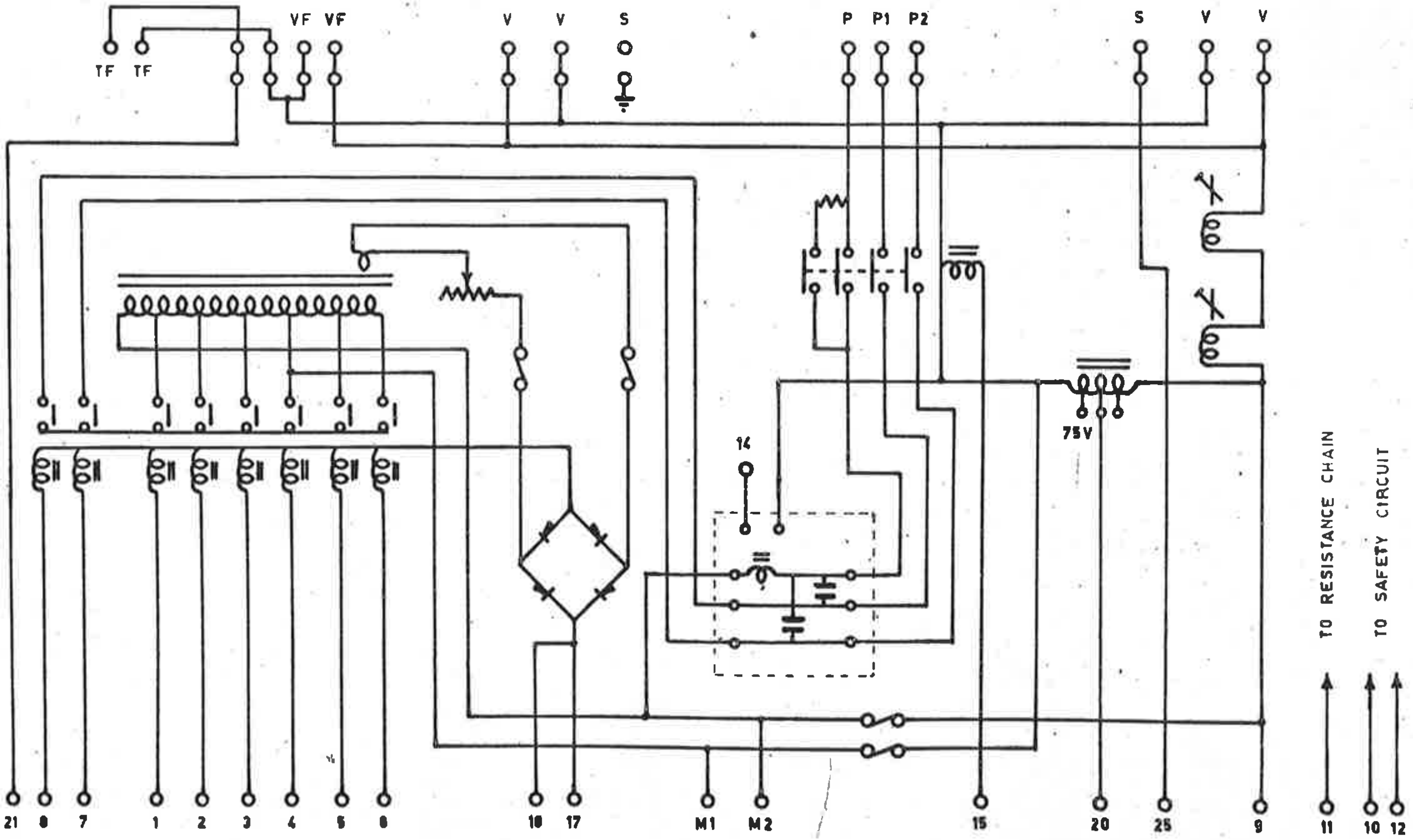

Fig. 1b. Primary circuit.

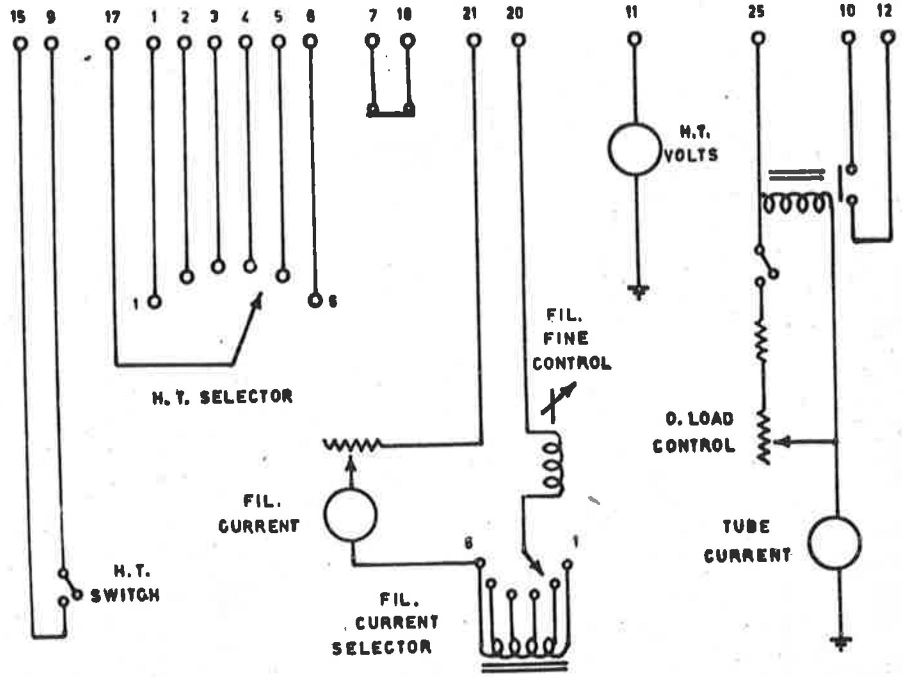

Fig. 1c. Control circuit.

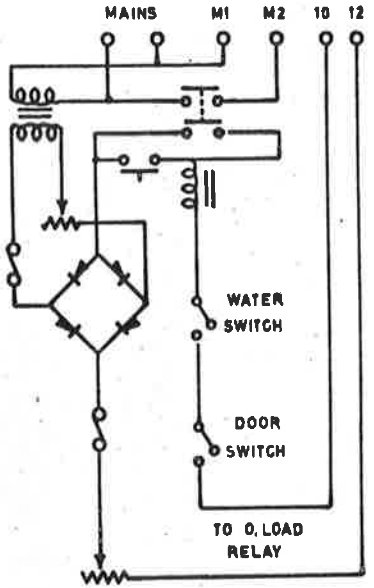

Fig. 1d. "Safety" circuit.

1.2 Measurement of intensities.

Diffracted spectra were recorded on Ilford Blue Label "Industrial G" X-ray film using either a Unicam S25 rotation, or S35 Weissenberg camera. Development was with ID42 for 10 min. at 68°F.

1.2.1 Integrated intensities.

On occasion a two dimensional integrating attachment designed by Dr. Medlin for the Weissenberg camera was used in conjunction with a Zeiss microphotometer to measure intensities more accurately. When integrating, the length of traverse was not less than the corresponding overall dimension of the largest reflection, and care was taken to avoid errors in background intensity due either to white radiation from neighbouring reflections on the same lattice row, or to exhaustion of the developer in the vicinity of strong reflections. The X-ray intensities were regarded as directly proportional to the measured optical densities for densities up to 1.2, a linear range given by Acta Cryst., 9, 520, and also confirmed in this laboratory by Gurr (1961).

1.2.2 Eye estimated intensities.

For those intensities estimated by eye, standard intensity strips were made by allowing a prominent reflection of moderate Bragg angle to pass through its reflection position an increasing number of times, the film being translated a few millimetres between each exposure.

1.2.3 Film factors.

The "film factor" which defines the attenuation in the X-ray beam as it passes from one film to the next in a film pack must be known if intensities of reflections measured on differing films of the pack are to be put on a common scale. Since a reflection consists of monochromatic radiation it is expected that within one film pack the film factors will be constant. Furthermore, knowing R(0) the film factor for radiation incident normal to the film, it should be possible to predict R(θ) the film factor for radiation incident at an angle θ from normal.

From geometrical considerations we expect *

$$\log R(0) \;=\; \cos\theta .\ \log R(\theta) \qquad (1.1)$$

To verify this relation R(θ) was measured for several layers by averaging the individual integrated intensity ratios of pairs of reflections whose density was less than 1.1 and measurable on adjacent films. Within any film pack R(θ) did not vary by more than 4% from film to film, and the constancy of cosθ.logR(θ) is illustrated below.

Layer	θ	R(θ)	cosθ.logR(θ)
h01	0	3.05	.484
h11	6°33'	3.11	.490
h21	13°11'	3.20	.492
h31	20°0'	3.34	.492
h41	27°8'	3.52	.487

Film factors used in Chapter 3 were derived from this table which was constructed from those measured and used in the work described in Chapter 2.

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* Since writing, verification of (1.1) has been seen in a note by Grenville-Wells (1955); also Rossmann (1956) has suggested a modification to include photochemical absorption effects.

CHAPTER 2.

THE CRYSTAL AND MOLECULAR STRUCTURE OF THE SODIUM SALT OF 5-PHENYL-THIAZOLIDINE-2:4-DIONE.

2.1 Introduction.

At the commencement of this investigation a compound was sought that was of biological interest and whose structure determination would be amenable to the two dimensional methods in use in this Department at that time. Dr. Medlin suggested the sodium salt of phenyl thiazolidine dione which had been shown by Shulman (1957) to have potential use in preventing epileptic seizures.

A search of the literature revealed that this compound had not been investigated by X-ray methods and that furthermore the 5-membered thiazolidine ring had occurred in only one X-ray investigation, that being the analysis of the crystal structure of penicillin (Crowfoot et.al., 1949). In penicillin the shape of the thiazolidine ring is undoubtedly influenced by the β-lactam ring, part of which is common with the thiazolidine ring. An investigation of the crystal structure of phenyl thiazolidine dione was therefore desirable not only because of its pharmacological interest but also as an independent determination of the dimensions of the unstrained thiazolidine ring.

Although the contribution of the sulphur scattering relative to that of the rest of the molecule would be somewhat less than that generally recommended for a successful structure determination (Lipson and Cochran, 1957, p.207) it was decided to proceed with this compound. (Since this work was commenced the crystal structures of rhodanine (van der Helm, Lessor and Merritt, 1962), merocyanine (Germain, Piret and Van Meerssche, 1962) and vitamin B_1 (Kraut and Reed, 1962) have been published; these compounds all contain the thiazolidine ring but with widely different substituents in each case.)

Two Patterson projections were misinterpreted and the "heavy atom" wrongly placed. After unsuccessful attempts to determine the remainder of the structure, generalized Patterson projections revealed the error in the sulphur position. By this time improved computing facilities had become available and these made it possible to overcome the limitations of projections by using three dimensional syntheses.

This chapter will in general be devoted to the successful solution and refinement in three dimensions, although a brief resumé of the unsuccessful attempt using projections will be included.

2.2 Properties of 5-phenyl-thiazolidine-2:4-dione.

2.2.1 Physical properties.

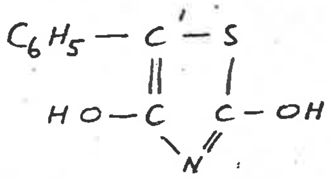
A sample of the sodium salt of phenyl thiazolidine dione (hereafter NaPTD) was donated by Nicholas (Aust.) Pty. Ltd. This appeared as colourless microscopic flakes which were insoluble in ethanol and acetone, slightly soluble in methanol, but very soluble in water.

Crystals were grown from water, the saturated solution being kept in a stoppered container in a constant temperature room for several weeks. The crystals always occurred as thin irregular plates formed parallel to (001) and often twinned on this plane. Cleavage parallel to (001) was most marked, while the crystal plates could also be split parallel to [010] in approximately the (100) plane. Other attempts to cleave or cut the crystal plates invariably resulted in multiple cleavage parallel to (001).

Additional physical properties are summarised in Table 2.

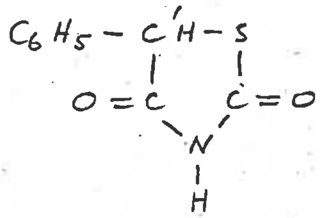
2.2.2 Chemical properties.

The chemical properties of NaPTD have been reported by Davies, MacLaren and Wilhemson (1950). Shulman (1957) points out that PTD can be written in the tautomeric forms I and II.



PTD (I)

2:4 Dihydroxy-5-phenylthiazole



PTD (II)

5-Phenylthiazolidine-2:4-dione

An X-ray structure determination would readily distinguish between the two, for even if the carbon-oxygen bond lengths were not sufficient evidence, the tetrahedral or planar bonding of C' would be quite conclusive.

Microanalysis of hand-picked cyrstals by the Organic Micro-analytical Laboratory of the C.S.I.R.O. confirmed the chemical composition $C_9H_6NO_2SNa$ as shown below.

Element	% Observed	% Calculated
C	50.60	50.23
H	3.01	2.79
N	6.43	6.51
O	15.9	14.87
S	12.58	14.90
Na	10.6 *	10.69

* Calculated from sulphate ash.

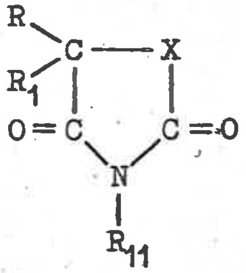
2.2.3 Pharmacological properties.

When written in its keto-tautomeric form, (i.e. as PTD (II) above), PTD has a close structural similarity to many of the antiepileptiform drugs in current use. This may

TABLE 1.

A structural comparison between PTD and other common antiepileptiform drugs.

General formula



Drug	R	R_1	R_{11}	X
PTD.	C_6H_5	H	H	S
Phenobarbitone	C_6H_5	C_2H_5	H	NH-CO
Dilantin	C_6H_5	C_6H_5	H	NH
Mesantoin	C_6H_5	C_2H_5	CH_3	NH
Epidon	C_6H_5	C_6H_5	H	O

be seen in Table 1. taken from Shulman (1957).

Shulman experimentally demonstrates the following properties of PTD.

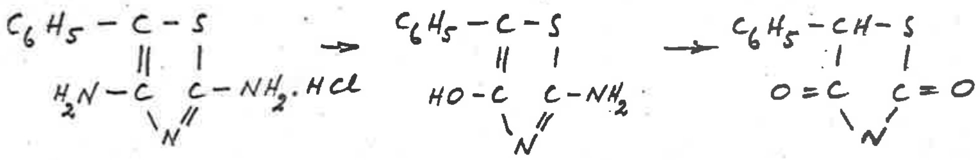
a. PTD produces narcosis in mice which is reversed by the barbiturate antagonist Bemegride (β-methyl-β-ethyl glutarimide). It also promotes the hypnotic action of phenobarbitone sodium in mice.

b. PTD protects mice against the convulsant action of Leptazol. (This property and a structural similarity to many of the commonly employed antiepileptiform drugs suggests that this and related substances may merit investigation in the treatment of epileptiform seizures.)

c. PTD antagonizes the respiratory stimulant and convulsive properties of its parent substance 2:4-diamino-5-phenythiazole hydrochloride (DAPT), (shown below) in mice. This is followed by an increased depth of narcosis, and an increased incidence and rapidity of death.

The result c. is taken as indicating that DAPT may be metabolized to PTD during the process of antagonism. Shulman also suggests that this conversion may proceed through the intermediate substance 2-amino-4-hydroxy-5-phenylthiazole (AHPT), which itself exhibits weak hypnotic properties and potentiates the hypnotic action of PTD and phenobarbitone.

The suggested method of conversion is shown below.



DAPT AHPT PTD

2.2.4 Space group and unit cell.

Zero, first and second layer Weissenberg photographs taken about the a and b axes showed the unit cell to be monoclinic, of approximate dimensions

$$a = 9.54\ \text{A}$$
$$b = 6.76\ \text{A}$$
$$c = 14.7\ \text{A}$$
$$\beta = 101^{\circ}$$

A molecular weight of 215.1 a.m.u. and a measured density of 1.53 gm/cm^3 indicated 4 molecules in general positions in the unit cell. The systematic absences - h0l for h odd, and 0k0 for k odd - gave the space group unequivocally as P2$_1$/a.

The cell dimensions were later determined more accurately by the extrapolation method of Farquhar and Lipson (1946). There were several reasons why the precision attained in their example was not achieved in this determination.

a. Organic crystals exhibit greater thermal vibrations than inorganic; therefore there are fewer sufficiently intense high angle reflections.

b. Copper radiation only was used. This limits the number of reflections in the high sinθ range and therefore forces a choice of reflections with less favourable indices.

c. For reasons which will be discussed later, good crystals could only be obtained suitable for rotation about the monoclinic axis. Reflections of the type (h0l) were therefore used to determine a, c and β. Use of these reflections has the inherent disadvantage that unless (h00) type reflections only can be used the value of a, for example, is influenced by errors in the values of c and cosβ. This can in theory be overcome by using a cyclic process to improve the accuracy of each parameter in turn, however in this case after three cycles the parameters began to oscillate rather than to converge to definite limiting values.

d. Not all reflections used were recorded on both sides of the "sinθ = 1" position on the film. At least two doublets were recorded symmetrically in the conventional way and then the "sinθ = 1" position taken as the average value obtained from these four reflection pairs. The positions of other reflections only recorded once on the film were then measured relative to this point. Since the four independent determinations of the "sinθ = 1" position always agreed within the experimental limit of measurement of position, any errors introduced are probably not more than those arising from positional uncertainties.

The crystal used to determine a, c and β measured .08 x .05 mm. in cross section; b was found using 0kl spectra from a crystal of approximate cross section b = 0.08 mm. and c = 0.4 mm. used "edge on".

The specially adapted camera described by Farquhar and Lipson (1946) was not available; instead, a hole for the collimator was cut in the film which was then loaded "back to front" in the Unicam S25 oscillation camera.

Figures 2a to 2d illustrate the final results which are summarised in Table 2.

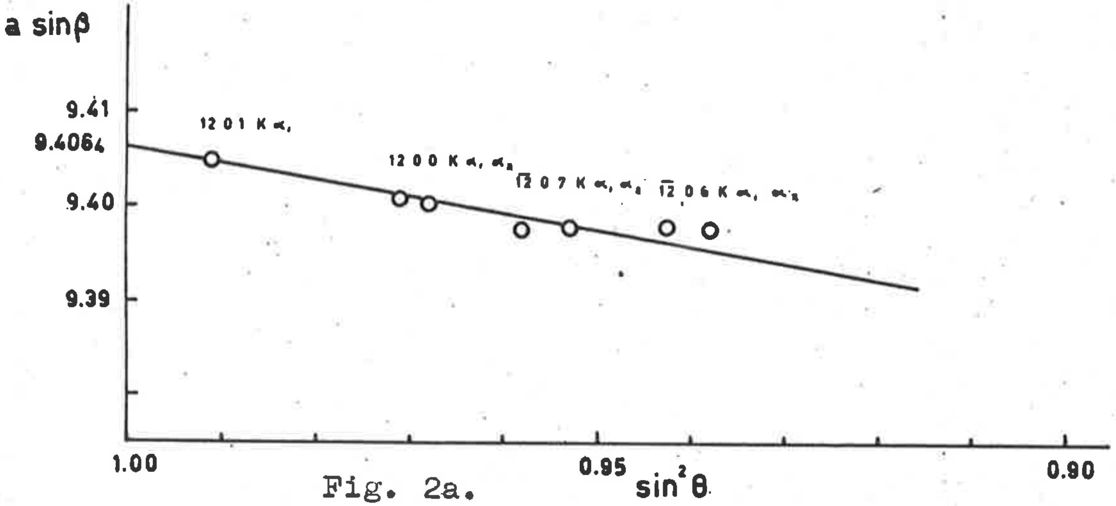

a sinβ
9.41
9.4064
9.40
9.39
12 0 1 Kα1
12 0 0 Kα1, α2
$\bar{12}$ 0 7 Kα1, α2
$\bar{12}$ 0 6 Kα1, α2
1.00
0.95
0.90
sin²θ

Fig. 2a.

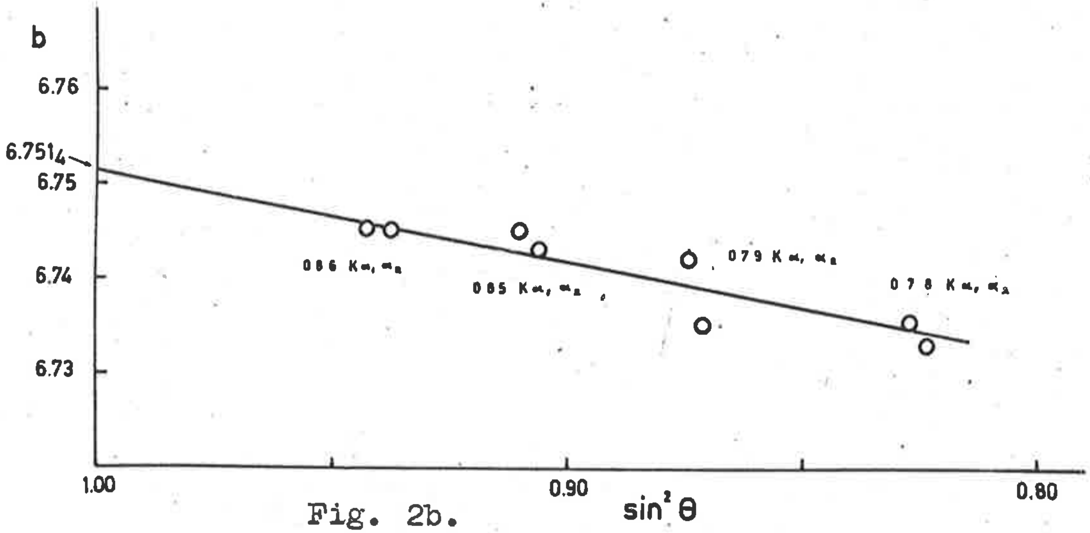

b
6.76
6.7514
6.75
6.74
6.73
0 8 6 Kα1, α2
0 8 5 Kα1, α2
0 7 9 Kα1, α2
0 7 8 Kα1, α2
1.00
0.90
0.80
sin²θ

Fig. 2b.

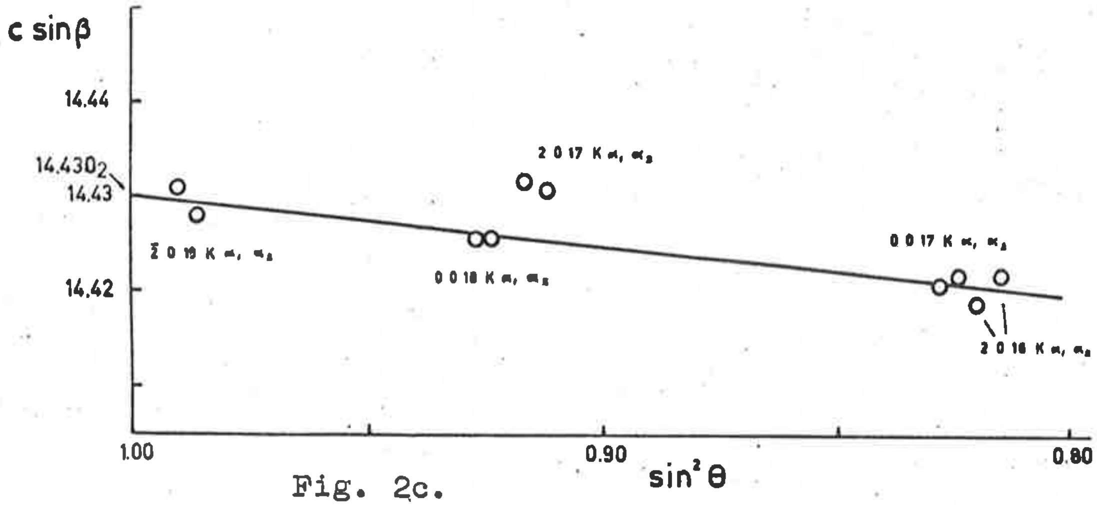


Fig. 2c.

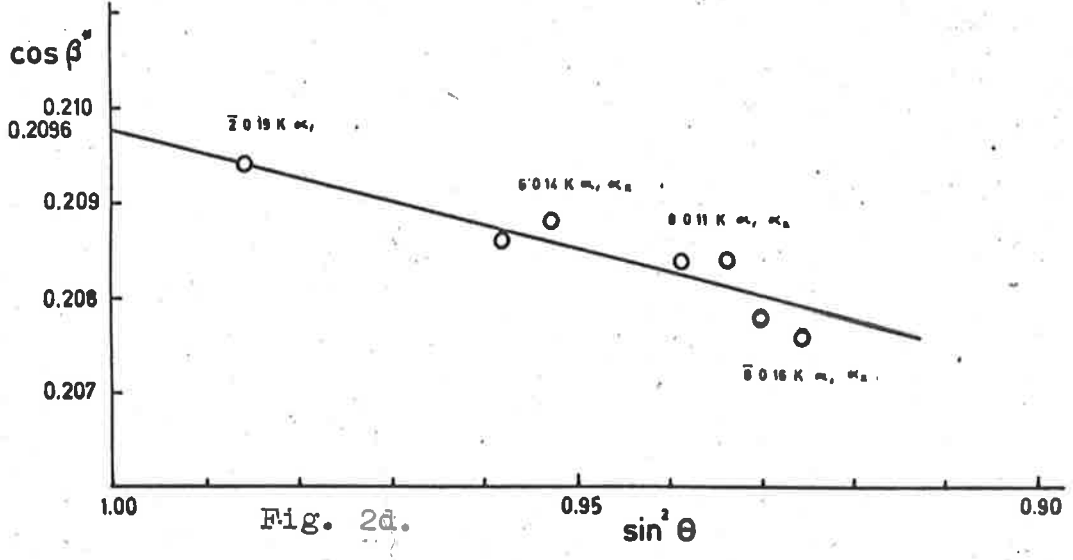


Fig. 2d.

Fig. 2. Determination of unit cell parameters for NaPTD.

TABLE 2.

Physical and crystallographic properties of NaPTD.

Space Group $P2_1/a$

$a.\sin\beta = 9.4064 \pm 0.0012$ A*	$a = 9.620 \pm 0.002$ A
$b = 6.7514 \pm 0.0019$ A	$b = 6.751 \pm 0.002$ A
$c.\sin\beta = 14.4302 \pm 0.0021$ A	$c = 14.758 \pm 0.003$ A
$\cos\beta = -0.20967 \pm 0.00021$	$\beta = 102^\circ\ 6.2' \pm 0.8'$
$\sin\beta = 0.97777 \pm 0.00004$	

Unit cell volume : 937.3 A^3

Observed density (by flotation) : 1.53 gm/cm^3

Calc. density (4 molecules/unit cell) : 1.537 gm/cm^3

Melting point : 306°C (decomp.)

Absorption coefficient $\mu(CuK\alpha)$: 31.5 cm^{-1}

Assumed wavelengths : $\lambda(CuK\alpha_1) = 1.54051$ A
$\lambda(CuK\alpha_2) = 1.54433$ A

* The uncertainties given equal the calculated standard deviations.

2.3 Collection of intensity data.

2.3.1 Selection of crystals.

Some of the difficulties experienced in obtaining good crystals have been mentioned previously. Although the plate-like crystals could be split fairly readily parallel to b, few of them were of sufficient thickness to give a reasonably uniform cross section suitable for b axis rotation. One batch of crystals grown over several months contained an exceptionally large plate about 1.5 mm. square and of thickness up to 0.13 mm. This plate which proved to be free from twinning provided all the crystals used for subsequent intensity and unit cell determinations.

The crystal selected for rotation about the b axis measured 0.08 x 1.5 x 0.05 mm. For CuKα radiation μ = 31.5 giving maximum and minimum absorption of 24% and 15%. It was thought that the error in intensity of any reflection due to neglecting absorption would not be greater than the difference between maximum and minimum absorption, i.e. 12% & 76%, 10.5% & 85% 9%. As this would result in a maximum error in F_o of only 6% 4.5%, absorption corrections were not thought necessary.

Since all attempts to cut crystals suitable for rotation about the a axis resulted in plastic-like deformations it was decided to collect all accurate intensities from the b axis crystal, and to use a axis data only to bring these intensities to a common scale. As this scaling might not be accurate the individual scaling factors for each layer of constant k would be treated as independent variables in any subsequent refinement.

The crystal used for a axis rotation measured 1.0 x 0.13 x 0.13 mm., implying 44% maximum and 34% minimum absorption for CuKα radiation. Although the absorption was considerable, no correction was made as the crystal was not used to obtain accurate intensities.

2.3.2. Measurement of intensities.

Diffracted spectra were recorded for the layers h0l to h5l and 0kl using a combination of two exposures each of about 100 hours for each layer.

For the first exposure the integrating attachment was used and by using a pack of four films even the most intense reflections fell within the linear density - intensity region on at most the fourth film. (The (001) reflection was just outside the linear range but was also unreliable as it appeared to be partly reduced by the beam trap.) Those integrated reflections of sufficient intensity were then measured using the micro-photometer.

From the second exposure which was not integrated many of those reflections too weak to be photometered were measured by visual comparison with a standard intensity strip. Intensities measurable by both methods gave the necessary correlation factor.

For non-zero layers integration makes the correction of Phillips (1954) for spot extension and contraction unnecessary; neither was this factor used for those spots estimated by eye, for they are generally of high Bragg angle where the correction becomes negligible.

An attempt was made to allow subjectively for the $K\alpha_1$-$K\alpha_2$ splitting; where the splitting was complete the $K\alpha_1$ component alone was measured and multiplied by 1.5.

Within the limiting sphere for copper radiation there were 2107 independent reflections. Of the 1743 theoretically observable in the layers h0l through h5l, 1137 were observed to have non-zero intensity and approximately half of these had sufficient intensity to be photometered.

2.3.3 Accuracy.

All intensities were taken as the average of at least two measurements made at different times; if the two measurements appeared to differ significantly they were repeated until consistent values were obtained.

Although the difference between repeated density measurements consistently had an R.M.S. value of only 2.1%, the probable errors in intensity are greater than this might seem to imply. A sample of pairs of reflections whose intensities were equal by Friedel's law, but not necessarily with equal absorption, gave an R.M.S. intensity difference of 6% which is a better indication of the accuracy of the photometered intensities.

Intensities estimated by eye are generally thought accurate within 10%.

2.3.4 Geometrical factors.

Graphical calculation of the Lorentz and polarization factors for the h01, h11, h21 and 0kl data is described in 2.4.3 and 2.4.5. Correction factors for the remainder of the data were evaluated using the I.B.M. 7090 computer described in 2.4.7.

2.3.5 Scaling.

After the 0kl data had been used to bring ~~the~~ six layers of b axis data to an approximately common scale, the method of Wilson (1942) was used to put this scaling on an absolute basis. The resultant plot shown in figure 3. gave an overall temperature exponent 2B = 6.8.

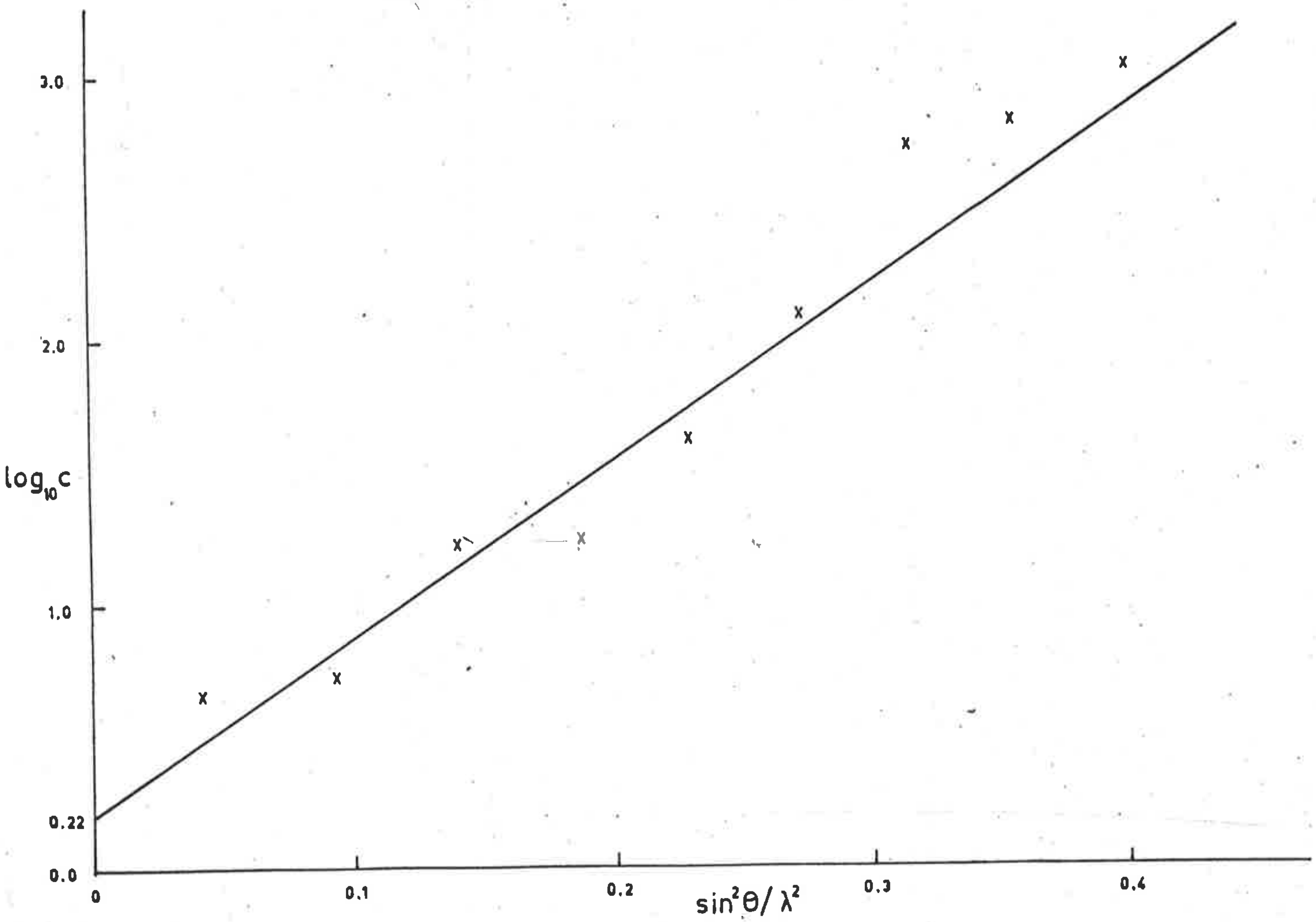


Fig. 3. Absolute scaling of NaPTD data.

2.4 An attempt to solve the structure in projection.

2.4.1 Introduction.

This section is meant only to be a summary - Detail will be given only where the technique in question does not arise in the three dimensional approach. E.g. discussion on the use of generalized projections will be included here, whereas that on the weighting system of Woolfson will be deferred.

2.4.2 Preliminary.

From preliminary considerations two reasons favoured concentration on the (h0l) projection.

a. The b axis length of 6.7 A was shortest and therefore suggested least overlap.

b. Because of the crystal habit, (h0l) data could be gathered most readily, completely and accurately.

With these considerations in mind, (h0l) data were collected by a combination of integrated and non integrated exposures as described in 2.3.2.

Rather than relying entirely on one projection to determine the sulphur position, additional 0kl data were gathered from a somewhat imperfect crystal by using eye estimation of intensities, however few spectra with $\sin\theta > 0.65$ were observed.

2.4.3 Geometrical factors.

For each h0l and 0kl reciprocal lattice point the values of sinθ and the various atomic scattering factors were obtained by using the graphical method of Cochran (1948). Knowing sinθ, the Lorentz and polarization factors were then found from the International Tables for X-ray Crystallography (Vol. 11 p.268) and applied to the observed intensities.

2.4.4 Patterson projections.

If we suppose an atom (say sulphur) to be placed at (x_1, y_1, z_1), then the vector interactions between this atom and the other symmetry related sulphur atoms within the $P2_1/a$ unit cell can be predicted. Projecting onto the (y, z) plane, we expect vector peaks at $(\frac{1}{2}, 2z_1)$, $(\frac{1}{2}\pm 2y_1, 0)$ and $(\pm 2y_1, 2z_1)$. Projecting onto (x,z), only one peak at $(2x_1, 2z_1)$ is expected.

A search for the heavy atom position can therefore be made by inspecting the (0,y,z) and (x,0,z) Patterson projections for a set of four peaks related in the manner suggested above. Following this procedure, four plausible peaks were chosen from the two (non sharpened) Patterson projections, and these are shown in fig.4.

Although the x and z sulphur atom coordinates derived from these peaks subsequently proved to be in error, it is interesting to note that even in retrospect the choice of the "wrong" peaks seems to be completely justified by the evidence available - yet another reminder of the possible

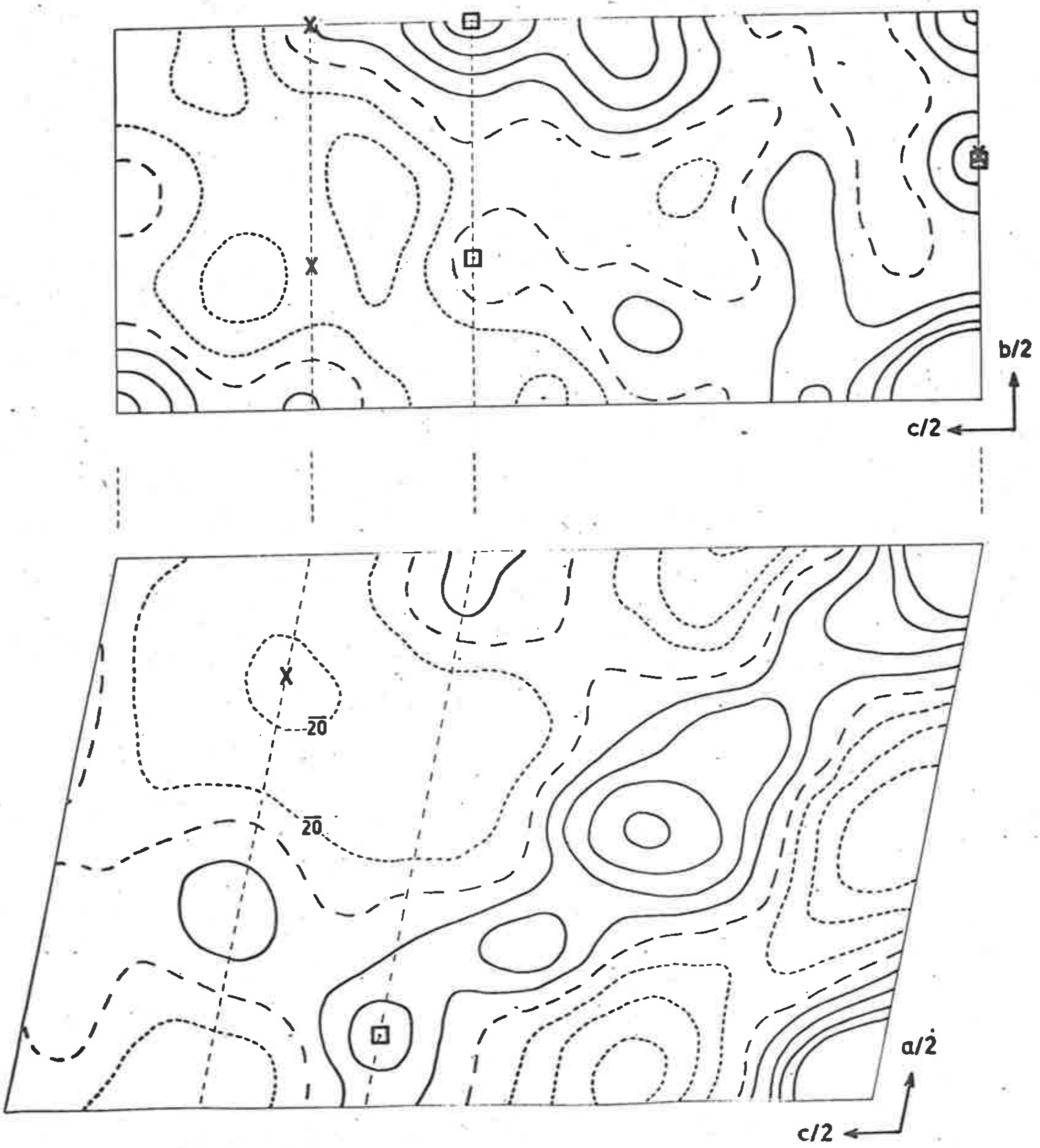


Fig. 4. 0kl and h0l Patterson projections.

(Note: In the 0kl synthesis, the direction of projection is parallel to "a", but the projection is onto the plane defined by (b,c) rather than $(b, c\sin\beta)$ as is usual.)

⊡ : Supposed sulphur-sulphur vector positions

X : True sulphur-sulphur vector positions danger in an "obvious" interpretation!

2.4.5 Fourier projections.

Having placed the sulphur atom, structure factors were calculated for the h0l and 0kl zones. The reliability factor R had the respective values of 0.56 and 0.49 for the h0l and 0kl zones; the summation was here taken over those structure amplitudes observed as non zero.

After weighting the observed structure amplitudes according to the scheme of Woolfson (1956), and using phases based on those of the heavy atom, the first two Fourier projections were calculated. From these an attempt was made to recognize further portions of the structure. After five further projections down $\underset{\sim}{b}$, (and as many difference syntheses) the sodium atom plus thiazole ring were "placed", and R reduced to 0.31, but nothing resembling the remainder of the structure could be seen.

Since the impasse which had been reached indicated major errors in the proposed atomic positions, attention was redirected toward the evidence leading to the original determination of the heavy atom position. It was now realized that the limitations of the 0kl data as mentioned in 2.4.2 had probably resulted in a vector distribution arising from the gross molecular structure rather than individual atoms. Providing that a reasonable proportion of high order spectra were observable, this defect could be partly remedied by sharpening the coefficients to emphasise the atom - atom interactions.

Rather than persevering with the poor quality 0kl data it was decided to collect higher layer b axis data which would enable the use of generalized projections to confirm or disprove the proposed sulphur position. Accurate h1l and h2l data were therefore collected and the Lorentz-polarization factors found by the graphical method of Cochran (1948).

2.4.6 Generalized projections.

A method of extracting information from non zero layers of the weighted reciprocal lattice by "generalized projections" has been given by Cochran and Dyer (1952). Although their discussion relates to generalized projections of the electron density they point out that generalized Patterson projections may be useful in special circumstances (e.g. Dyer, 1951).

Corresponding to the Patterson density (Patterson, 1935)

$$P(x,y,z) = \frac{1}{V_c} \Sigma\Sigma\Sigma \, |F(h,k,l)|^2 \exp[2\pi i(hx+ky+lz)] \quad (2.1)$$

the Kth generalized projection of this distribution on a plane perpendicular to the b axis is defined as

$$P_K(x,z) = b\int_0^1 P(x,y,z)\exp(2\pi iKy)dy \quad (2.2)$$

K is here considered only as a positive integer, however the subsequent discussion will show that the right hand side of (2.2) can be expressed as a two dimensional summation over the structure amplitudes F(h,K,l) where K is constant.

From (2.1), and the fact that

$$\int_0^1 \exp[2\pi i(K-k)y]dy \quad \begin{aligned} &= 1 \quad \text{if } k = K \\ &= 0 \quad \text{if } k \neq K \end{aligned} \tag{2.3}$$

we obtain

$$P_K(x,z) = \frac{1}{A} \sum_{hl}\sum |F(h,K,l)|^2 \exp[-2\pi i(hx+lz)] \tag{2.4}$$

Collecting the coefficients in ~~pairs~~, hKl and $\bar{h}K\bar{l}$

$$P_K(x,z) = \frac{2}{A} \sum_{hl}\sum |F(h,K,l)|^2 \exp[-2\pi i(hx+lz)] + |F(\bar{h},K,\bar{l})|^2 \exp[2\pi i(hx+lz)] \tag{2.5}$$

For the space group $P2_1/a$ which has a two fold axis parallel to b, $F(h,K,l) = F(\bar{h},K,\bar{l})$, so

$$P_K(x,z) = \frac{1}{A} \sum_{hl}\sum |F(h,K,l)|^2 \cos 2\pi(hx+lz) \tag{2.6}$$

Since $P_K(x,z)$ and $P(x,y,z)$ are both real, (2.2) becomes

$$P_K(x,z) = b\int_0^1 P(x,y,z)\cos(2\pi Ky)dy \tag{2.7}$$

From (2.7) the physical interpretation of the Kth generalized Patterson projection of P(x,y,z) on (010) can be seen. For K not too large (e.g. K=1,2,3), the value of $\cos(2\pi Ky)$ will not change rapidly as a function of y.

Therefore, to a first approximation, we can say that if in (2.7) we are integrating along a line passing through a peak of the Patterson function, then the contribution of this peak to the integral will be approximately proportional to the product of the peak value of $P(x,y,z)$ and the value of $\cos 2\pi Ky$ at this peak position. Hence if a Patterson peak arises from atoms at (x_i,y_i,z_i) and (x_j,y_j,z_j), then this peak appears in the projection $P_K(x,z)$ at (x_i-x_j, z_i-z_j), but its magnitude is multiplied by the factor $\cos 2\pi(y_i-y_j)$.

In particular, for atoms related by a screw axis parallel to b, $y_i-y_j = \frac{1}{2}$, and they therefore give rise to peaks in the generalized projections of heights shown below, Zo being the height of the unmodified peak.

Projection	Peak Height
h0l	$Zo \cos(2\pi.0.\frac{1}{2}) = Zo$
h1l	$Zo \cos(2\pi.1.\frac{1}{2}) = -Zo$
h2l	$Zo \cos(2\pi.2.\frac{1}{2}) = Zo$

Since each peak has the same x and z coordinates, a search can be made for heavy atom - heavy atom peaks by superimposing successive generalized projections drawn on transparent sheets and noting peaks of approximately equal numerical magnitude but oscillating sign.

For numerical calculation (2.6) can be further simplified (for the space group $P2_1/a$) to

$$P_K(x,z) = \frac{2}{A}\Big\{ \sum_{h=1}^{\infty} |F(h,K,0)|^2 \cos 2\pi hx + \sum_{l=1}^{\infty} |F(0,K,l)|^2 \cos 2\pi lz + \sum_{h,l=1}^{\infty}\sum [|F|^2+|\bar{F}|^2]\cos 2\pi hx \cos 2\pi lz - [|F|^2-|\bar{F}|^2]\sin 2\pi hx \sin 2\pi lz\Big\} \qquad (2.8)$$

where $F = F(h,K,l)$ and $\bar{F} = F(\bar{h},K,l)$.

Before calculation the coefficients were "sharpened" in a manner similar to that of Patterson (1935). (The sharpening function used is discussed more fully in section 2.5.1).

The origin peak of the h0l sharpened Patterson projection (which had not heretofor been calculated) was removed by the method of Lipson and Cochran (1957, p.174).

Inspection of the h0l, h1l and h2l Patterson syntheses shown in figs. 5,6 and 7 not only confirmed the suspected misinterpretation of the original Patterson syntheses but strongly indicated the true sulphur - sulphur interactions.

Now that the presumably correct heavy atom position had been determined a second attempt to locate the remainder of the structure in projection could have been initiated; however better computational aids had become available and it was decided to extend the structure investigation into a three dimensional analysis.

It may be noted that although this new sulphur position subsequently proved to be the correct one, a successful interpretation of further (010) projections may have been

(Note: In this and all other projections the positive contours are drawn unbroken, zero drawn as long dashes and negative drawn as short dashes. Unless stated otherwise, the contours are drawn at arbitrary equal intervals.)

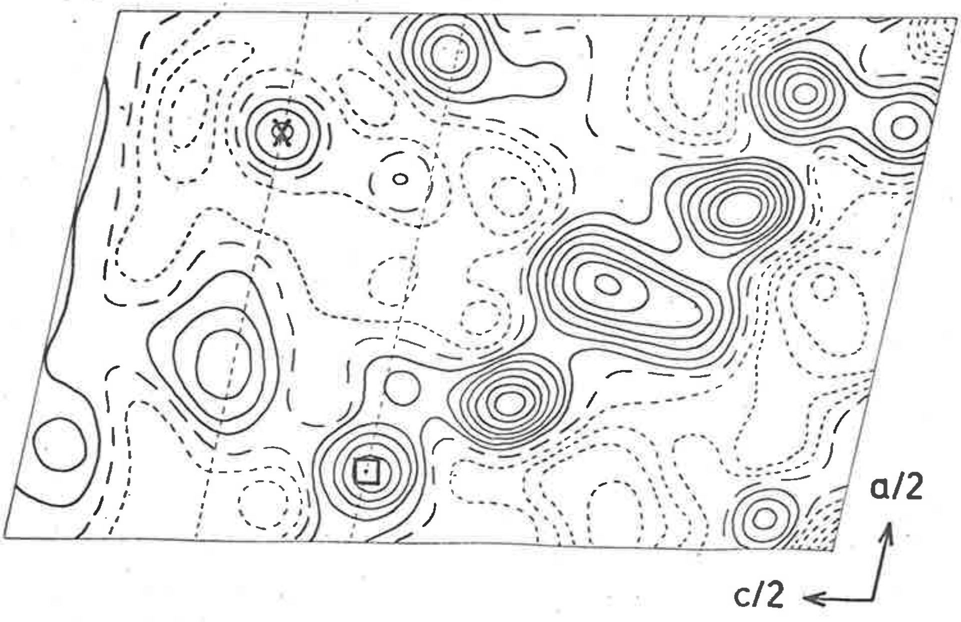


Fig. 5. h0l Sharpened Patterson projection.

□ : Supposed S-S vector position

X : True S-S vector position

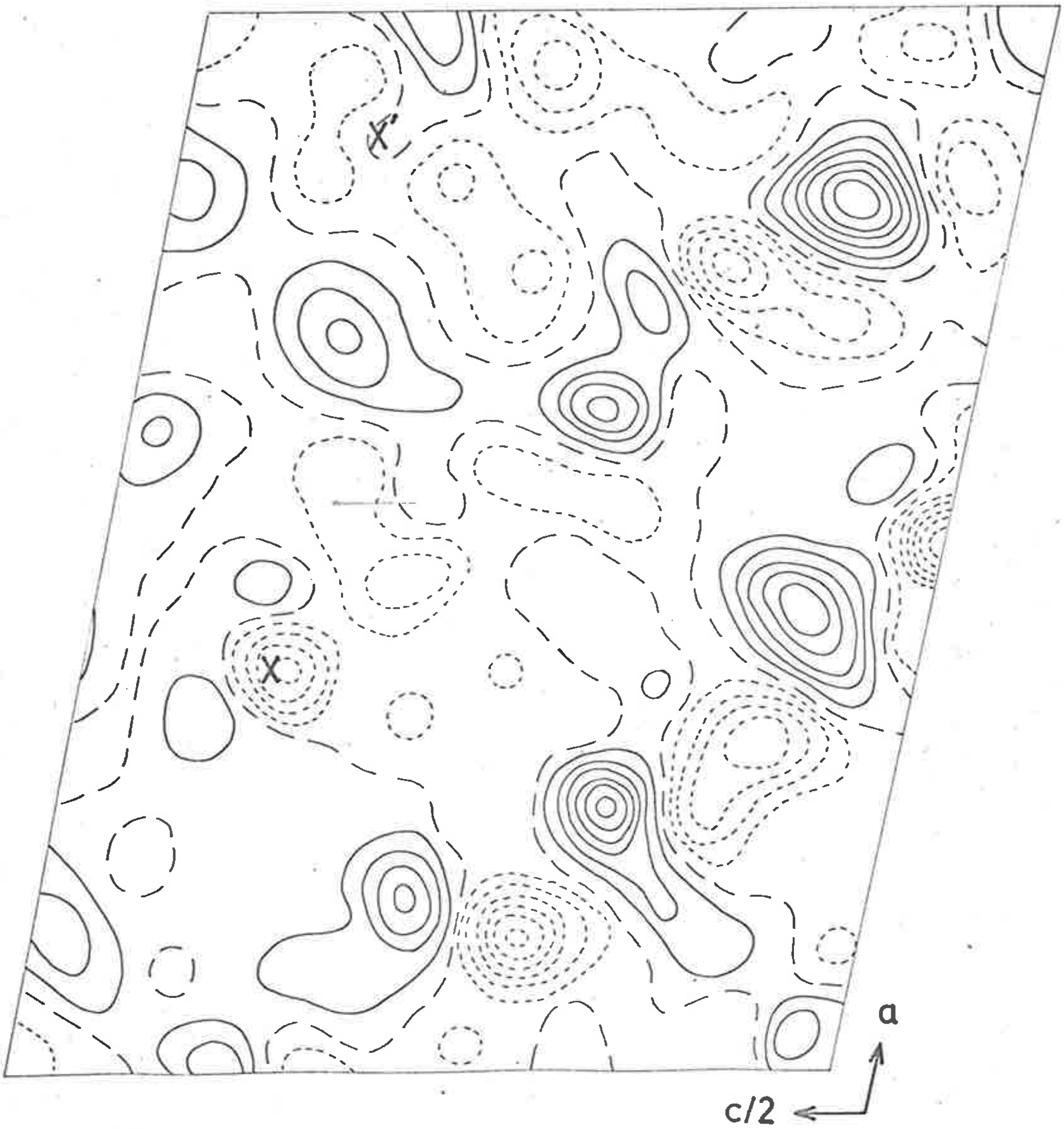


Fig 6. h11 Generalized Patterson projection.

X : S-S vector position.
(Atoms related by a screw operation)

X' : S-S vector position.
(Atoms related by a centre of symmetry)

Fig. 7. h2l Generalized Patterson projection
X and X' as for Fig. 6.

difficult, for the two rings of the NaPTD molecule proved to be almost "edge on" to this plane. There was also considerable overlap in the other principal projections.

2.4.7 Improved computing facilities: The IBM 7090

Prior to this time all calculations had been done either by hand or by the Sydney University's computer SILLIAC. Although the hand calculations were facilitated by the "Structure Factor Tables" of Buerger (1941), Beevers and Lipson strips, and a desk calculator, they were at best time consuming; on the other hand geographical separation from SILLIAC had obvious disadvantages. The advent of a large computer near Adelaide now made it possible to remove these limitations.

Recently the Weapons Research Establishment had installed an IBM 7090 Digital Computer (hereafter called the 7090) at Salisbury, a few miles from the city, and had made limited time on this machine available to the University. Since this machine had a large store (32,000 words) and was faster than most other computers (e.g. see "Computing Methods and the Phase Problem in X-ray Crystal Structure Analysis"), its successful use would allow a considerable increase in the magnitude and scope of any investigations; in particular the manipulation of complete sets of three-dimensional data was now feasible.

Although some crystallographic programs for the 7090 had been written and were in use elsewhere, applications to other organisations for copies of these programs did not initially prove successful; this ultimately resulted in the author writing all the programs mentioned in the remainder of this thesis.

2.5 Three dimensional Patterson synthesis.

2.5.1 Sharpening.

If the Patterson density is represented by a summation over an infinite number of non-zero coefficients then by suitably modifying these terms it is possible to "sharpen" the peaks of the Patterson function. This process was first suggested by Patterson (1935) as a means of resolving overlapping peaks, however in practice only a limited range of the coefficients can be observed and a compromise must therefore be made between the degree of sharpening and the increased diffraction ripples introduced into the Patterson density by termination of the Fourier series.

If the sharpening is of the form

$$|F_o^*|^2 = (1/\bar{f})^2 . \exp\left(-\frac{\pi^2}{p}\frac{4\sin^2\theta}{\lambda^2}\right) . |F_o|^2 \qquad (2.9)$$

where $\bar{f} = \sum_{j=1}^{N} f_j / \sum_{j=1}^{N} Z_j$ is the average, unitary scattering amplitude including temperature effects, and the other symbols have their usual meaning, then Lipson and Cochran (p.173) suggest that $p = 7.3$ has been found satisfactory in practice.

Substituting for p and putting

$$\bar{f} = \bar{f}_o \exp(-B\sin^2\theta/\lambda^2) \qquad (2.10)$$

where $\bar{f}_o$ is the average unitary scattering amplitude without temperature effects,

$$|F_o^*|^2 = (1/\bar{f}_o)^2 \exp[(-5.4+2B)\sin^2\theta/\lambda^2] . |F_o|^2 \qquad (2.11)$$

Although the value 2B = 6.8 had been determined statistically, the sharpening corresponding to 2B = 5.4 was finally used, i.e.

$$|F_o^*|^2 = (1/\bar{f}_o)^2 \cdot |F_o|^2 \qquad (2.12)$$

This simplified expression was chosen firstly for ease of computation and secondly because it was thought that the relatively low fraction of high order spectra observed did not justify the usual degree of sharpening.

Those spectra unobserved were given zero intensity.

2.5.2 Computation and representation.

Synthesis of the Patterson function was carried out by the 7090 at intervals of a/40 = 0.24A°, b/20 = 0.34A° and c/60 = 0.25A°. It may be noted that if, following Lipson and Cochran (1957, p.88), the optimum number of intervals along a cell edge a is

$$n_a = \frac{a \sin\theta_{max}}{0.12\lambda} \qquad (2.13)$$

$$= 0.37h_{max} \text{ for an effective } \sin\theta_{max} = 0.9,$$

then $n_a = 41$, $n_b = 19$, and $n_c = 59$. Since $k_{max} = 5$, a finer division of b would serve little purpose.

Alternate sections along b were plotted out and the contours traced onto transparent celluloid sheets which were supported by vertical rods in an attempt to represent the function in three dimensions. In retrospect the time spent was hardly justified as the model has had little more than didactic uses, all useful information being subsequently extracted from the Patterson function by an exhaustive inspection of its 80 or so positive peaks.

Approximate peak positions were found from the density at the nearest grid points, either by subjective estimation, or objectively by using the parabolic approximation of Booth (1948, p.64).

2.5.3 Interpretation.

If an atom is placed at (x,y,z) in a unit cell of symmetry $P2_1/a$, then equivalent atoms will be placed at the four sites given below.

$$(x,y,z),\ (-z,-y,-z),\ (\tfrac{1}{2}+x,\tfrac{1}{2}-y,z),\ (\tfrac{1}{2}-x,\tfrac{1}{2}+y,-z).$$

Let us suppose that we have four heavy atoms each containing Z_h electrons placed at (x,y,z) and its equivalents, and in addition four light atoms containing Z_l electrons at (u,v,w) and its equivalents.

Then if, following Buerger (1959, p.26), we suppose that the product $Z_h.Z_l$ gives an approximate measure of the height of a single heavy atom - light atom Patterson peak, we can determine the positions and heights of all the independent vector peaks generated by these two atom types. They are summarised below

Peak Coordinates	Peak Height
$\frac{1}{2}-2x$, $\frac{1}{2}$, $-2z$	$4Z_h.Z_h$
$\frac{1}{2}$, $\frac{1}{2}\pm y$, 0	$4Z_h.Z_h$
$2x$, $\pm 2y$, $2z$	$2Z_h.Z_h$
(and three similar light atom - light atom peaks)	
$u+x$, $v+y$, $w+z$	$4Z_h.Z_l$ (i)
$u+x+\frac{1}{2}$, $v-y-\frac{1}{2}$, $w+z$	$4Z_h.Z_l$ (ii)
$u-x$, $v-y$, $w-z$	$4Z_h.Z_l$ (iii)
$u-x-\frac{1}{2}$, $v+y-\frac{1}{2}$, $w-z$	$4Z_h.Z_l$ (iv)

Inspection of the Patterson peaks immediately confirmed the sulphur position suggested by the generalized projections.

Since each of the thirteen light atoms in the structure generated four light atom - sulphur vector peaks an attempt was made to search for these interactions systematically using the relations between the peaks given by (i) - (iv).

Firstly a search was made for pairs of peaks of approximately equal height and of equal z coordinates, but with x coordinates differing by $\frac{1}{2}$. This reduced all the peaks to those potentially satisfying either (i) and (ii), or (iii) and (iv). A second search was then made by taking one pair and searching for a second pair whose y coordinates differed from those of the search pair by $\frac{1}{2}$. A final test on the resultant set of four peaks was provided by their internal consistency. For example, half the difference of coordinates (i) and (iii) should equal the heavy atom coordinates; the light atom coordinates are then half the sum of (i) and (iii).

Five sets of tentative peak coordinates were derived from the Patterson synthesis and are listed below with the final parameters included in braces.

Peak identification	Coordinates (x,y,z)		
Sulphur - S	0.444	0.098	0.192
(S	0.4433	0.0927	0.1933)
Sodium - Na	0.186	0.009	0.023
(Na	0.1890	0.0102	0.0236)
Oxygen - O_1	0.996	0.097	0.098
(O	0.9975	0.1003	0.0985)
Oxygen - O_2	0.268	0.900	0.385
(C	0.2667	0.9183	0.3844)
Nitrogen - N	0.913	0.706	0.517*
(-	-	-	-)

* No atom was subsequently found with coordinates near these.

2.6 Structure factors.

2.6.1 Trigonometric factors.

The structure factor F(h,k,l) may be expressed in the general form

$$F(h,k,l) = V_c\iiint_0^1 \rho(x,y,z)\exp[2\pi i(hx+ky+lz)]dxdydz \qquad (2.14)$$

$$= \sum_n f_n(h,k,l)\exp[2\pi i(hx+ky+lz)] \qquad (2.15)$$

where the summation is over all atoms in the unit cell.

If we put

$$A = \sum_m \cos[2\pi(hx_m+ky_m+lz_m)]$$

and $\qquad (2.16)$

$$B = \sum_m \sin[2\pi(hx_m+ky_m+lz_m)]$$

where the summation is over the different equivalent positions of any one atom, then

$$F(h,k,l) = \sum_n f_nA_n + i\sum_n f_nB_n \qquad (2.17)$$

the summation now being only over those atoms within the asymmetric unit.

For $P2_1/a$, A and B reduce to

$$A = 4(\cos2\pi hx.\cos2\pi lz - \sin2\pi hx.\sin2\pi lz)\cos2\pi ky$$

for h+k even $\qquad (2.18)$

$$A = -4(\cos2\pi hx.\sin2\pi lz + \sin2\pi hx.\cos2\pi lz)\sin2\pi ky$$

for h+k odd

$$B = 0$$

2.6.2 Scattering factors.

Atomic scattering factors were represented by the sixth degree polynomial approximations of Freeman and Smith (1958) which are accurate within 1%, simple to calculate, and require little computer storage space.

2.6.3 Computation.

The basic structure factor program was written to accept and store the range of spectra to be calculated, the observed structure amplitudes $F_o(h,k,l)$, the scattering factor polynomial coefficients, and the various atomic parameters. The calculated structure amplitudes $F_c(h,k,l)$ and $F_c(\bar{h},k,l)$ were then calculated together and printed out with F_o and $||F_o|-|F_c||$.

As an indication of the agreement between the observed and calculated structure factors the reliability factor R defined as

$$R = \Sigma|F_o-F_c| / \Sigma|F_o| \qquad (2.19)$$

was also calculated. Generally the summation was taken in two ways

a. Summation (hereafter called Ra) over all spectra with those not observed put equal to zero. It is thought that this is the most useful form for the reliability index, in the early stages of structure determination when F_o may equal zero but F_c be of appreciable magnitude.

b. Summation (hereafter called R) only over those spectra observed as non zero.

Two modifications to the basic structure factor program were subsequently made.

a. Since output was relatively slow an option was included to suppress the printing of F_o and F_c, the R values only being printed for each layer.

b. Provision was made to allow calculation of the Woolfson weighting factors (Woolfson, 1956) and to punch out the coefficients preparatory to the calculation of Fourier or Difference Fourier syntheses.

2.6.4 Test of trial coordinates.

As a check on the five "atoms", the coordinates of which had been found from the Patterson function, the appropriate set of structure factors was calculated. The resultant reliability index Ra was 71% which was only slightly less than the 83% expected from a completely random set of coordinates (Wilson, 1950).

In the hope that some, at least, of the proposed coordinates were correct, the following structure factor calculations were made.

Atoms Included	Reliability Index Ra(%)
$S+Na+O_1+O_2+N$	71
$S+Na+N_1+N_2+N_3$	59
S	69

(Cont.)

(Cont.)

Atoms Included	Reliability Index Ra(%)
S+Na	61
S+Na+N_1	58
S+Na+N_2	61
S+Na+N_3	62

The coordinates of the atoms N_1, N_2 and N_3 were respectively put equal to the coordinates of the O_1, O_2 and N atoms.

From these results it appeared that the sulphur and sodium atoms had been correctly located and that "N_1" was probably a real atom, but that "N_2" and "N_3" were as likely to be wrong as right. It was therefore decided to calculate the first Fourier synthesis on the basis of the first group of three atoms, i.e. S+Na+N_1.

2.7 Fourier syntheses.

2.7.1 Trigonometric factors.

Previously the structure factor $F(h,k,l)$ was expressed in terms of the electron density $\rho(x,y,z)$; we now write the inverse relationship

$$\rho(x,y,z) = \frac{1}{V_c}\sum\sum\sum_{hkl\,-\infty}^{\infty} F(h,k,l)\exp[-2\pi i(hx+ky+lz)] \qquad (2.20)$$

For the space group $P2_1/a$,

$F(h,k,l) = F(h,\bar{k},l)$ and $F(\bar{h},k,l) = F(h,k,\bar{l})$ for $h+k$ even,

$F(h,k,l) = -F(h,\bar{k},l)$ and $F(\bar{h},k,l) = -F(h,k,\bar{l})$ for $h+k$ odd. (2.21)

Using these relations the expression for the electron density becomes

$$\begin{aligned}\rho(x,y,z) = \frac{4}{V_c}\Bigg\{ & \overset{(h+k\,=\,2n)}{\sum\sum\sum_{hkl}{}_0^{\infty}} [C(h,k,l)\cos2\pi hx\cos2\pi lz \\ & \qquad - D(h,k,l)\sin2\pi hx\sin2\pi lz]\cos2\pi ky \\ & + \overset{(h+k\,=\,2n+1)}{\sum\sum\sum_{hkl}{}_0^{\infty}} [-C(h,k,l)\cos2\pi hx\sin2\pi lz \\ & \qquad - D(h,k,l)\sin2\pi hx\cos2\pi lz]\sin2\pi ky \end{aligned} \qquad (2.22)$$

where $C(h,k,l) = F(h,k,l) + F(\bar{h},k,l)$ for $h,\ k,\ l \neq 0$

$D(h,k,l) = F(h,k,l) - F(\bar{h},k,l)$ "

and $C(0,k,l) = \frac{1}{2}(F(0,k,l) + F(0,k,l))$ etc.

2.7.2 Weighting of coefficients.

In the "heavy atom" method of solving crystal structures the Fourier series summed has coefficients of modulus equal to those of the heavy atom contribution. Woolfson (1956) has shown that improved resolution of the light atoms can be achieved by weighting each coefficient of the Fourier series according to the probability that its phase is correct.

The weighting factor in the form given by Woolfson was found to be not very convenient for practical use, and instead the equivalent expression given below was derived and used.

$$F(\text{weighted}) \;=\; S_c.|F_o|.\tanh\left(\frac{|F_o.F_c|}{\sum\limits_j (f_j)^2}\right) \qquad (2.23)$$

where S_c is the sign of F_c (i.e. ± 1), and f_j $(=f_j(h,k,l))$ is the scattering factor including temperature modification, the summation being over all atoms in the unit cell excluding the "heavy atoms".

When written in this form the fact is emphasised that for a given Bragg angle the probability of a calculated phase being correct depends only on the product of F_o and F_c and not on the agreement of their magnitudes.

In practice it was found convenient to evaluate Σf_j^2 at intervals of 0.05 in $\sin\theta/\lambda$ and hence to construct a graph of the function. For hand calculations the method of Cochran (1948) could then be used, while for automatic computation linear interpolation between the known values gave sufficient accuracy.

2.7.3 First Fourier synthesis.

The first synthesis using coefficients weighted in the manner described above was calculated over the asymmetric unit at intervals of a/40, b/20, c/60 and printed out on sheets ready for direct contouring. Although the total time taken was 24 mins. about 75% of this represents output time. (At this time since no off-line listing facilities were available any program with a large amount of output was generally most inefficient.)

To represent the calculated electron density, balls were supported on metal rods of the appropriate length; from this model the remainder of the structure could be seen quite unambiguously. Structure factors based on this model gave a residual Ra = 33% which left little doubt that the proposed structure was an approximation to the correct one.

The weighting system of Woolfson was most successful in this application, for, although the lowest peak density was 2.6 e/A^3, the background density did not exceed 1.3 e/A^3.

2.7.4 Further syntheses.

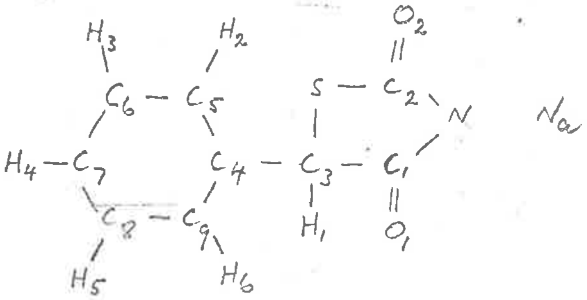
Two further Fourier syntheses were calculated at intervals of a/30, b/20, c/40 in which the coefficients were not weighted; the residuals in the alternative forms described before were then Ra = 28% and R = 17%. It may be noted that when all the atoms have been placed, i.e. they all become "heavy atoms," $\Sigma f_j^2 = 0$, and the weighting factors all become unity. If, however, some of the coordinates are likely to be in error, it is probably useful to give the summation values corresponding to several light atoms, thereby introducing weighting which seems at least to be physically reasonable even if not mathematically optimized.

Since these two syntheses were substantially the same, it was apparent that subsequent refinement would have to proceed along different lines.

2.8 Refinement using isotropic temperature factors.

Refinement of the approximately known atomic parameters was carried out on the 7090 computer by utilizing "differential difference" Fourier syntheses. An outline of the general features of the refinement programs along with the underlying theory is given in Chapter 4.

In subsequent discussion the following numbering will be used



2.8.1 Initial refinement.

After two cycles of refinement had reduced R to 13% the most striking feature was the apparent large thermal vibration of the benzene ring. Although C_3 had B = 4.0 the value of this exponent increased progressively across the benzene ring until for C_7 it reached 9.0 which implied an R.M.S. thermal displacement of 0.34A (James, 1958, p.193).

At this stage the University's I.B.M. 1620 computer (see 2.4.7 below) had just come into operation and was used to compute and print out in full the observed and calculated structure factors, a calculation which had been avoided on the 7090 because of the large amount of output involved.

A careful inspection of these F's revealed several arithmetic errors and wrong indexing of high angle reflections; when these had been corrected no serious discrepancies between F_o and F_c remained.

2.8.2 Extinction.

James (1958, p.293) has suggested a correction for secondary extinction of the form

$$I_c = \frac{I_o}{1-2gI_o} \qquad (2.24)$$

Plotting $(1 - I_o/I_c)$ against I_o $(=F_o^2)$ for the more intense reflections the best straight line gave $2g = 0.000019$ which was then used to correct all F_o's of magnitude greater than 40.

Thus, apart from scaling, the only corrections made to the F_o's were for Lorentz-polarization and secondary extinction effects.

2.8.3 Hydrogen atoms.

Since the six hydrogen atoms were bonded directly to the NaPTD molecule their approximate positions were found geometrically by assuming a C-H bond length of 1.05A (Allen and Sutton, 1950).

2.8.4 Further refinement.

After correcting the F_o's for extinction the contribution of the 6 hydrogen atoms was included while the other 14 atoms were refined for three cycles during which R remained at 10.4% but the sum of squares of the coefficients $(F_o-F_c)^2$ fell from 3267 to 3057. The average coordinate shift during the last cycle was 0.0011A and the greatest shift 0.0040A which was a quarter of the corresponding coordinate standard deviation at that stage. A summary of the results of this isotropic refinement is given in Appendix 2.

During the five cycles of refinement the greatest nett coordinate shift was 0.064A.

2.8.5 The need for anisotropic temperature factors.

As the refinement with isotropic thermal parameters had progressed it was apparent that although the mean value of the three principal derivatives of the difference density was small, the individual derivatives had appreciable values for some atoms. To verify that there were in fact significant anisotropic thermal vibrations, and also as a general check on the correctness of the structure, a three dimensional difference synthesis was calculated. The necessary coefficients (F_o-F_c) were calculated and punched out by the 7090 and the Fourier summation then carried out in three stages by the 1620 (see 2.4.7 below).

Generally the hydrogen atom positions were confirmed, although toward the extremity of the benzene ring the electron density was modified by (presumably) vibrational effects.

A section of this synthesis close to the sulphur atom is shown in fig. 15: the presence of anisotropic vibration, which appears to be approximately normal to the plane of the thiazolidine ring, can readily be seen.

In view of these rather obvious inadequacies of the refinement of the structure thus far, it was decided to include anisotropic thermal parameters.

2.8.6 Further computing facilities : The IBM 1620.

As has been mentioned above the University had recently acquired the use of an IBM 1620 digital computer.

This machine has been found most useful for data conversion, for Fourier syntheses, and in fact for all crystallographic calculations with the exception of structure refinement. Structure factor calculation was found to be rather slow (1 sec./atom/reflection) and where possible was better done by the 7090. This especially applied to the coefficients for Fourier or difference Fourier syntheses which could be calculated and then punched out in a condensed form ready for input to the 1620. A more complete description of a 1620 $P2_1/a$ structure factor program allowing individual isotropic temperature factors is included in Appendix 3.

The 1620 $P2_1/a$ Fourier synthesis program was very similar to that for $P2_1/n$ described in Appendix 3 and took 5 hours to sum over 1700 F's at 8,000 grid points.

2.9 Refinement using anisotropic temperature factors.

2.9.1 Structure factors.

If the motion of an atom is represented by an ellipsoid of vibration, then since this ellipsoid is itself centrosymmetric, the scattering of this atom will be identical with that of similar atoms related by translation or inversion; this will not in general be the case for atoms related by a mirror or glide operation.

Trueblood (1956) has shown that if the temperature factor of an atom is written

$$T_1 = \exp\{-[B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl]\} \qquad (2.25)$$

then the temperature factor of an atom related by the $P2_1/a$ glide plane is

$$T_2 = \exp\{-[B_{11}h^2+B_{22}k^2+B_{33}l^2-B_{12}hk+B_{13}hl-B_{23}kl]\} \qquad (2.26)$$

The structure factor for centrosymmetric space groups is given by

$$F(h,k,l) = \sum_n f_n T_n \cos[2\pi(hx_n+ky_n+lz_n)] \qquad (2.27)$$

where the summation is over all atoms within the unit cell; f_n is the scattering factor of atom n at rest. By using (2.25) and (2.26), (2.27) can be reduced for $P2_1/a$ to the following summations over atoms within the asymmetric unit (the subscript n being omitted for clarity).

$$F(h,k,l) = \Sigma\ 2f\{(T_1+T_2)(\cos2\pi hx.\cos2\pi lz-\sin2\pi hx.\sin2\pi lz).\cos2\pi ky$$

$$+ (T_2-T_1)(\sin2\pi hx.\cos2\pi lz+\cos2\pi hx.\sin2\pi lz).\sin2\pi ky\}$$

for h+k even (2.28)

$$F(h,k,l) = \Sigma\ 2f\{(-T_1-T_2)(\sin2\pi hx.\cos2\pi lz+\cos2\pi hx.\sin2\pi lz).\sin2\pi ky$$

$$+ (T_1-T_2)(\cos2\pi hx.\cos2\pi lz-\sin2\pi hx.\sin2\pi lz).\cos2\pi ky\}$$

for h+k odd

As a check on the correctness of these results it may be noted that the required relations between the structure factors (i.e. (2.21)) hold.

2.9.2 Initial thermal parameters.

To express the anisotropic parameters B_{ij} in terms of the isotropic parameter B we write

$$T = \exp(-B\sin^2\theta/\lambda^2)$$

$$= \exp\left\{-\frac{B}{\lambda^2}\left[\left(\frac{a^*}{2}\right)^2h^2+\left(\frac{b^*}{2}\right)^2k^2+\left(\frac{c^*}{2}\right)^2l^2+2\left(\frac{a^*}{2}\frac{c^*}{2}\right)\cos\beta^*.hl\right]\right\} \quad (2.29)$$

Equating coefficients with (2.25);

$$B_{11} = \frac{B}{\lambda^2}\left(\frac{a^*}{2}\right)^2 = \frac{B}{4(a.\sin\beta)^2}$$

$$B_{22} = \frac{B}{\lambda^2}\left(\frac{b^*}{2}\right)^2 = \frac{B}{4.b^2}$$

B_{33} : as B_{11}, c replacing a. (2.30)

$$B_{12} = B_{23} = 0$$

$$B_{13} = \frac{B}{\lambda^2}\left(\frac{a^*c^*\cos\beta^*}{2}\right) = \frac{B.\cos\beta^*}{2(a.\sin\beta)(c.\sin\beta)}$$

```
FIXED ATOMS

TYPE 1. X= 0.4790 Y= 0.7340 Z= 0.1590  B11=    1189. B22=   2303. B33=    483. B12=    -0. B13=    317. B23=    -0.
TYPE 1. X= 0.0950 Y= 0.9730 Z= 0.2680  B11=    1881. B22=   3642. B33=    764. B12=    -0. B13=    502. B23=    -0.
TYPE 1. X= 0.2430 Y= 0.3960 Z= 0.2970  B11=    1990. B22=   3853. B33=    809. B12=    -0. B13=    531. B23=    -0.
TYPE 1. X= 0.2720 Y= 0.0650 Z= 0.4060  B11=    2517. B22=   4874. B33=   1023. B12=    -0. B13=    672. B23=    -0.
TYPE 1. X= 0.4120 Y= 0.4890 Z= 0.4370  B11=    2517. B22=   4874. B33=   1023. B12=    -0. B13=    672. B23=    -0.
TYPE 1. X= 0.4250 Y= 0.8220 Z= 0.4910  B11=    2547. B22=   4931. B33=   1035. B12=    -0. B13=    679. B23=    -0.


INITIAL PARAMETERS TO BE REFINED, STANDARD DEVIATIONS UNDERNEATH

TYPE 6. X= 0.4435 Y= 0.0926 Z= 0.1932  B11=    1059. B22=   2419. B33=    548. B12=   140. B13=    544. B23=    74.
           0.00037    0.00044    0.00031
TYPE 5. X= 0.1892 Y= 0.0102 Z= 0.0236  B11=    1070. B22=   2073. B33=    435. B12=    -0. B13=    286. B23=    -0.
           0.00052    0.00058    0.00040
TYPE 4. X= 0.2050 Y= 0.6912 Z= 0.0797  B11=    1024. B22=   2342. B33=    542. B12=   -18. B13=    392. B23=   177.
           0.00097    0.00109    0.00081
TYPE 4. X= 0.9077 Y= 0.0996 Z= 0.0984  B11=    1290. B22=   2499. B33=    524. B12=    -0. B13=    344. B23=    -0.
           0.00107    0.00115    0.00082
TYPE 3. X= 0.1230 Y= 0.3761 Z= 0.0805  B11=    1003. B22=   1942. B33=    409. B12=    -0. B13=    268. B23=    -0.
           0.00108    0.00120    0.00083
TYPE 2. X= 0.1309 Y= 0.5636 Z= 0.1088  B11=     961. B22=   1261. B33=    391. B12=    -0. B13=    256. B23=    -0.
           0.00122    0.00140    0.00095
TYPE 2. X= 0.0284 Y= 0.2755 Z= 0.1168  B11=     992. B22=   1534. B33=    469. B12=  -242. B13=    106. B23=   -97.
           0.00119    0.00134    0.00096
TYPE 2. X= 0.0506 Y= 0.6248 Z= 0.1839  B11=    1189. B22=   2303. B33=    483. B12=    -0. B13=    317. B23=    -0.
           0.00144    0.00160    0.00111
TYPE 2. X= 0.1331 Y= 0.6778 Z= 0.2724  B11=    1253. B22=   2425. B33=    509. B12=    -0. B13=    334. B23=    -0.
           0.00151    0.00167    0.00116
TYPE 2. X= 0.1627 Y= 0.8684 Z= 0.3041  B11=    1881. B22=   3642. B33=    764. B12=    -0. B13=    502. B23=    -0.
           0.00230    0.00238    0.00175
TYPE 2. X= 0.2481 Y= 0.5401 Z= 0.3202  B11=    1990. B22=   3853. B33=    809. B12=    -0. B13=    531. B23=    -0.
           0.00246    0.00252    0.00187
TYPE 2. X= 0.2670 Y= 0.9187 Z= 0.3833  B11=    2517. B22=   4874. B33=   1023. B12=    -0. B13=    672. B23=    -0.
           0.00338    0.00331    0.00255
TYPE 2. X= 0.3429 Y= 0.5941 Z= 0.4013  B11=    2517. B22=   4874. B33=   1023. B12=    -0. B13=    672. B23=    -0.
           0.00338    0.00331    0.00255
TYPE 2. X= 0.3514 Y= 0.7803 Z= 0.4300  B11=    2466. B22=   5277. B33=    910. B12= -1971. B13=   -276. B23=  -187.
           0.00275    0.00304    0.00196




LAYER                HOL   H1L   H2L   H3L   H4L   H5L    ...ETC.
SCALE FACTORS   =  0.971 1.005 1.017 1.008 1.000 0.995
R (INC. FO = 0) =  0.132 0.142 0.152 0.145 0.170 0.206
R (EXC. FO = 0) =  0.084 0.098 0.096 0.097 0.107 0.100

SUM OF F OBS   =   16768.4

INCLUDING F OBS = 0
SUM OF F CALC =    17759.8
SUM OF FO - FC =    2536.1
RELIABILITY INDEX R =0.1512

EXCLUDING F OBS = 0
SUM OF F CALC =    16768.4
SUM OF FO - FC =    1544.7
RELIABILITY INDEX R =0.0921

SUM OF SQUARES OF FO-FC FOR ALL PLANES OBSERVED   14123.8

 TOTAL NUMBER OF SPECTRA CALCULATED =  1986
 TOTAL NUMBER OF OBSERVED NON ZERO SPECTRA =  1243
 NUMBER OF F CALC GREATER THAN TWICE THE MIN F OBSERVABLE =   3

FOR THE NEXT CYCLE
 NUMBER OF COEFFS WITH F NOT OBSERVED AS ZERO INCLUDED =  1215
 NUMBER OF COEFFS WITH F CALC GREATER THAN THE MIN F OBSERVABLE INCLUDED =   23
 SUM OF ALL COEFFS INCLUDED =    1412.8
 SUM OF SQUARES OF ALL COEFFS INCLUDED =    2834.2


END OF CYCLE =0
```

Fig. 8. Typical results of "Structure Refinement" program.

```
COORDINATE SHIFTS IN ANGSTROMS AND CHANGES IN THE TEMPERATURE FACTOR PARAMETERS  B IJ

ALSO THE DENSITY IN ELECTRONS PER CUBIC ANGSTROM OF THE DIFFERENCE SYNTHESIS SIGMA(FO-FC) AT THE ATOMIC POSITION


   COORDINATE SHIFTS                                  CHANGES IN  B IJ                              DIFFERENCE DENSITY

      X          Y          Z             B11       B22       B33       B12       B13       B23           DENS

  -0.0003    0.0004   -0.0011             -7.       75.        2.       10.        9.       16.         -0.067
  -0.0007   -0.0010    0.0007            -99.      121.       63.     -151.       42.      122.         -0.387
   0.0015    0.0011    0.0007             -3.       38.        1.       14.      -24.      -11.         -0.074
  -0.0033    0.0041    0.0017            -47.     -162.        6.     -103.     -201.       67.          0.124
   0.0008    0.0048    0.0012             -8.     -142.       45.      140.      -35.       26.         -0.139
   0.0031   -0.0014    0.0044            -34.      -51.       41.      213.     -100.      201.         -0.194
  -0.0006   -0.0016   -0.0035             -9.       16.        2.       34.        8.        2.          0.004
   0.0016   -0.0032    0.0010           -119.      416.       10.      260.      -26.      -52.          0.085
  -0.0041    0.0019   -0.0021            -62.      272.       34.      -33.       18.     -248.         -0.147
   0.0001   -0.0017   -0.0058            398.     -326.     -172.     -386.     -229.       61.         -0.029
   0.0063   -0.0087    0.0060           -232.     1249.      -99.      874.     -823.     -229.         -0.090
  -0.0020   -0.0013    0.0036            715.    -1080.     -192.    -1520.     -219.     -471.         -0.016
   0.0176    0.0043    0.0005           -171.     1641.     -305.     1077.    -1564.     -209.         -0.149
   0.0039    0.0014    0.0006              6.      235.      -18.     -160.      -73.     -135.         -0.042


MEAN SHIFTS
DX=  0.0033 DY=  0.0026 DZ=  0.0023   GREATEST SHIFT =  0.0176 ANGSTROM



FIXED ATOMS

TYPE 1. X= 0.4790 Y= 0.7340 Z= 0.1590  B11=    1189. B22=   2303. B33=    423. B12=     -0. B13=    317. B23=    -0.
TYPE 1. X= 0.0950 Y= 0.9730 Z= 0.2680  B11=    1881. B22=   3642. B33=    764. B12=     -0. B13=    502. B23=    -0.
TYPE 1. X= 0.2430 Y= 0.3960 Z= 0.2970  B11=    1990. B22=   3353. B33=    809. B12=     -0. B13=    531. B23=    -0.
TYPE 1. X= 0.2720 Y= 0.0650 Z= 0.4060  B11=    2517. B22=   4874. B33=   1023. B12=     -0. B13=    672. B23=    -0.
TYPE 1. X= 0.4120 Y= 0.4890 Z= 0.4370  B11=    2517. B22=   4874. B33=   1023. B12=     -0. B13=    672. B23=    -0.
TYPE 1. X= 0.4250 Y= 0.8220 Z= 0.4910  B11=    2547. B22=   4931. B33=   1035. B12=     -0. B13=    679. B23=    -0.


REFINED PARAMETERS, STANDARD DEVIATIONS UNDERNEATH

TYPE 6. X= 0.4434 Y= 0.0927 Z= 0.1931  B11=    1052. B22=   2494. B33=    550. B12=    150. B13=    553. B23=    90.
           0.00036    0.00041    0.00030
TYPE 5. X= 0.1391 Y= 0.0100 Z= 0.0236  B11=     971. B22=   2194. B33=    498. B12=   -151. B13=    328. B23=   122.
           0.00050    0.00055    0.00038
TYPE 4. X= 0.2052 Y= 0.6913 Z= 0.0792  B11=    1021. B22=   2380. B33=    543. B12=     -4. B13=    362. B23=   166.
           0.00093    0.00104    0.00077
TYPE 4. X= 0.9374 Y= 0.1002 Z= 0.0985  B11=    1243. B22=   2336. B33=    530. B12=   -103. B13=    143. B23=    67.
           0.00103    0.00107    0.00078
TYPE 3. X= 0.1231 Y= 0.3768 Z= 0.0806  B11=     995. B22=   1200. B33=    453. B12=    140. B13=    233. B23=    26.
           0.00103    0.00114    0.00079
TYPE 2. X= 0.1312 Y= 0.5634 Z= 0.1091  B11=     927. B22=   1910. B33=    432. B12=    213. B13=    156. B23=   201.
           0.00117    0.00132    0.00090
TYPE 2. X= 0.0293 Y= 0.2752 Z= 0.1166  B11=     983. B22=   1550. B33=    471. B12=   -208. B13=    114. B23=   -95.
           0.00114    0.00127    0.00091
TYPE 2. X= 0.0508 Y= 0.6243 Z= 0.1840  B11=    1070. B22=   2719. B33=    493. B12=    260. B13=    231. B23=   -52.
           0.00138    0.00152    0.00105
TYPE 2. X= 0.1527 Y= 0.6781 Z= 0.2723  B11=    1191. B22=   2697. B33=    543. B12=    -33. B13=    352. B23=  -248.
           0.00145    0.00158    0.00110
TYPE 2. X= 0.1627 Y= 0.8680 Z= 0.3037  B11=    2279. B22=   3316. B33=    592. B12=   -386. B13=    273. B23=    61.
           0.00221    0.00224    0.00165
TYPE 2. X= 0.2488 Y= 0.5388 Z= 0.3206  B11=    1758. B22=   5102. B33=    710. B12=    874. B13=   -292. B23=  -229.
           0.00237    0.00239    0.00177
TYPE 2. X= 0.2668 Y= 0.9185 Z= 0.3835  B11=    3232. B22=   3794. B33=    231. B12=  -1520. B13=    453. B23=  -471.
           0.00325    0.00314    0.00241
TYPE 2. X= 0.3447 Y= 0.5947 Z= 0.4013  B11=    2346. B22=   6515. B33=    718. B12=   1077. B13=   -392. B23=  -209.
           0.00325    0.00314    0.00241
TYPE 2. X= 0.3518 Y= 0.7805 Z= 0.4301  B11=    2472. B22=   5512. B33=    892. B12=  -2131. B13=   -349. B23=  -322.
           0.00264    0.00289    0.00186
                                                                         /



LAYER                  H0L   H1L   H2L   H3L   H4L   H5L    ...ETC.
SCALE FACTORS   =  0.967 1.067 1.014 1.006 0.989 0.980
R (INC. FC = 0) =  0.124 0.126 0.137 0.132 0.154 0.180
R (EXC. FC = 0) =  0.077 0.074 0.082 0.076 0.092 0.079

SUM OF F OBS   =   16708.5

INCLUDING F OBS = 0
SUM OF F CALC =    17672.9
SUM OF FO - FC =    2293.8
RELIABILITY INDEX R =0.1367

EXCLUDING F OBS = 0
SUM OF F CALC =    16708.5
SUM OF FO - FC =    1319.4
RELIABILITY INDEX R =0.0790

SUM OF SQUARES OF FO-FC FOR ALL PLANES OBSERVED   12310.7

 TOTAL NUMBER OF SPECTRA CALLULATED =  1986
 TOTAL NUMBER OF OBSERVED NON ZERO SPECTRA =  1248
 NUMBER OF F CALC GREATER THAN TWICE THE MIN F OBSERVABLE =   2


FOR THE NEXT CYCLE
 NUMBER OF COEIFS WITH F NOT OBSERVED AS ZERO INCLUDED =  1221
 NUMBER OF COEFFS WITH F CALC GREATER THAN THE MIN F OBSERVABLE INCLUDED =   19
 SUM OF ALL COEFFS INCLUDED =    1211.0
 SUM OF SQUARES OF ALL COEFFS INCLUDED =     2111.6


END OF CYCLE  1
```

Fig. 8.

These relations gave the initial B_{ij} for the heavy atoms; those for the hydrogen atoms were taken equal to the appropriate bonding carbon atom.

2.9.3 First refinement.

During the first three cycles of refinement of the 14 heavy atoms (with hydrogens included but held constant), the reliability index R fell from 10.4% to 7.7%. Some of the coordinate changes seemed appreciable; however, the greatest overall shift of 0.023A for C_8 did not exceed its coordinate standard deviation of 0.032A.

Although the reliability index R was determined for each cycle, during this and subsequent refinement the primary criterion for improvement was the least squares residual

$$R(L.S) = \Sigma w(F_o-F_c)^2$$

where w is the weight given to $(F_o-F_c)^2$. This summation equals the sum of the squares of all coefficients included in the refinement equations. R(L.S) fell from 3057 to 1960 during the first refinement of anisotropic thermal parameters.

2.9.4 Hydrogen refinement.

In the first instance the hydrogen positions had been estimated from bonding considerations; it was therefore desirable to confirm and refine these positions using the observed data. No attempt was made to improve the thermal parameters which were held constant throughout, while to guard against divergence all the coordinate shifts were reduced by a half.

During refinement only those F's within the reciprocal sphere sinθ = 0.4 were included and for these R(L.S) fell from 872 to 826 during 4 cycles. All the coordinate changes converged, the mean shift falling from 0.055 to 0.011A and the greatest from 0.17 to 0.036A.

2.9.5 Choice of sodium f-curve.

In an effort to decide whether the sodium scattering was best represented by a neutral or ionized sodium f-curve, all other atoms were held constant while two refinements of the sodium atom were carried out using the alternative f-curves. The neutral atom scattering was represented as in 4.3.2 while the corresponding ionized f-curve was taken from Boys (1961).

After two cycles all the parameter changes were negligible, and the results (which indicated a neutral atom) are summarised below.

f-curve	R(L.S) Initial	R(L.S) Final	$(\rho_o-\rho_c)_{Na}$ (e./A^3)	R (%)
Na	1914	1910	-0.17	7.6
Na^+	1971	1959	-0.21	7.7

The result that the ionized atom has the more negative residual electron density is not anomalous when it is remembered that removal of the outermost electron will cause little change to the electron density at the centre of the atom.

2.9.6 Extinction.

Following an inspection of the more intense F's, a second determination of the secondary extinction correction was made in a manner similar to 2.8.2. The resultant plot which indicated a correction factor 2g = .000031 is shown in fig. 9. Primary cause of the initial insufficient correction was the fact that the correction increased ΣF_o and therefore decreased the corresponding scaling factor which in turn reduced the individual F_o's. The "over-estimation" of 2g which is apparent in fig. 9 was made for the same reason.

Since there appeared to be no justification for correcting only selected intense reflections, the extinction modification was made to all reflections for which it was significant, i.e. to all F_o's greater than 30.

2.9.7 Final refinement.

Because it was thought that the extinction modifications might affect both the heavy atom thermal parameters and the hydrogen atom coordinates, two further refinement runs were performed. Firstly, three cycles including the 14 heavy atoms reduced R(L.S) from 1643 to 1561 for the 1233 coefficients included, and secondly four cycles refining the coordinates of the 6 hydrogen atoms reduced R(L.S) from 700 to 664 for the 279 coefficients with $\sin\theta<0.4$ included in this refinement.

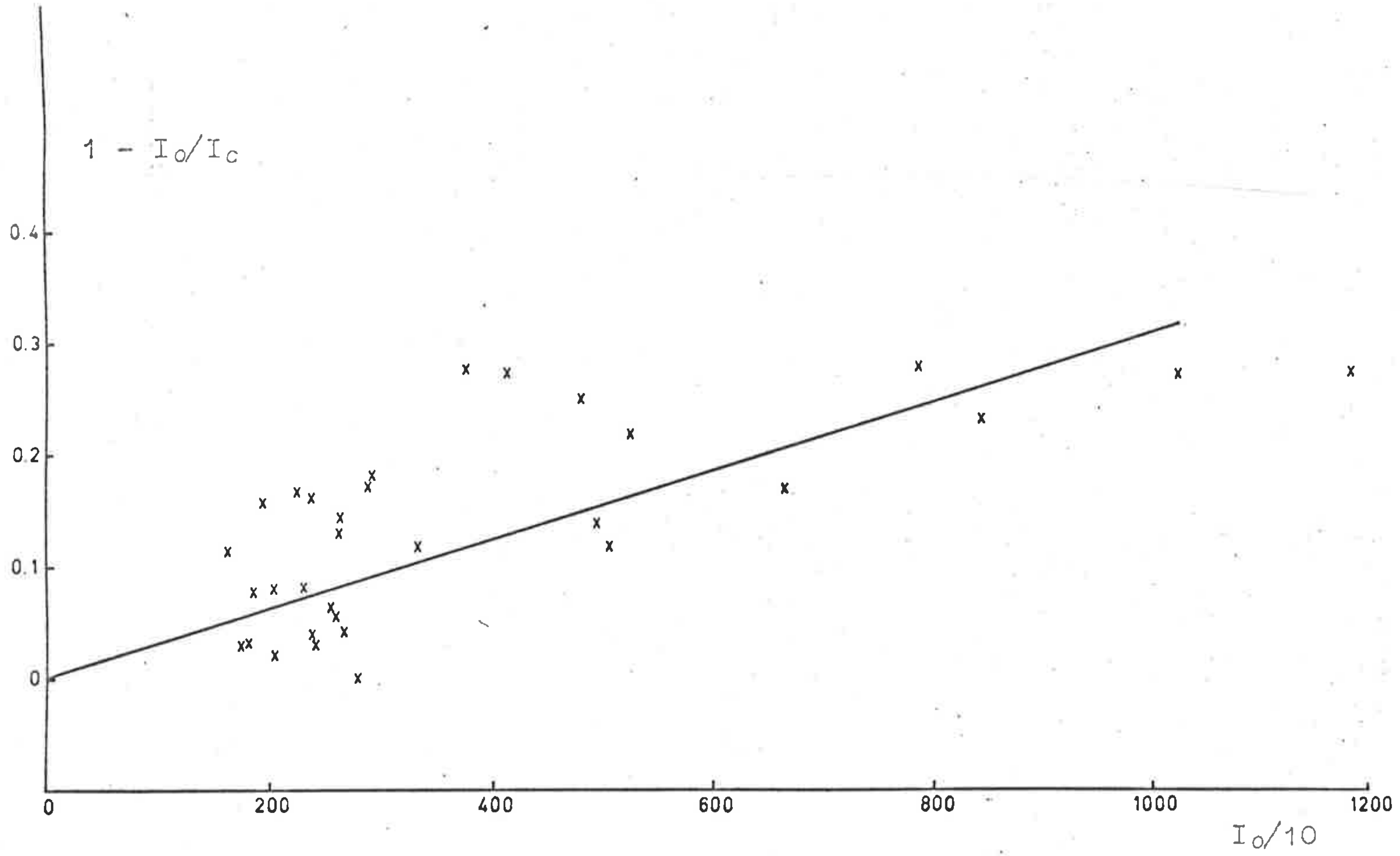


Fig. 9. Secondary extinction determination.

During the last cycle the mean heavy atom shift was 0.003A and the greatest shift 0.0017A, less than one tenth of the corresponding coordinate standard deviation; the greatest relative B_{ij} change was 2% except for some of the small B_{12} and B_{23} where the absolute changes were small. For the hydrogen atoms the final mean shift was 0.0059A and the greatest 0.019A, being one seventh of the corresponding standard deviation.

The final coordinates, standard deviations and temperature factors are given in Tables 3 and 4, the final F_o and F_c are listed in Appendix 4, and a summary of the final R values is given below.

Layer:	h01	h11	h21	h31	h41	h51
R(%)	6.6	6.2	7.0	7.0	8.0	7.4

R (final overall) $\doteq$ 6.87%

Table 3. Final positional parameters in fractional coordinates, and their standard deviations x 10^3.

Atom	x/a	y/b	z/c	σ(x/a)	σ(y/b)	σ(z/c)
S	.44328	.09272	.19331	.36	.40	.29
Na	.1891	.0102	.0236	.49	.55	.41
O_1	.2048	.6917	.0793	.91	.99	.74
O_2	.9975	.1003	.0986	.94	.99	.74
N	.1226	.3769	.0803	1.0	1.1	.79
C_1	.1314	.5627	.1093	1.1	1.3	.90
C_2	.0285	.2741	.1165	1.1	1.2	.90
C_3	.0510	.6236	.1838	1.3	1.5	1.0
C_4	.1529	.6782	.2725	1.4	1.6	1.1
C_5	.2472	.5374	.3197	1.8	2.2	1.3
C_6	.3452	.5929	.4003	2.3	2.9	1.5
C_7	.3520	.7834	.4302	2.7	2.9	1.8
C_8	.2667	.9183	.3844	3.8	2.7	2.0
C_9	.1626	.8683	.3040	2.3	2.0	1.4
H_1	.495	.779	.163	15	15	12
H_2	.250	.374	.306	17	18	13
H_3	.412	.458	.432	18	20	14
H_4	.438	.805	.501	19	20	15
H_5	.256	.034	.402	22	19	15
H_6	.103	.949	.274	18	17	14

Table 4. Final anisotropic thermal parameters x 10^4.

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	110	269	55	17	58	9
Na	95	243	53	-14	34	14
O_1	110	245	53	- 2	37	19
O_2	123	228	58	1	17	8
N	107	173	48	21	23	15
C_1	91	218	45	36	13	31
C_2	100	187	48	- 5	11	2
C_3	108	284	47	51	23	13
C_4	121	319	51	-15	37	-30
C_5	184	506	71	106	-47	-57
C_6	250	676	74	150	-85	-21
C_7	266	593	82	-203	-31	-34
C_8	395	392	80	-219	36	-58
C_9	259	341	57	-70	28	-12

H_1	as	C_3
H_2	as	C_5
H_3	as	C_6
H_4	as	C_7
H_5	as	C_8
H_6	as	C_9

2.10 Accuracy.

2.10.1 Standard deviation of coordinates.

Use was made of the formulae given by Cruickshank (1949), e.g.

$$\sigma(x_n) = \frac{2\pi}{aV_c}\{\sum_q h^2(F_o-F_c)^2\}^{\frac{1}{2}} \Big/ \left(\frac{\partial^2\rho_c}{\partial x^2}\right)_n \qquad (2.31)$$

The various curvatures, $\left(\frac{\partial^2\rho_c}{\partial x^2}\right)_n$ etc., were found by using (4.24).

2.10.2 Standard deviation of bond lengths and angles.

Since the standard deviations (s.d.) of the x, y and z coordinates of some atoms differed appreciably this was taken into account by using the expressions given by Ahmed and Cruickshank (1953). For a bond of length d, the s.d. is given by

$$\sigma^2(d) = \left(\frac{x_2-x_1}{d}\right)[\sigma^2(x_1)+\sigma^2(x_2)] + \text{similar terms in y and z.} \qquad (2.32)$$

For an angle θ,

$$\sigma^2(\theta) = (1/d_1 d_2 \sin\theta)^2[(x_2-x_3)^2\sigma^2(x_1) + (x_1-2x_2+x_3)^2\sigma^2(x_2) + (x_2-x_1)^2\sigma^2(x_3) + \text{similar terms in y and z}] \qquad (2.33)$$

2.10.3 Significance tests.

Cruickshank and Robertson (1953) have stressed the need for numerically specifying levels of significance when discussing the agreement between experimental and predicted values of various parameters; their classification was used here. If the hypothesis is made that an experimental parameter l_e equals 1, then from the statistic $\frac{(l_e - 1)}{\sigma(l_e)}$, where $\sigma(l_e)$ is the s.d. of l_e, the probability P of a difference at least as large as that between l_e and 1 being due to chance experimental errors can be found.

Cruickshank and Robertson suggest the following levels of significance

$P > .05$	corresponding to	$t < 1.960$	- not significant
$.05 > P \geqq .01$	"	$1.960 < t \leqq 2.576$	- possibly significant
$.01 > P \geqq .001$	"	$2.576 < t \leqq 3.291$	- significant
$.001 > P$	"	$3.291 < t$	- highly significant

Even if we are in the category $P < .001$ it does not mean that the original hypothesis is true, rather only that it has not been disproved.

2.10.4 The case for intensity measurement by methods other than eye estimation.

An inspection of the final coordinate deviations shown in Table 3 will reveal that they are larger than one would anticipate for a final residual of R = 6.9% which is usually considered to be very good (e.g. compare with Gerdil, 1961). Although the large thermal vibrations of some of the atoms, especially those at the extremity of the benzene ring, result in increased s.d.'s, this is not the crux of the problem. From an inspection of the final observed and calculated structure amplitudes shown in

Appendix 4, it can be seen that the differences between F_o and F_c are largely independent of both the magnitude and indices of F_o and F_c. This is a consequence of the fact that the larger F_o's were measured by the method of integration and photometry and are therefore relatively more accurate than the smaller F_o's which were measured by the method of eye estimation. These eye estimated F_o's occur mainly in the regions of larger Bragg angle, i.e. for spectra $F_o(h,k,l)$ with larger indices.

From (2.31) it is apparent that the differences (F_o-F_c) for the reflections of large indices will dominate the summation for the coordinate s.d.'s because the summation is over terms of the form $h^2(F_o-F_c)^2$. This is in fact the situation for NaPTD where the s.d.'s are essentially determined by the accuracy of the eye estimated intensities alone.

It may therefore be said in this case, that, although the accurate measurement of some of the intensities has resulted in a low residual, it has not resulted in a corresponding improvement in the accuracy of the structure analysis. There seems to be little to justify the time spent in measuring intensities by the method of integration and photometry unless this method can also be used for the high angle reflections.

It may also be noted that apart from the discussion above, a considerable fraction (about 50%) of the high order

F_o's for NaPTD were not experimentally observed at all; this reduces the peak curvature term in the denominator of (2.31) and, therefore, increases the standard deviations.

2.11 Discussion of the structure.

2.11.1 The molecular arrangement.

There are no water molecules associated with the NaPTD molecules which are held together by a system of bonds between the sodium and oxygen atoms. Each sodium atom is bonded to four oxygen atoms; conversely O_1 is bonded to two sodium atoms at distances of 2.35A and 2.30A, and O_2 to sodium atoms at distances of 2.38A and 2.42A. Each sodium atom is thereby bonded to four different NaPTD molecules; figs. 10 and 11 illustrate how this bonding forms endless chains of molecules parallel to the b screw axis and also extending in the "a" direction. In this chain formation there are two Na - N bonds, of length 2.73A and 2.76A.

The only other bonding between the molecules is of the weak van der Waals type; fig. 11 shows the shortest of these inter-molecular contacts,

The molecular bonding corresponds with the crystal habit; the system of bonding through the sodium atoms is in keeping with the plate-like nature of the crystals while the weak van der Waals contacts would allow ready cleavage in the (001) plane. The magnitude of the individual atomic thermal parameters also reflects the degree of bonding. Atoms of the thiazolidine ring are relatively tightly bound and therefore have smaller thermal parameters; progressing across the benzene ring the atoms are more free to vibrate

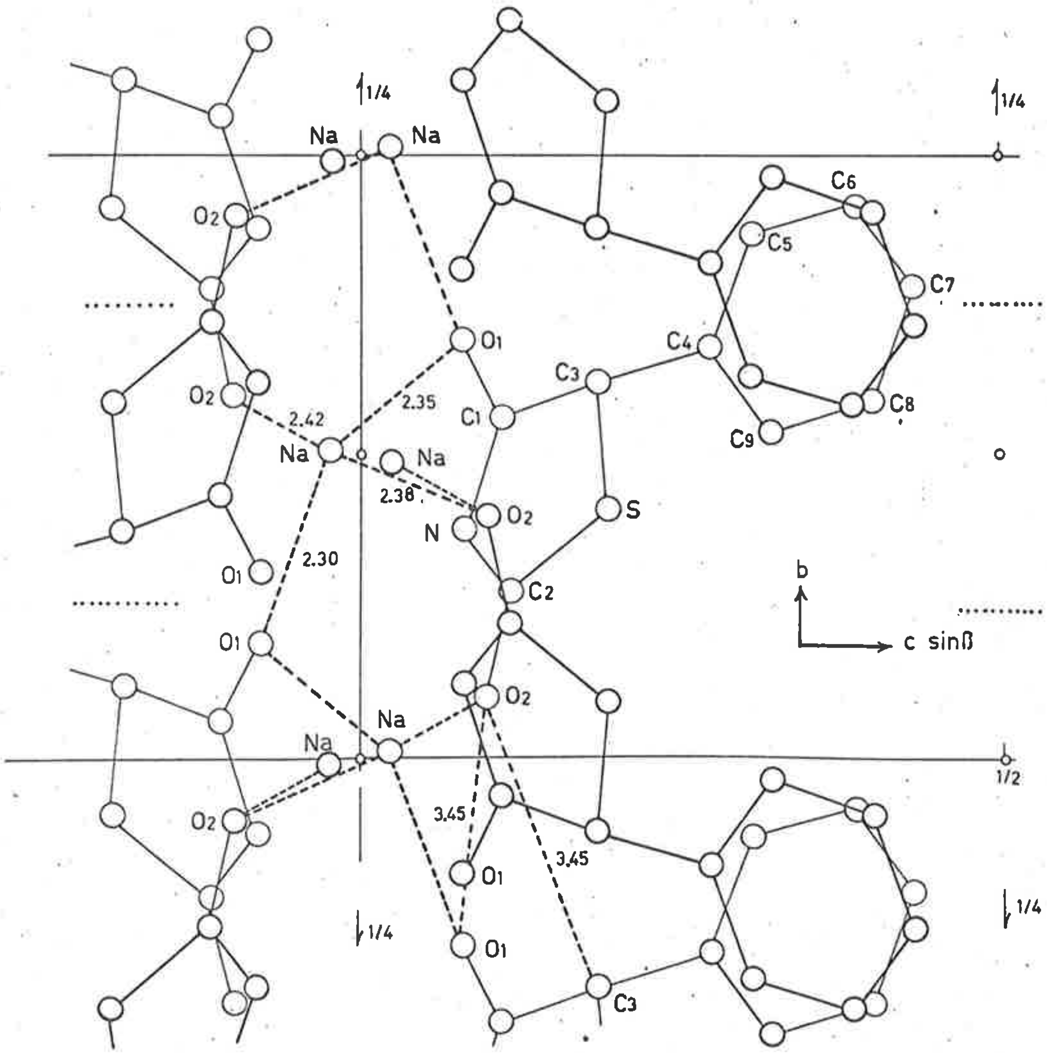


Fig. 10. Sodium atom bonding.

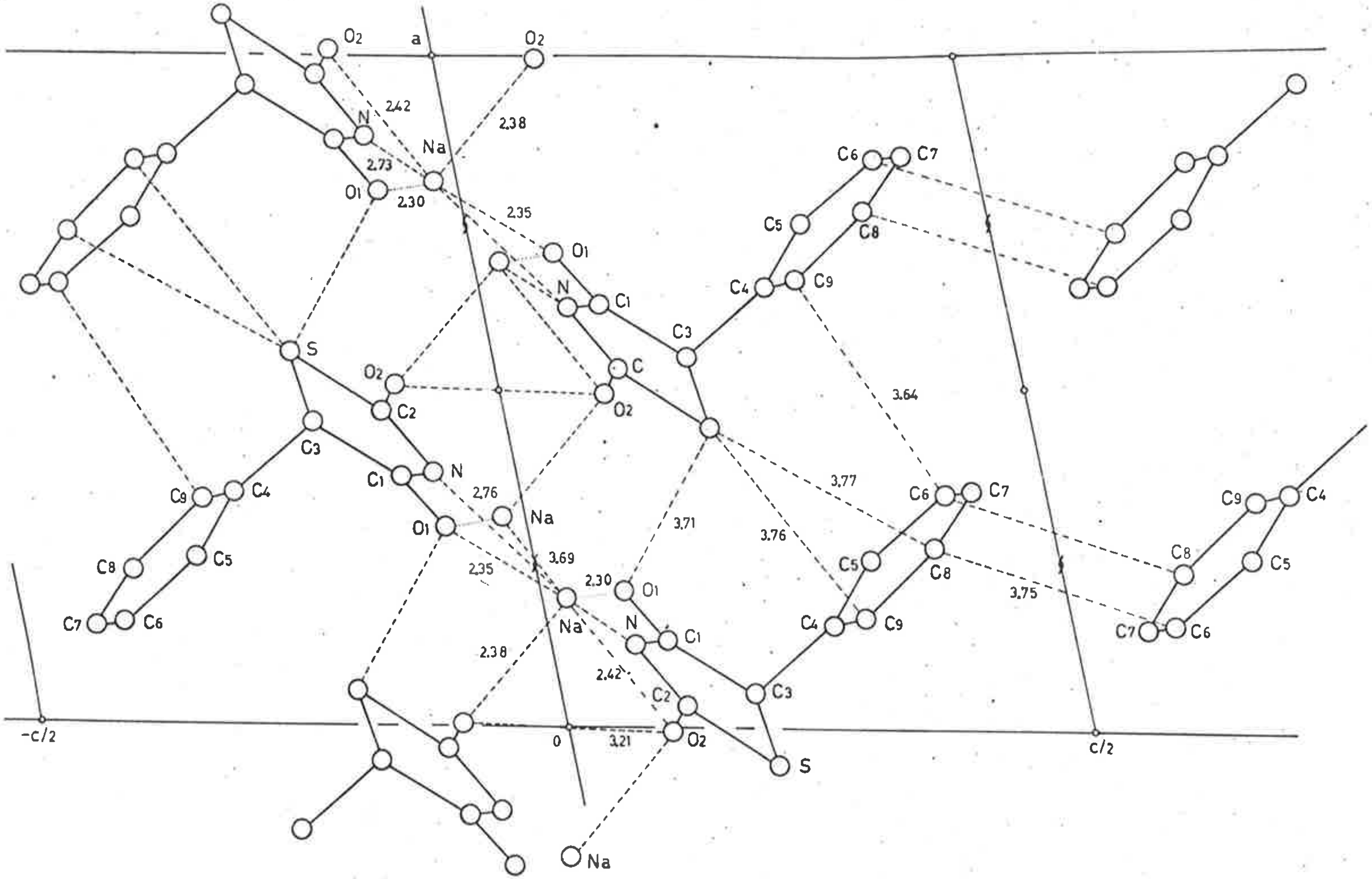


Fig. 11. Intermolecular distances less than 4.0 A°.

(Two close approaches that cannot be shown here are shown in Fig. 10.)

and therefore have larger themal constants.

2.11.2 The phenyl thiazolidine molecule.

The spatial arrangement of the NaPTD molecule is illustrated in fig. 12 while the intra-molecular bond lengths and angles are listed in Table 5 and illustrated diagrammatically in fig. 13, and fig. 14.

Although the bond lengths within the benzene ring vary considerably, only for the short C_7 - C_8 bond (1.314A) is the difference from the expected value of 1.395A "possibly significant". (The "expected" values for bond lengths are taken from the International Tables for X-ray Crystallography, Vol.111, p.276.) Because the carbon atoms in this part of the benzene ring have extreme thermal vibrations and large coordinate standard deviations the author prefers to think that any apparent departures of the benzene ring from regularity are due to this thermal motion, (e.g. see Cruickshank, 1956a).

Since the thiazolidine ring can be considered as "resonating" between several different canonical forms, each contributing to the actual observed structure, a close agreement between the dimensions of thiazolidine rings occurring in NaPTD and other crystal structures is not necessarily expected.

To give some quantitative measure of the degree of resonance of a bond between the single and double bond

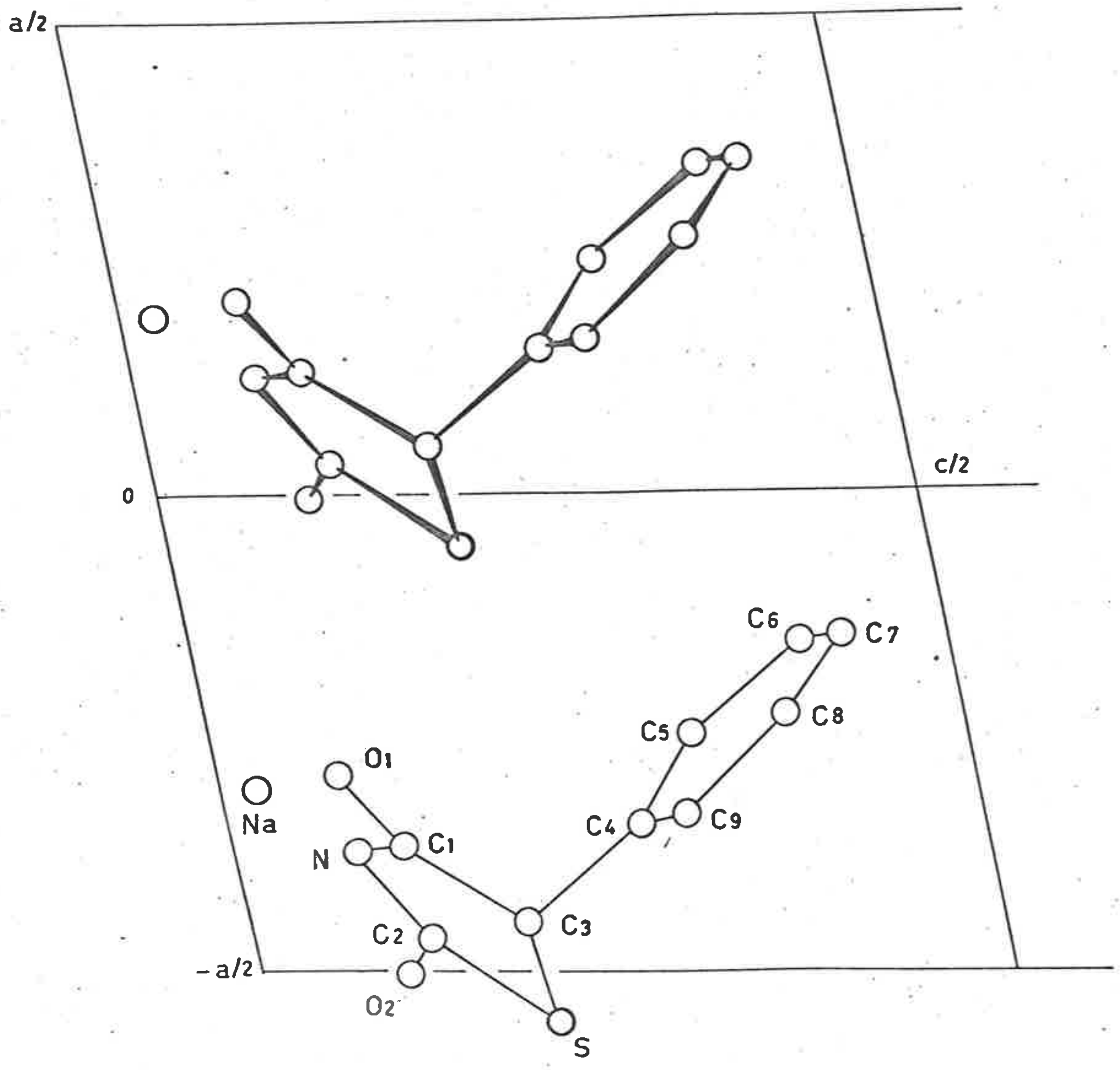


Fig. 12. Spatial arrangement of the NaPTD molecule.

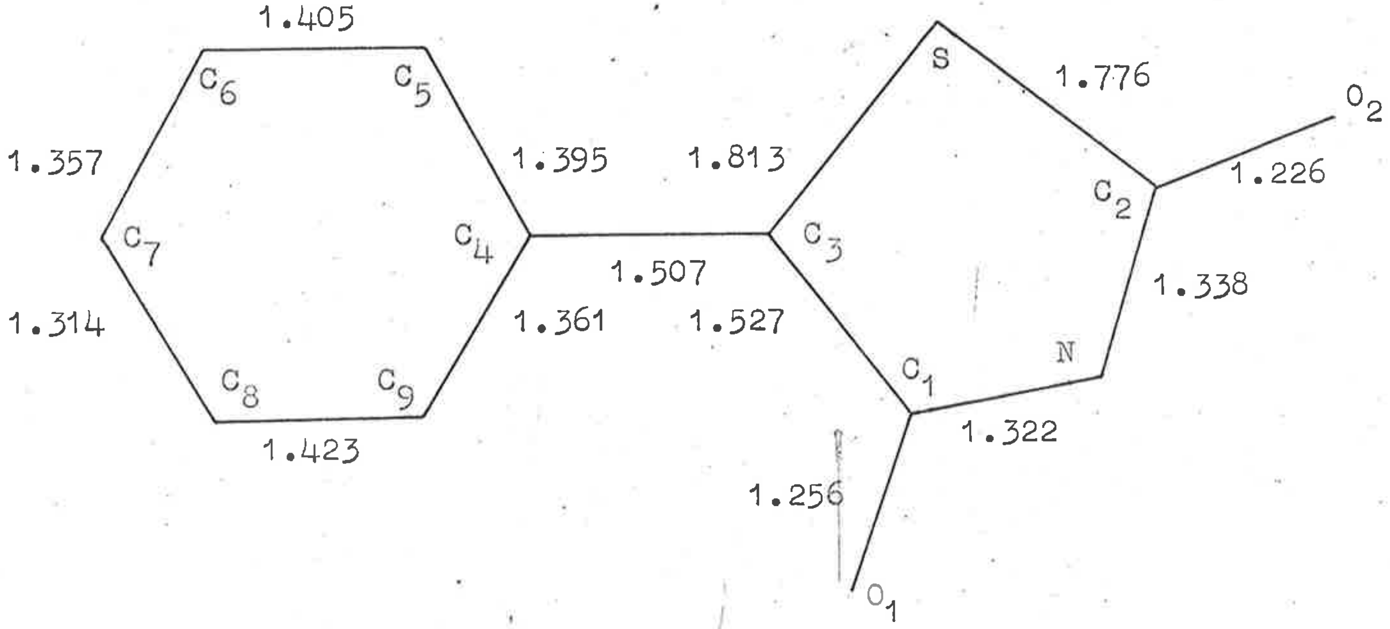


Fig. 13. Intramolecular bond lengths of NaPTD.

(In Angstroms)

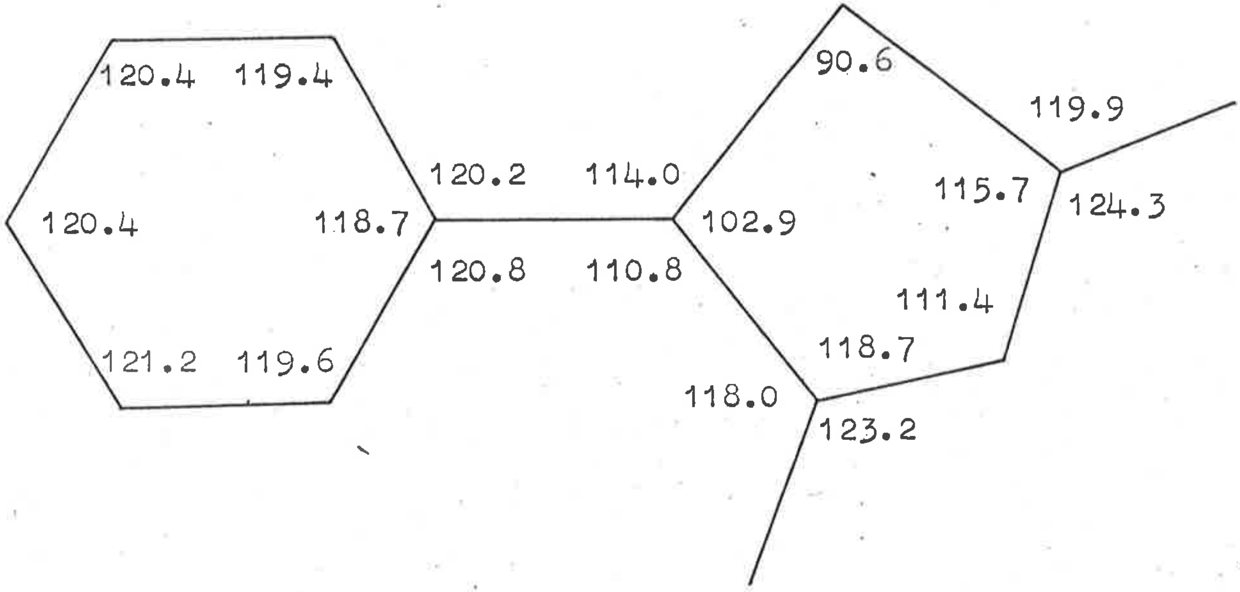


Fig. 14. Intramolecular bond angles of NaPTD.

(In degrees)

Atoms placed as in Fig. 13.

Table 5. Final bond lengths and angles.

Lengths in Angstroms, angles in degrees.

Atoms	Bond Length	Standard Deviation
$S-C_2$	1.776	.011
$S-C_3$	1.813	.011
$N-C_2$	1.322	.012
$N-C_1$	1.338	.014
C_1-C_3	1.527	.016
C_1-O_1	1.256	.013
C_2-O_2	1.226	.011
C_3-C_4	1.507	.018
C_4-C_5	1.395	.020
C_5-C_6	1.405	.025
C_6-C_7	1.357	.027
C_7-C_8	1.314	.034
C_8-C_9	1.424	.034
C_9-C_4	1.361	.018
C_3-H_1	.87	.12
C_5-H_2	1.12	.12
C_6-H_3	1.15	.15
C_7-H_4	1.20	.18
C_8-H_5	.84	.13
C_9-H_6	.85	.15

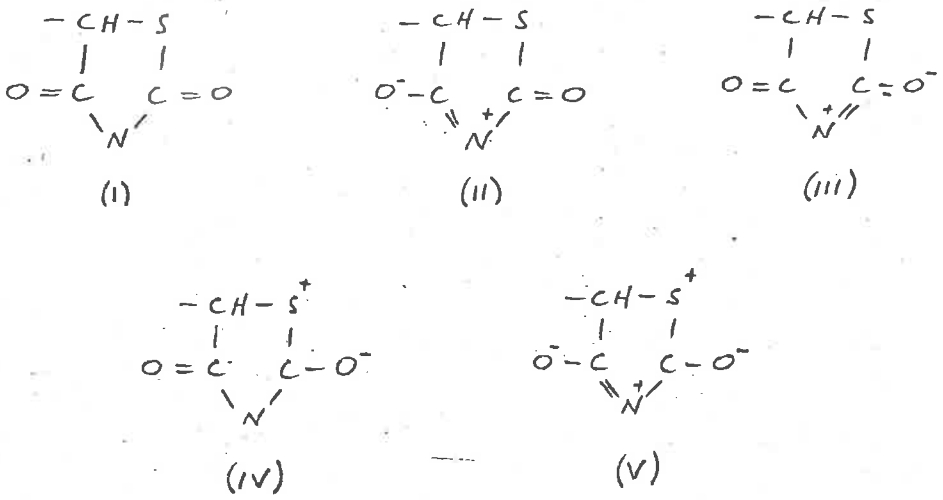
Atoms	Angle	Standard Deviation
$S-C_3-C_1$	102.9	1.3
C_3-C_1-N	118.7	1.6
C_1-N-C_2	111.4	1.5
$N-C_2-S$	115.7	1.3
C_2-S-C_3	90.6	0.9
O_1-C_1-N	123.2	1.6
$O_1-C_1-C_3$	118.0	1.6
O_2-C_2-N	124.3	1.7
O_2-C_2-S	119.9	1.4
$C_4-C_3-C_1$	110.8	1.6
C_4-C_3-S	114.0	1.4
$C_3-C_4-C_5$	120.2	2.0
$C_3-C_4-C_9$	120.8	2.1
$C_4-C_5-C_6$	119.4	2.5
$C_5-C_6-C_7$	120.4	3.1
$C_6-C_7-C_8$	120.4	3.7
$C_7-C_8-C_9$	121.2	3.9
$C_8-C_9-C_4$	119.6	3.0
$C_9-C_4-C_5$	118.7	2.3

extremes, Pauling (1948) defines the percent double-bond character, p, of a bond by

$$D = D_s - (D_s - D_d)(\frac{3p}{2p + 100}) \qquad (2.34)$$

where D is the observed length of the actual bond and D_s and D_d are the lengths of the pure single and pure double bonds between the two atoms in question. Pauling also gives tables of single and double bond radii from which the values of D_s and D_d can be calculated. In using Pauling's equation, the following bond lengths were assumed, C-C = 1.54A; C=C = 1.33A; C-N = 1.47A; $C{=}N^+$ = 1.24A; $C{-}O^-$ = 1.45A; C=O = 1.20A; C-S = 1.81A and $C{=}S^+$ = 1.61A. Except for the carbon - sulphur bond lengths which were derived from Pauling's tables, these bond lengths are the same as those used by Gerdil (1961) in discussing the resonance of thymine monohydrate.

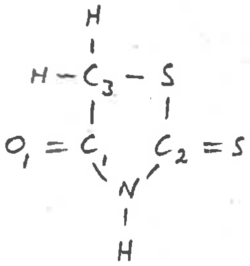
It was found (although this solution is not unique) that it was possible to account for the bond lengths observed in the thiazolidine ring by assuming that the canonical formulae shown below contribute to the resonant state in the following proportions, I, 30%; 11, 40%; 111, 25%; IV, 5% and V, 0%.



Some canonical formulae for the thiazolidine ring.

By summing over the canonical forms in the proportions indicated, the corresponding double bond character of each bond was found. Then, by using Pauling's equation in an inverse form, the "calculated" bond lengths were evaluated.

These calculated bond lengths and double bond characters are listed below together with the observed bond lengths; for comparison the corresponding bond lengths observed for rhodanine (van der Helm, 1962) are also included.



Rhodanine

Bond	Double bond character	Calc. bond length	Obs. bond length	Obs. for Rhodanine
S $-C_3$	0 %	1.81 A	1.81 A	1.82 A
S $-C_2$	5	1.78	1.78	1.74
C_3-C_1	0	1.54	1.53	1.51
C_1-N	40	1.32	1.32	1.38
C_2-N	25	1.35	1.34	1.37
C_1-O_1	60	1.24	1.26	1.23
C_2-O_2	70	1.23	1.23	-

Although the bond length differences between rhodanine and NaPTD can be satisfactorily explained by different double bond character, they may be partly due to experimental errors. If the latter is the case then the results obtained from this investigation appear to be the more reliable. (It is difficult to assess the reliability of the rhodanine bond lengths because the standard deviations quoted were obtained from an inspection of the changes during the final cycle of refinement - a most unsatisfactory procedure.)

With the exception of the benzene ring, the observed NaPTD bond lengths and angles agree well with the "expected" values. The S-C_3 single bond has an observed length of 1.81A, in exact agreement with the expected value. The C_2-S-C_3 angle is observed to be 90.6^o, the slight increase from 90^o being expected because of the partial double bond character of the S-C_2 bond. The change of the C_1-N-C_2 bond from 120^o

to the observed value of 111.4° can also be accounted for by the double bond character of the C_1-N and C_2-N bonds.

As is expected the six carbon atoms of the benzene ring do not depart significantly from planarity. The best plane through these atoms calculated by the least squares method of Schomaker et. al. (1959) is

$$7.670x + 1.420y - 10.631z = 0.753$$

where the distance from this plane to the origin is 0.753A. The weight given to each atom site was proportional to the inverse of the corresponding coordinate variance; the departures of the atoms from this plane average 0.010A and are listed below.

Several references have been made to possible errors in atom coordinates due to refinement with isotropic rather than anisotropic temperature factors (e.g. Grenville Wells, 1956; Cruickshank, 1960). It was therefore valuable to compare the benzene ring planes before and after the use of anisotropic temperature factors. Using the same weights as above, the best plane was similar, i.e.

$$7.692x + 1.386y - 10.618z = 0.767$$

but the sum of squares of the weighted residuals increased from 1.6×10^{-4} to 5.1×10^{-4} A^2. For comparison the individual residuals which averaged 0.017A are listed below.

Atom	C_4	C_5	C_6	C_7	C_8	C_9
Deviation (after final refinement)	-.007	.014	-.012	-.007	.017	.002 A°
Deviation (before anisotropic temperature factors)	-.008	.024	-.032	-.007	.024	-.007 A°

On assuming that the benzene ring should be planar, it is apparent that appreciable (even if "not significant") errors in atomic coordinates can result through the neglect of anisotropic thermal motion.

The best plane through the five atoms in the thiazolidine ring is

$$-5.536x + 2.013y - 9.209z = 0.651$$

where the origin to plane distance is 0.651A. The departures of the ring atoms and also the two O_1 and O_2 atoms are as follows:

Atom	S	C_3	C_1	N	C_2	O_1	O_2	
Deviation	.0045	-.069	.050	-.009	-.028	.176	-.041	A°

The departures of both C_1 and C_3 from the plane are considerable. In order to test whether the ring is, in fact, significantly aplanar, the "χ^2" test was applied (Wheatley, 1953).

By definition

$$\chi^2 = \Sigma\,(\Delta/\sigma)^2$$

where Δ is the deviation from planarity and σ is the corresponding coordinate standard deviation. Summing over the five ring atoms, $\chi^2 = 61.2$. From the table of Fisher (1954, p.112), this corresponds to a probability P less than 0.01; P is the probability of the observed value of χ^2 occurring, or being exceeded, by chance. Using the usual levels of significance (P less than 0.02 being "significant"), it must be concluded that the thiazolidine ring departs "very significantly" from planar.

Only four of the five ring atoms are involved in resonance (i.e. S, C_1, N, C_2) and are expected to be planar. The best fit plane through these atoms is

$$-5.597x + 1.757y - 9.319z = 0.768$$

In this case their departures from planarity are much less, viz.

Atom	S	C_1	N	C_2	C_3	O_1	O_2
Deviation	-.0002	.003	-.004	.005	-.134	.095	.040

The value of χ^2 is 0.44, corresponding to P = 0.50; thus these four atoms do not depart significantly from planar.

The best fit plane through the six atoms S, C_1, N, C_2, O_1 and O_2 (i.e. excluding C_3) was also found. In this case $\chi^2 = 61.3$, indicating "highly significant" aplanarity.

2.11.3 Thermal vibrations.

In order to examine the anisotropy of the atom vibrations more conveniently, the vibrations were expressed in terms of the principal axes of the ellipsoids of vibration by using the transformation of Rollett and Davies (1955). They define the ellipsoid of vibration of an atom as the ellipsoid in reciprocal space on which the temperature factor is constant. The temperature factor for an atom is then written as

$$T = \exp[-\sum_{i=1}^{3} q_i h_i^2] \qquad (2.35)$$

where i = 1, 2, 3 for each of the three principal axes of the ellipsoid of vibration, and h_i is the component of $(2\sin\theta/\lambda)$ in the direction i. Then if g_{i1}, g_{i2} and g_{i3} are the direction cosines of the principal axes with respect to a*, b* and c*, the temperature factor can be written as

$$T = \exp[-\sum_{i} q_i (hg_{i1}a^* + kg_{i2}b^* + lg_{i3}c^*)^2] \qquad (2.36)$$

The values of the q_i and g_{ij}, determined from the B_{ij} by the method of Rollett and Davies are given in Table 6.

Although a detailed interpretation of each of the thermal ellipsoids was not attempted, some general conclusions were reached. Generally, adjacent atoms have similar modes of vibration; for example, the thermal ellipsoids for the bonded atoms C_1 and O_1 are similar, as are those for C_2 and O_2. The vibrations of atoms in the thiazolidine ring are not far from isotropic while at the extremity of the benzene ring the anisotropy is considerable. Of these extreme ring

TABLE 6. Principal axis thermal parameters.

Atom	i	q_i	g_{i1}	g_{i2}	g_{i3}
S	1	.343	.790	-.055	-.432
	2	.538	.447	.733	.595
	3	.490	.420	-.678	.678
Na	1	.344	.944	.213	-.049
	2	.497	.018	.731	.670
	3	.440	.330	-.648	.741
O_1	1	.399	.846	.279	-.266
	2	.506	.130	.718	.696
	3	.435	.517	-.638	.667
O_2	1	.426	.664	-.626	.539
	2	.442	.602	.772	.325
	3	.556	-.443	.111	.777
N	1	.406	.887	.407	.398
	2	.314	-.349	.900	-.328
	3	.437	-.301	.155	.857
C_1	1	.289	.769	-.469	.587
	2	.470	.102	.761	.648
	3	.409	-.632	-.448	.486
C_2	1	.346	.853	.293	.601
	2	.359	-.227	.954	-.241
	3	.465	-.470	.071	.762
C_3	1	.365	.853	-.352	.555
	2	.572	.366	.930	.114
	3	.425	-.371	.109	.824

TABLE 6. (Cont.)

Atom	i	q_i	g_{i1}	g_{i2}	g_{i3}
C_4	1	.447	.981	.160	.310
	2	.633	-.122	.948	-.313
	3	.418	-.148	.276	.898
C_5	1	.425	.740	-.007	.813
	2	1.190	.493	.685	-.420
	3	.776	-.457	.728	.404
C_6	1	1.109	.459	-.729	-.400
	2	1.524	.574	.680	-.326
	3	.422	.678	-.082	.857
C_7	1	.543	.655	.315	.687
	2	1.407	.673	-.656	-.341
	3	1.016	-.343	-.686	.642
C_8	1	1.611	.930	-.302	-.009
	2	.554	.366	.718	.656
	3	.809	-.029	-.627	.755
C_9	1	1.019	.941	-.239	-.037
	2	.638	.177	.951	-.212
	3	.491	.289	.198	.976

Note: These direction cosines apply to atoms with coordinates given in Table 3. For symmetry equivalent atoms related by a glide operation the sign of g_{i2} must be reversed.

atoms the vibrations of C_5, C_6, C_7 and C_8 are somewhat similar and although the directions of the axes of maximum vibration vary, they are directed approximately out of the ring plane. Also, the minimum vibration directions lie reasonably near the direction of the $C_3 - C_4$ bond as might be expected.

It was also interesting to compare the directions of the axes of the vibrational ellipsoids as calculated from the B_{ij} with the directions of maximum and minimum thermal vibration as indicated by the final difference synthesis calculated after refinement with isotropic temperature factors. This was done for the sulphur atom by projecting the three principal axes of its ellipsoid of vibration onto the (x, z) plane.

It follows from the properties of spherical triangles that if g_{i1}, g_{i2} and g_{i3} are the direction cosines as defined above, then the angle between the projection of the (g_{i1}, g_{i2}, g_{i3}) direction on the (x, z) plane and a^* is φ, where

$$\varphi = \arccos[\, g_{i1}/\sqrt{(1-g_{i2}^2)}\,] \qquad (2.37)$$

By using this result the necessary projections for the sulphur ellipsoid were made and are shown in fig. 15. A_1, A_2 and A_3 represent the projections of the three principal axis directions and it can be seen that there is excellent agreement with the anisotropy indicated by the electron density

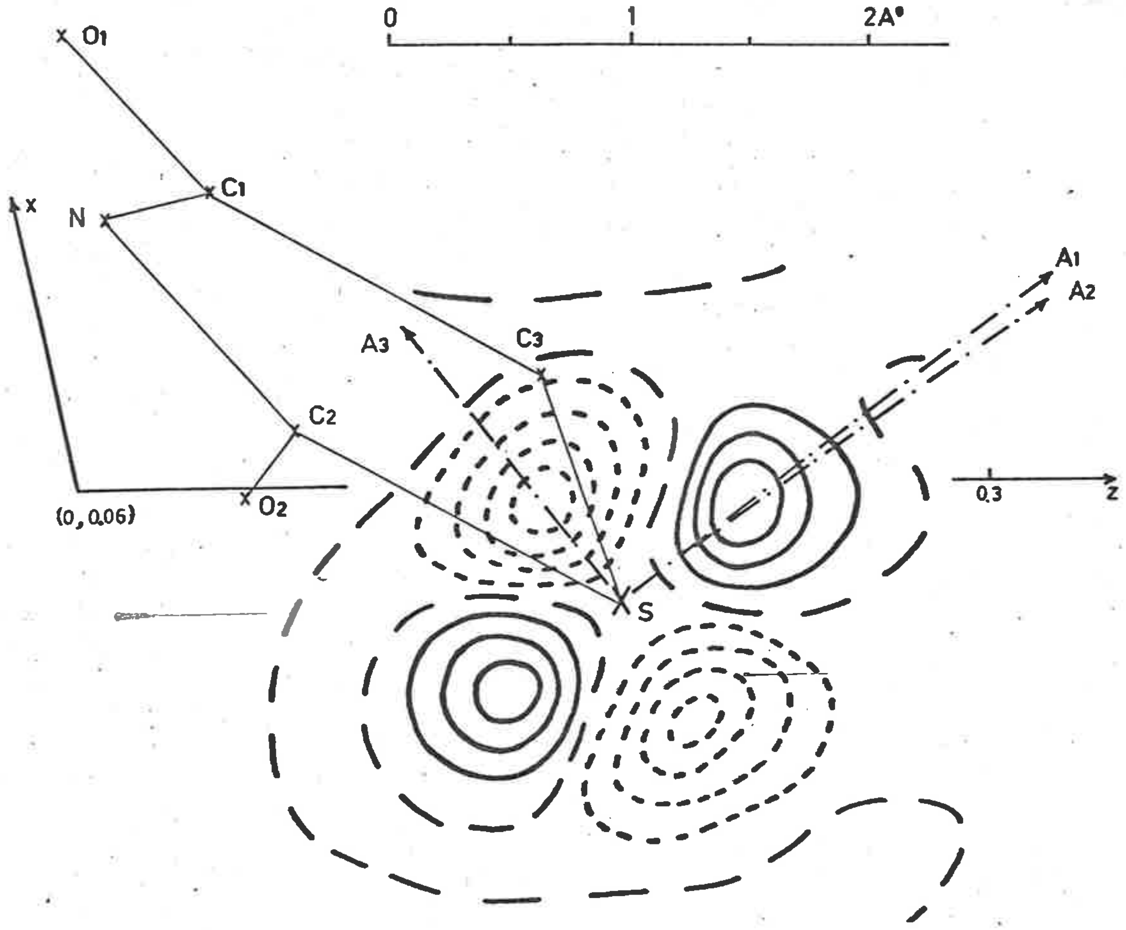


Fig. 15. Anisotropic vibration of the sulphur atom. Contours at intervals of 0.2 e./A^3.

maxima and minima. The axes corresponding to A_1, A_2 and A_3 are respectively directed at 47° downwards, 43° upwards, and 3° upwards from the section plane. In three dimensions, there is an annulus of positive electron density around the sulphur position, which corresponds with the fact that the A_1 and A_2 axes are of similar magnitude, and are both considerably greater than A_3 (respective values being 0.538, 0.490, and 0.343).

Fig. 15 also shows the projection of the thiazolidine ring onto the section plane. The orientation of the ellipsoid corresponds well with the directions in which the sulphur atom is bonded. The direction of minimum vibration is approximately coincident with the bisector of the $S - C_2$ and $S - C_3$ bond directions, and the vibration normal to this bisector is almost isotropic, as might be anticipated.

CHAPTER 3.

THE CRYSTAL AND MOLECULAR STRUCTURE OF A BENZIMIDAZOLE DERIVATIVE

3.1 Introduction.

At the conclusion of the work described in Chapter 2, techniques had been developed which would allow the investigation of any of a wide range of crystal structures. Excellent computing facilities had become available and programs had been written which, with some modification, would greatly facilitate the investigation of most organic compounds.

During discussion Dr. (now Professor) Clark-Lewis of the Organic Chemistry Department brought to the author's notice a unique chemical problem which had for some years not yielded to chemical analysis and which would be best resolved by X-ray techniques. Since the problem was essentially to distinguish between a five or six membered ring structure, and also since heavy atom derivatives were available, it was thought that a solution of the structure should be possible, thereby resolving the chemical problem without ambiguity.

Two very similar bromo derivatives were provided by Dr. Clark-Lewis with the hope that solution of either structure would solve the problem. The first derivative proved to be triclinic and possibly non-centric; the second was monoclinic ($P2_1/n$) with eight molecules in the unit cell. Although the monoclinic derivative had 46 non-hydrogen atoms in the asymmetric unit it was decided to proceed with the investigation of its structure, for in addition to the interest of the chemical problem it would be instructive to compare the consistency of chemically equivalent but crystallographically independent bonds and angles in the two molecules comprising the asymmetric unit.

This chapter describes the solution and refinement of the monoclinic structure, a structure which was found to be one not thought likely on chemical grounds. The original chemical dilemma has, in a sense, been resolved, but the solution leads one to speculate on other structural problems not well understood (e.g. the possibility of ring contractions and ring expansions under very mild conditions).

3.2 The nature of the problem.

3.2.1 Introduction.

To explain some of the products formed by o-phenylenediamines and alloxan in neutral solution, King and Clark-Lewis (1951 a,b) proposed a new type of ring formation not known heretofore. Although their hypothesis agreed with all the chemical evidence (and still does) there were still some unusual interconversions between different condensation products which were difficult to explain.

This section is intended to review the chemical problem, to show the need for X-ray diffraction techniques, and to mention the present understanding of the problem.

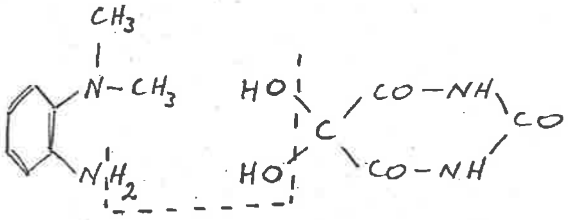
The author is most indebted to Dr. Clark-Lewis for much of the chemical background given in this section.

3.2.2 The chemical problem.

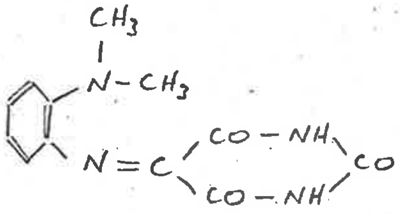
In aqueous ethanol o-aminodimethylaniline (I) reacts with alloxan hydrate (II) to give a mixture or products composed mainly of a yellow spiran and a colourless "carbinol-amine". These products will be referred to as compounds "A" and "B" respectively.

Rudy and Cramer (1938, 1939 a,b) proposed that A was the anil (III), formed by splitting off two water molecules as suggested by the dashed lines. Subsequently King and Clark-Lewis (1951 a,b) proved beyond all reasonable doubt that A was in fact the spiran (IV), formed in a ring -

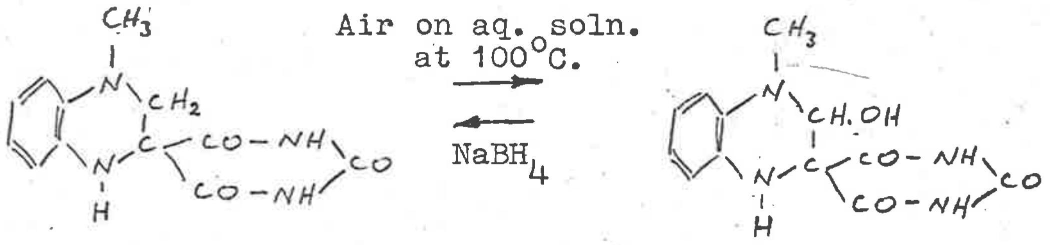
closure unique in the literature in that it involves an N-methyl group.



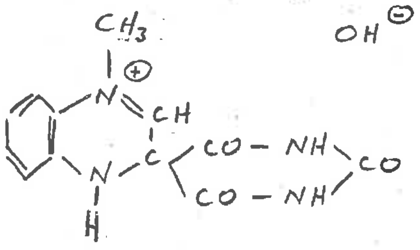
(I) (II)



(III)

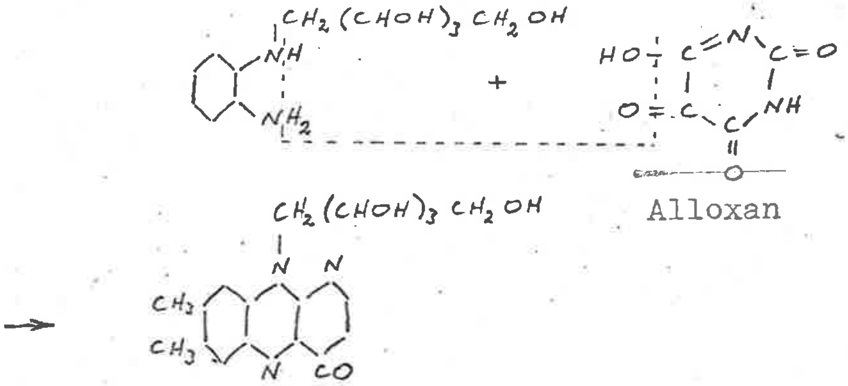


(IV) (V)



(VI)

The condensation is therefore somewhat similar to the synthesis of riboflavin (Vitamin B2) from 2-amino-4:5-dimethylphenyl-ribamine and alloxan. While this reaction is readily visualised by writing alloxan in its tautomeric form (as done below), the same simple picture does not describe the formation of (IV) because the N-hydrogen has been replaced by an N-methyl group.



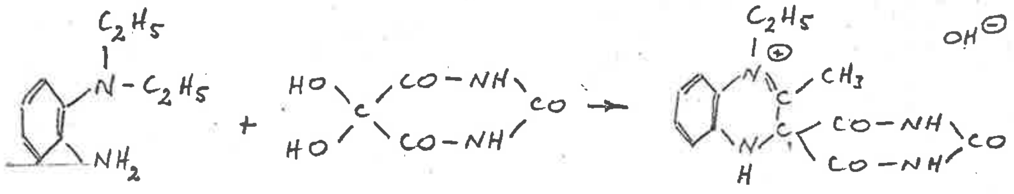
Alloxan

Riboflavin

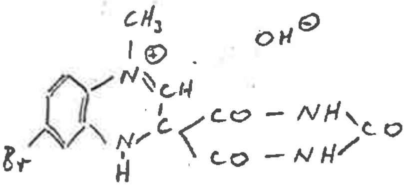
Returning to the original condensation, King and Clark-Lewis (1953) showed that the second product (B) was also obtained when air was passed through an aqueous solution of A (i.e. IV); formation under such mild conditions indicated that B must be closely related to (IV), and it was assigned the carbinol-amine structure (V).

The structures (IV) and (V) accounted satisfactorily for the chemical properties of the compounds A and B, but their electronic absorption spectra differed, and it was later considered desirable to alter the bonding shown in (V) to that in the related structure (VI), which was compatible with all the chemical and physical properties.

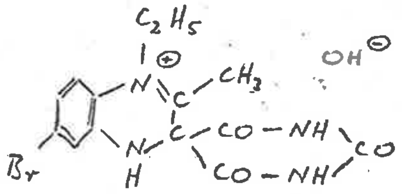
The chemical evidence for the structures (IV) and (VI) was not conclusive, however, and to obtain further data Thompson (1957) condensed o-aminodiethylaniline (VII) with alloxan hydrate. This gave a compound thought to be an analogue (VIII) of (VI) which differed from (V) in being remarkably resistant towards aqueous alkali; no analogue of (IV) was isolated.



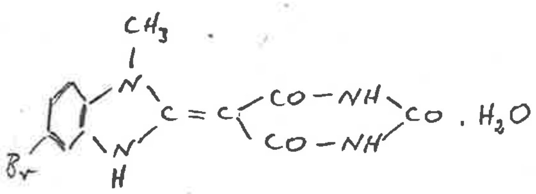
(VII) (VIII)



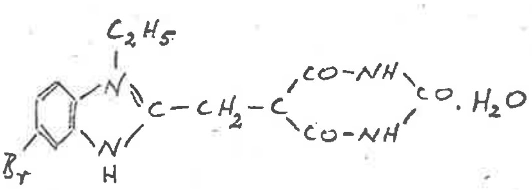
(IX)



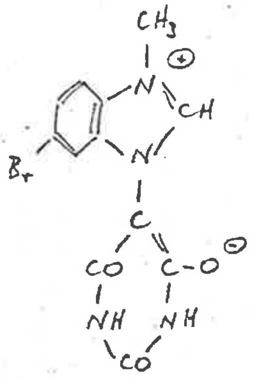
(X)



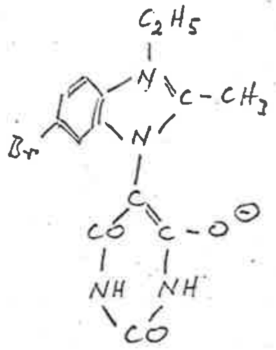
(XI)



(XII)



(XIV)



(XIII)

There were several factors which made chemical confirmation of the structures (VI) and (VIII) difficult. Firstly the compounds were in general very stable (melting points approaching 400°C not being uncommon), secondly all degradation products proved inconclusive and thirdly the compounds had very limited solubility in the usual organic solvents. For these reasons confirmation (or otherwise) of the structures (VI) or (VIII) by X-ray techniques was highly desirable, and availability of the corresponding bromo derivatives (IX) and (X) made this feasible. The alternative structures for which there was some chemical evidence are shown as (XI) and (XII).

Although it would have been preferable to investigate the structure B (i.e. IX) because of its close relation to the original condensation product A, it proved more convenient to use the diethyl condensation product (i.e. X).

Rather surprisingly the work described in the remainder of this chapter has revealed that the true structure is not the proposed structure (X) but in fact (XIII).

At the time of writing it is still thought that the six-membered ring structure (IV) is correct; on the other hand it is certain that the structure (XIII) with its five-membered ring cannot be wrong. To resolve this dilemma one must propose either that the reactions of alloxan with the dimethyl and diethyl amino aniline derivatives (I) and (VII) are substantially different, or alternatively that the conversion of A (i.e. IV) to B (i.e. XIV) by air on the aqueous solution at 100°C involves the contraction of a six to five-membered ring. Chemical analysis of the problem is still continuing, and if this still remains inconclusive it would be worth examining the bromo derivative of B by X-ray methods to ascertain whether this structure is in fact (XIV), the analogue of (XIII).

3.3 Choice of compound.

Crystals of the two bromo derivatives thought to be (IX) and (X) were supplied by Dr. Clark-Lewis; these will be referred to hereafter as B.Br(Me) and B.Br. (Dr. Clark-Lewis has pointed out that it is difficult to assign satisfactory names to these compounds and therefore no full chemical name will be given.)

Crystals of B.Br(Me) were well formed brittle colourless needles. From oscillation and Weissenberg photographs a triclinic unit cell of the following dimensions was chosen.

a = 7.23 A α = 63.5°
b = 9.08 A β = 106°
c = 12.07 A γ = 99.5°

Cell Volume = 683 A^3.

Referred to this cell the needles used were bounded by the faces (001) and ($\bar{1}10$). Assuming two molecules in the unit cell, the calculated density was 1.72 gm/cc which agreed with the value of 1.752 obtained by flotation.

To determine whether the two molecules in the unit cell were centrosymmetrically related, intensities were obtained by the method of eye estimation for the zone of reflections corresponding to rotation about the needle axis. A plot was then made of the distribution of intensities in the manner suggested by Howells, Phillips and Rogers (1950)

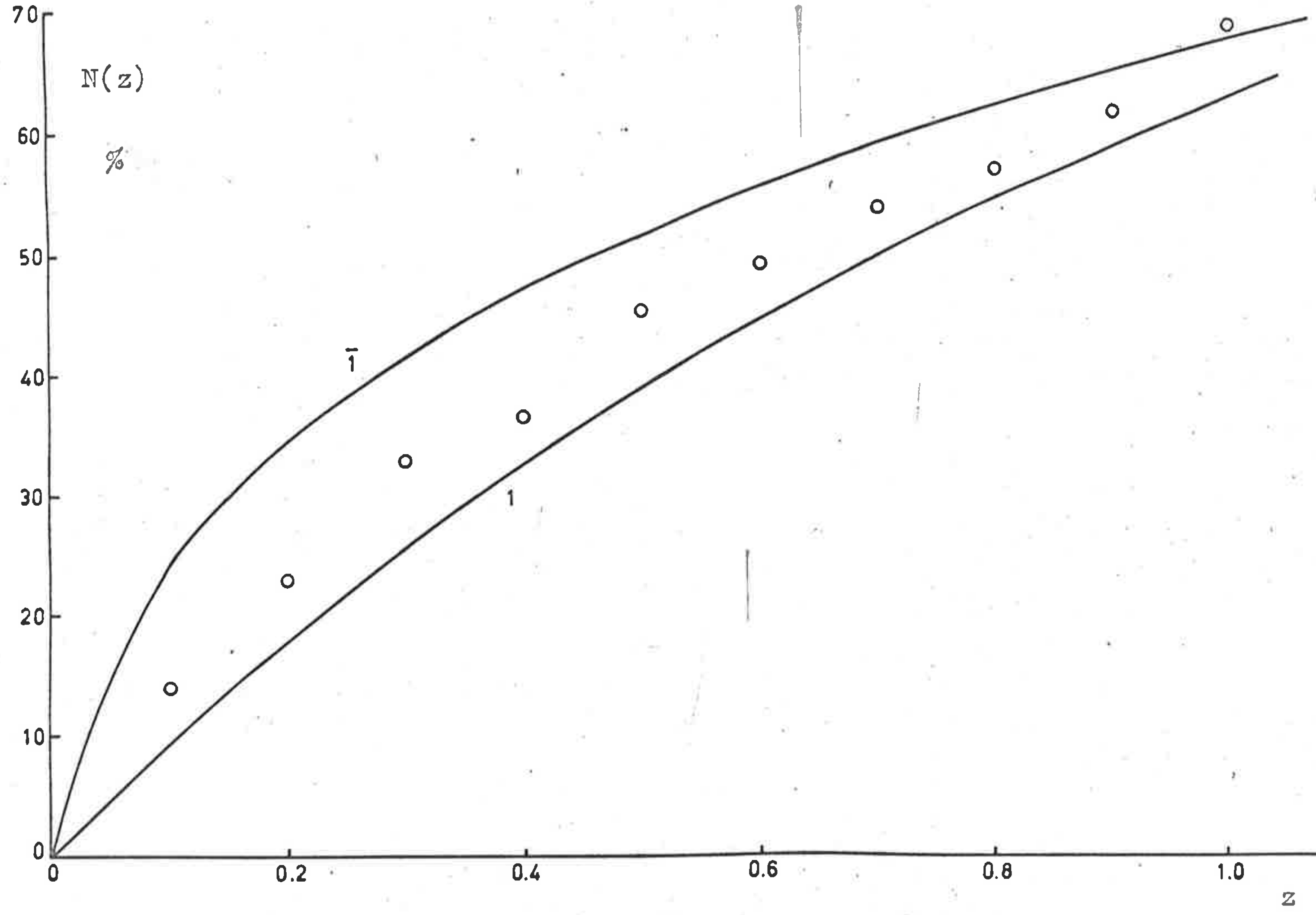


Fig. 16. Distribution of intensities of B.Br(Me)

and this is shown in fig. 16 along with the theoretical distributions for centric and non-centric structures. It can be seen that this plot was not conclusive. It was nevertheless felt that if the origin of coordinates was considered to be midway between the two heavy atoms, then since these atoms dominate the scattering the results would tend to indicate a centric structure irrespective of whether the remainder of the light atoms were centrosymmetrically related or not; thus a non-centric structure of 42 independent atoms seemed likely. Although this did not completely rule out an X-ray analysis, attention was directed toward the second possible compound (i.e. B.Br) which it was hoped would prove to be more tractable. Analysis of this benzimidazole derivative is described in the remainder of this chapter.

3.4 Properties of the benzimidazole derivative.

3.4.1 Physical properties.

Crystals of B.Br were generally well formed, brittle, and tabular, elongated along [100] and with the (010) and (001) faces most prominent. Cleavage was possible parallel to the principal faces and to (100), although care had to be taken not to lose the specimens as the cleavage was generally violent.

The crystals were monoclinic, and systematic absences - (h0l) for h+k odd and 0k0 for k odd - gave the space group unequivocally as $P2_1/n$.

From the cell volume, measured density and chemical composition of ($BrC_{14}N_4O_4H_{15}$), it was apparent that there were eight molecules in the unit cell, i.e. two independent molecules per asymmetric unit.

These and other physical properties are summarised in Table 7.

3.4.2 Unit cell dimensions.

The lattice parameters were determined by a method similar to the extrapolation back-reflection Weissenberg technique described by Buerger (1958, p.435). Since the appropriate camera was not available, a conventional camera was modified by removing the usual film - retaining clips and then mounting a slotted film "back to front".

0kl spectra were used to determine b and c sinβ, h0l to determine β and a sinβ. The crystals used were about 0.1 mm square in cross section and were the ones later used for intensity measurements. The final results are shown graphically in fig. 17, and are summarised in Table 7.

It may be noted that in retrospect the author is of the opinion that, for organic crystals, the accuracy obtained by either of the extrapolation methods described in Chapters 2 and 3 does not warrant the time spent. Although other accurate methods have not been used by the author, it would appear that by calibration against a standard, (e.g. Fridrichsons, 1959), unit cell parameters of comparable accuracy can be determined much more conveniently.

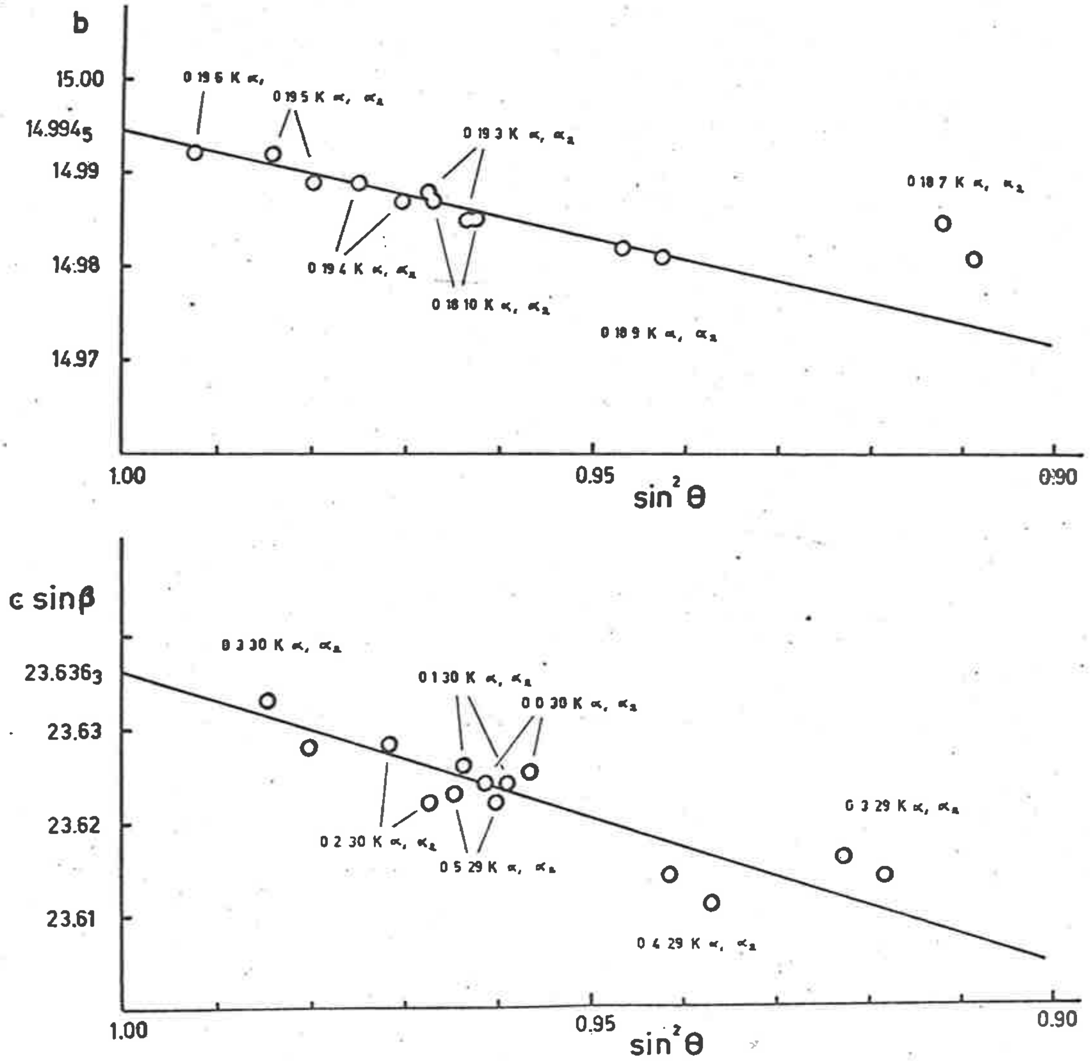

b
15.00
14.994₅
14.99
14.98
14.97
0 19 6 K α₁
0 19 5 K α₁, α₂
0 19 3 K α₁, α₂
0 18 7 K α₁, α₂
0 19 4 K α₁, α₂
0 18 10 K α₁, α₂
0 18 9 K α₁, α₂
1.00
0.95
0.90
sin²θ
c sinβ
23.6363
23.63
23.62
23.61
0 3 30 K α₁, α₂
0 1 30 K α₁, α₂
0 0 30 K α₁, α₂
0 3 29 K α₁, α₂
0 2 30 K α₁, α₂
0 5 29 K α₁, α₂
0 4 29 K α₁, α₂
1.00
0.95
0.90
sin²θ

Fig. 17.

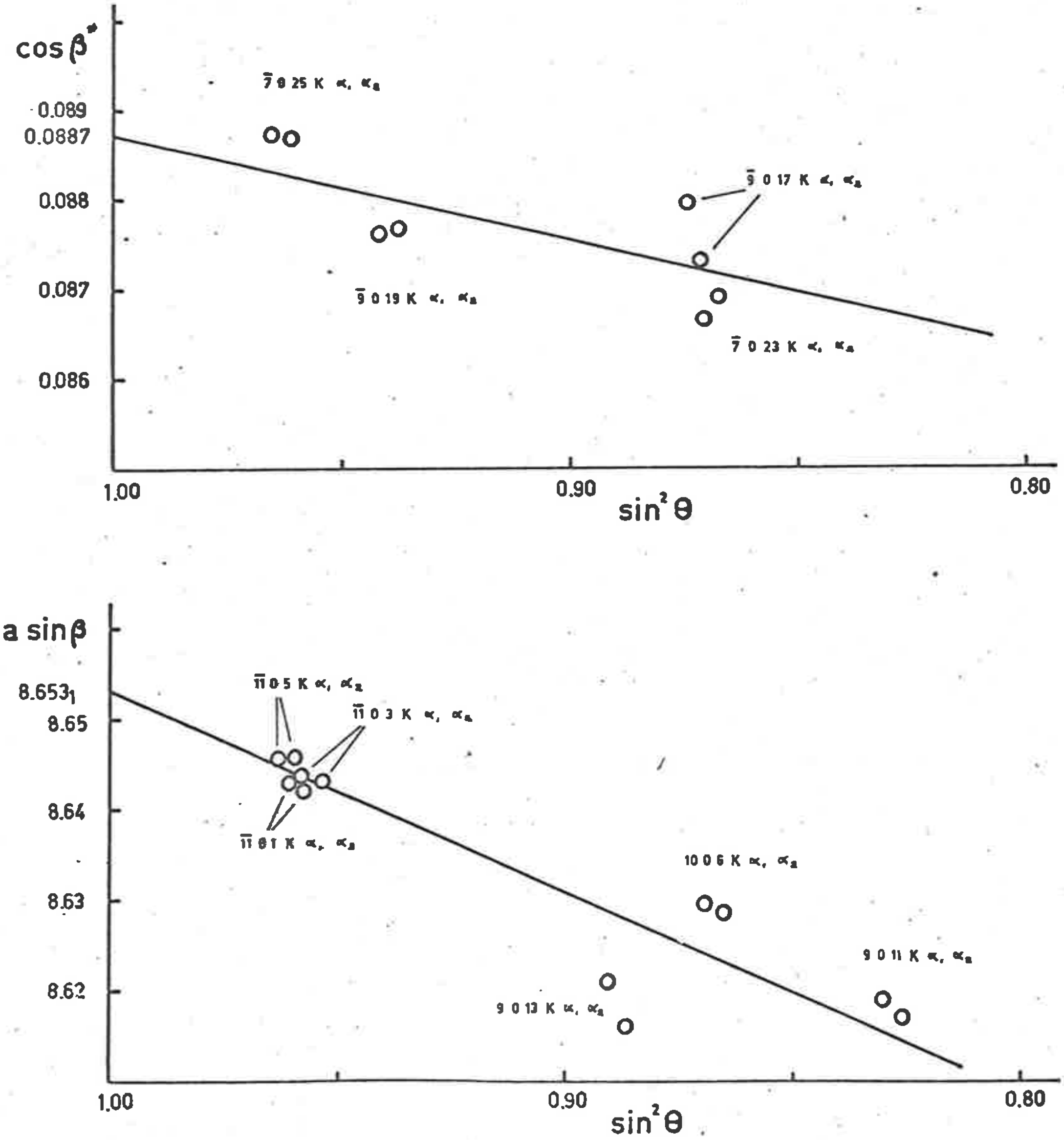


Fig. 17. Determination of unit cell parameters for B.Br.

TABLE 7.

Physical and crystallographic properties.

Space group $P2_1/n$

$a.\sin\beta = 8.6531 \pm .0036$ A*	$a = 8.687 \pm .004$ A
$b = 14.9945 \pm .0025$ A	$b = 14.995 \pm .003$ A
$c.\sin\beta = 23.6363 \pm .0027$ A	$c = 23.730 \pm .004$ A
$\cos\beta = - .08871 \pm .00044$	$\beta = 95^\circ\ 5.3' \pm 1.5'$
$\sin\beta = .996058 \pm .000040$	

Unit cell volume : 3079 A^3

Observed density (by flotation) : 1.652 gm/cm^3

Calc. density (8 molecules/unit cell) : 1.652 gm/cm^3

Absorption coefficient : 39.8 $cm.^{-1}$

---

* The uncertainties given equal the calculated standard deviations.

3.5 Collection of intensity data.

3.5.1 Selection of crystals.

Since the crystals were generally well formed and could be reduced to a suitable size by cleavage, the selection of a crystal to rotate about the a axis and another for b axis rotation was not difficult. The specimens chosen measured 1.0 x 0.13 x 0.13 mm and 0.13 x 0.6 x 0.13 mm respectively. This implies rather severe absorption, the maximum and minimum for transmitted radiation being 51% and 41% for radiation incident normal to the respective axes of rotation; however it was thought that since the crystals were approximately uniform in cross section the absorption would vary uniformly with $\sin\theta$ and therefore perhaps influence the thermal parameters but not those of atomic position, (e.g. see Lipson and Cochran, 1957, p.286).

3.5.2 Measurement of intensities.

Each layer of reflections was recorded without integration on a pack of four films, the exposure time being about 75 hours. To reduce the strongest reflections to a measurable density a second film pack was exposed for about 2 hours.

Intensities were recorded for the layers 0kl through 7kl, and h0l through h4l, and were measured by the method of eye estimation. Within the limiting sphere for copper radiation there were about 8,300 independent reflections; about 7,100 of these reflections were recorded and of these 72% observed to have a non-zero intensity.

3.5.3 Geometrical Factors.

Since the recorded intensities had not been integrated it was desirable to make a correction for the extension and contraction of the higher layer reflections characteristic of Weissenberg photographs (e.g. see Buerger, 1958, p.227). Phillips (1954) has given an expression for the modified length L' of a recorded reflection of the form

$$L' = L(1 + dW) \tag{3.1}$$

and recommends that this be applied only to the extended spots (i.e. where dW is always positive).

When recording intensities by rotating the crystal about the a axis it would have been necessary to oscillate the crystal through 270° to record all the (hkl) and $(hk\bar{l})$ spectra as extended spots on the one film, but this was impossible because 210° rotation was the maximum allowed by the Unicam camera. Rather than making separate exposures for the (hkl) and $(hk\bar{l})$ reflections it was decided to use one exposure only, the crystal being arranged so that oscillation through 180° would allow measurement of all the (hkl) spectra from one half of the film (i.e. the "extended" side), and all the $(hk\bar{l})$ spectra from the other half (i.e. the "contracted" side).

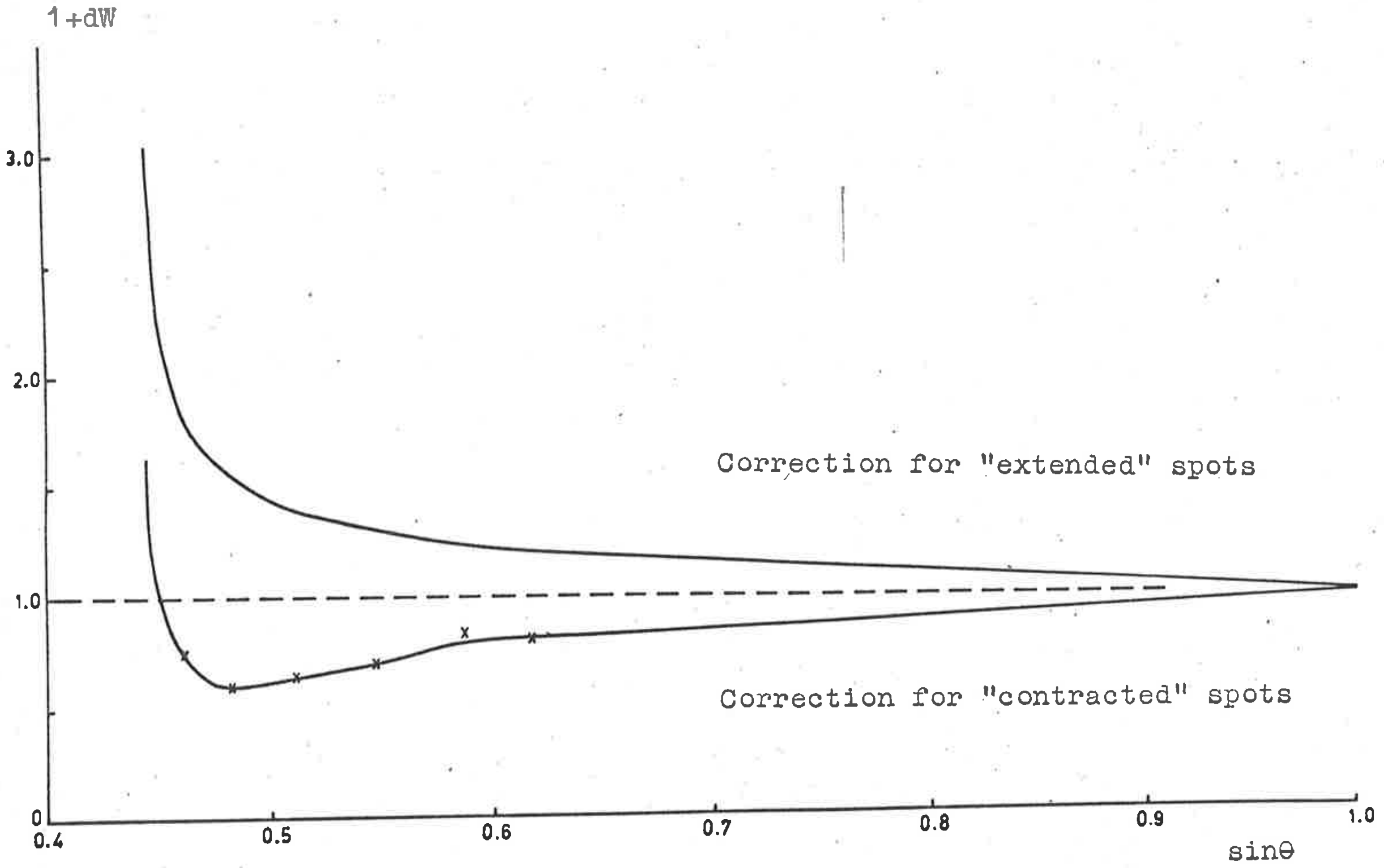


Fig. 18. Correction for spot shape : Layer 5kl.

x : measured values of (1 + dW)

The extended spots were corrected by using the analytical expression given by Phillips. For the contracted spots, with the exception of those near the centre of the film (i.e. of low sinθ), the fractional change in length (dW) is small; therefore the expression (3.1) will be essentially correct whether dW is positive or negative. For smaller values of sinθ, however, (3.1) may be grossly in error, especially for values of dW near -1. To overcome this uncertainty the lengths of a number of spots in this region of the film were measured, and by comparison with the length of equally intense spots near the edge of the film (i.e. with dW = 0) a semi-empirical correction curve built up. A typical curve used for correction of the 5kl intensities is shown in fig. 18. It may be noted that for reflections whose Bragg angles approach the minimum for the layer being considered (say 5kl) the correction becomes unreliable, however these reflections necessarily had a small value of k and therefore could be independently measured by using data obtained from the "b axis" crystal. Furthermore, since these reflections had a k index of 5, they occurred on the b axis photograph in a region where the spot extension correction was reliable.

After measuring the intensities and recording them on punched cards, the 1620 computer was used to evaluate the Phillips correction as described above along with the Lorentz and polarization factors; the modified intensities were then punched out on cards with the appropriate indices, $\sin\theta$ and $\sin^2\theta$ values.

3.5.4 Averaging and scaling.

By using all the intensities common to both a axis and b axis photographs, the individual layers of reflections were brought to a common scale.

For reflections recorded about the two axes, the final intensity was generally taken as the average of the two independent scaled values; there were, however, two exceptions to this rule. Firstly if a weak reflection was observed only on one film, its intensity was put equal to this one observed value. Secondly if a pair of measurements differed by more than the ratio 1.5 : 1, they were first checked for experimental and other errors (e.g. introduced by the spot shape correction) before a "best" value for the intensity was chosen. It was found that only about 5% of the reflections fell into this second category, and of these, only a few, all being weak, differed by more than 2 :1.

The multiplying factor necessary to put all the measured intensities on an absolute scale was found by the method of Wilson (1942) using about 3300 reflections from the layers 0kl through 3kl. The final plot which is shown in fig. 19 gave the value $2B = 7.0$ for the overall temperature exponent.

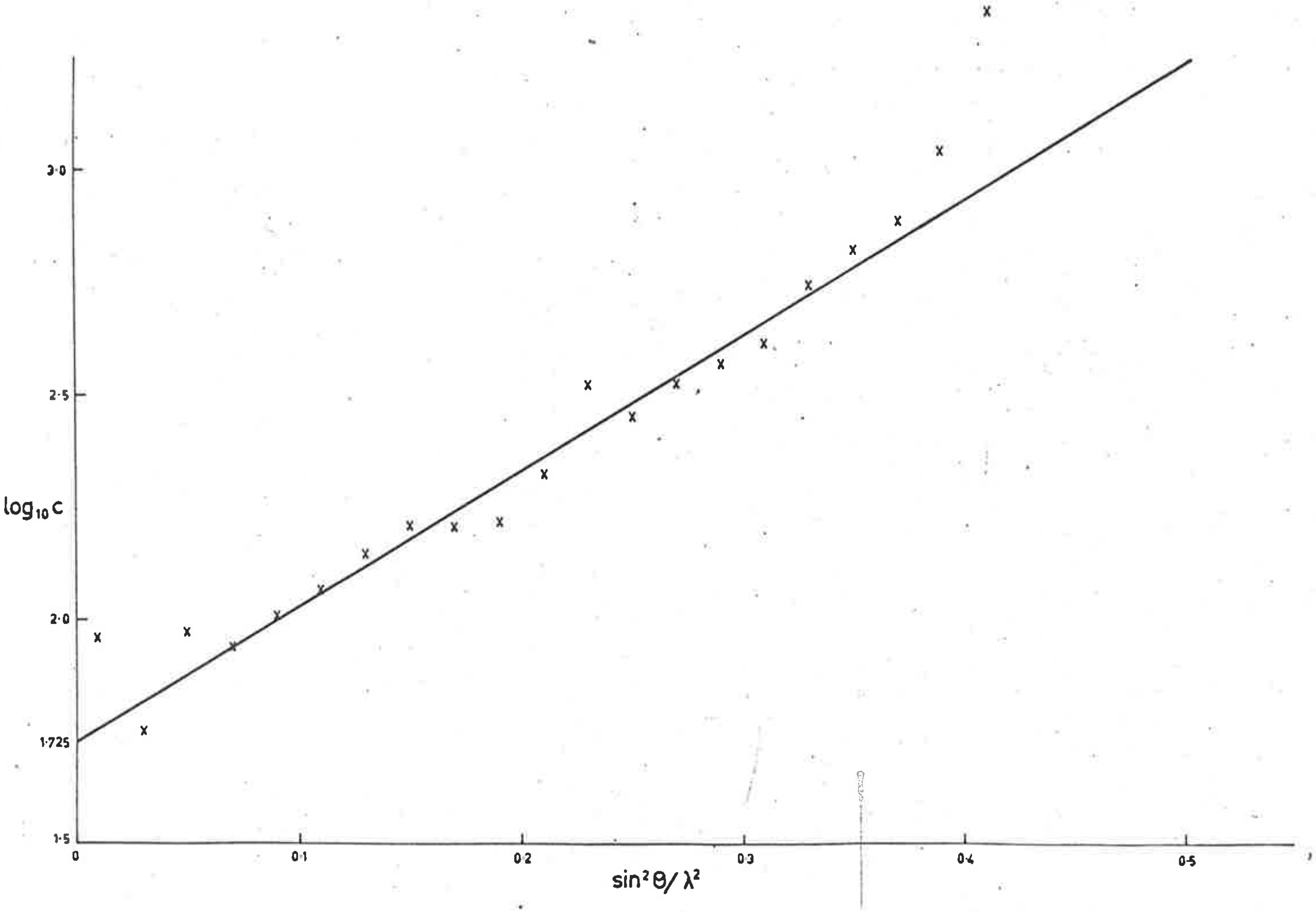


Fig. 19. Absolute scaling of B.Br data.

3.6 Determination of the heavy atom positions.

3.6.1 Introduction.

Although at this stage the full three dimensional Patterson function could have been calculated and used in an attempt to determine the coordinates of the two bromine atoms, it was realised that this computation would be a major one better avoided if a less tedious approach were possible.

Use of projections of the Patterson function was not seriously considered, firstly because a wide range of diffraction data was available, secondly because the author did not wish to repeat his experience described in Chapter 2; instead, attention was turned to the use of Harker sections.

3.6.2 Harker sections.

Shortly after the introduction of the Patterson function in 1935, Harker (1936) showed that certain symmetry operations result in useful information being concentrated on lines or planes of the three dimensional Patterson function. In particular in the space group $P2_1/n$, atoms related by the screw axis parallel to b will have vector interactions lying in the plane $y = \frac{1}{2}$; also atoms related by the n-glide plane normal to b will result in Patterson peaks lying on the line $x = \frac{1}{2}$, $z = \frac{1}{2}$.

If there is only one heavy atom (say Br_1) with fractional coordinates (x_1, y_1, z_1), then the Harker interactions between this atom and its symmetry related equivalents within the $P2_1/n$ unit cell occur at $(\frac{1}{2}-2x_1, \frac{1}{2}, \frac{1}{2}-2z_1)$ and $(\frac{1}{2}, \frac{1}{2}-2y_1, \frac{1}{2})$. Following the discussion of 2.5.3, the product $4Z_h.Z_h$ gives a measure of the height of both these Patterson peaks (Z_h being the number of electrons associated with the heavy atom). It is apparent that a knowledge of the two Harker peaks mentioned above would determine the heavy atom position without ambiguity.

If we now consider a second heavy atom (say Br_2) with coordinates (x_2, y_2, z_2), then as before Harker peaks of height $4Z_h.Z_h$ will be generated at $(\frac{1}{2}-2x_2, \frac{1}{2}, \frac{1}{2}-2z_2)$ and $(\frac{1}{2}, \frac{1}{2}-2y_2, \frac{1}{2})$. Now, however, there are two ambiguities which arise in the determination of the heavy atom coordinates. Firstly there is no direct method of correlating the pair of peaks in the plane $y = \frac{1}{2}$ with the pair of peaks on the line $x = \frac{1}{2}$, $z = \frac{1}{2}$; a wrong correlation would lead to heavy atom coordinates of the form (x_1, y_2, z_1) and (x_2, y_1, z_2). Secondly, for each Harker peak at $(\frac{1}{2}-2x_1, \frac{1}{2}, \frac{1}{2}-2z_1)$, there is another peak in the adjacent cell at $(1\frac{1}{2}-2x_1, \frac{1}{2}, \frac{1}{2}-2z_1)$; thus, the heavy atom can be placed at either (x_1, y_1, z_1) or $(x_1+\frac{1}{2}, y_1, z_1)$. This alternative is not important for the case of one heavy atom since it corresponds merely to a choice of origin; for two atoms, having placed Br_1 at say (x_1, y_1, z_1), the origin is fixed, and therefore Br_2 has the alternative coordinates (x_2, y_2, z_2) or $(x_2+\frac{1}{2}, y_2, z_2)$.

One approach to this problem might have been to compare the observed structure factors with those calculated for all the possible heavy atom positions. It was felt that this method was most unsatisfactory, and, instead, the ambiguities were resolved by using general line sections as described in the next section.

Before any Patterson sections were calculated, the coefficients (i.e. the observed intensities) were modified by the function suggested by Shoemaker et. al. (1953) and designed to "sharpen" the Patterson peaks but at the same time supress ripples in the Patterson density due to series termination effects. The modification used was of the form

$$I_o^* = I_o . M(\sin\theta) \qquad (3.2)$$

where I_o is the observed intensity and

$$M(\sin\theta) = C.\left(\frac{\sin^2\theta}{\lambda^2}\right)^2\left(\frac{1}{f_o^2}\right)\exp\{(2B-19.4)\frac{\sin^2\theta}{\lambda^2}\} \qquad (3.3)$$

where f_o $(=f_o(\sin\theta))$ is the scattering factor for oxygen. The temperature exponent 2B was equated to 7.0 as determined statistically. For the constant C equal to 1060, $M(\sin\theta)$ equals zero at $\sin\theta = 0$, rises to a maximum of 1.0 at $\sin\theta = 0.79$ and then falls to 0.48 at $\sin\theta = 1.0$.

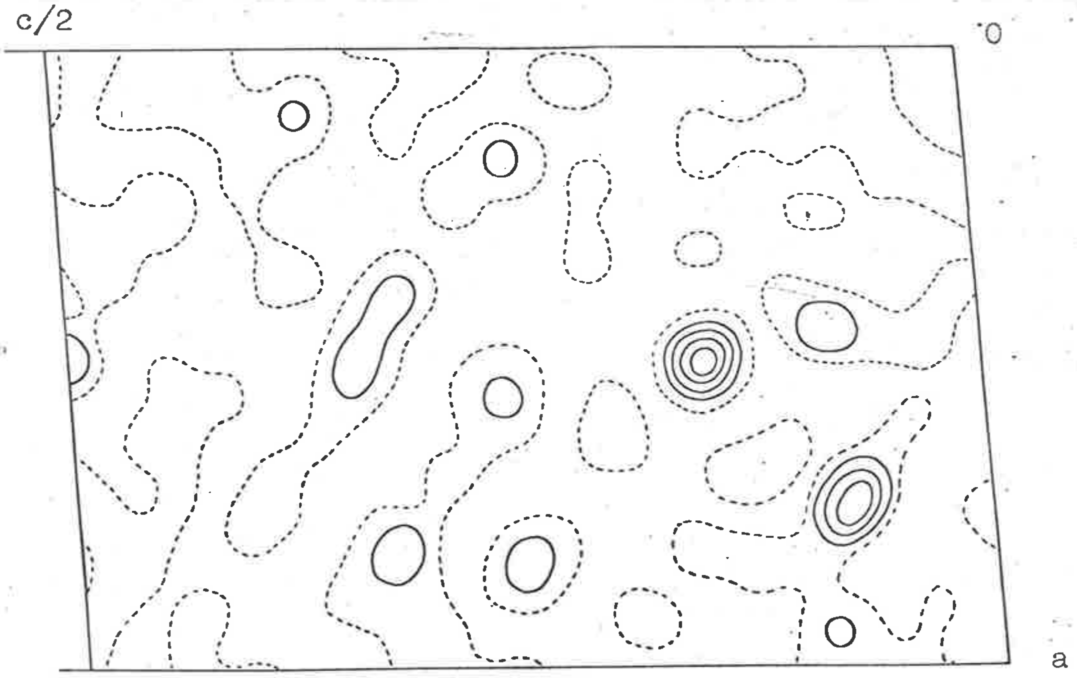


Fig. 20. Harker section $P(x,\frac{1}{2},z)$.

Zero contour dashed.

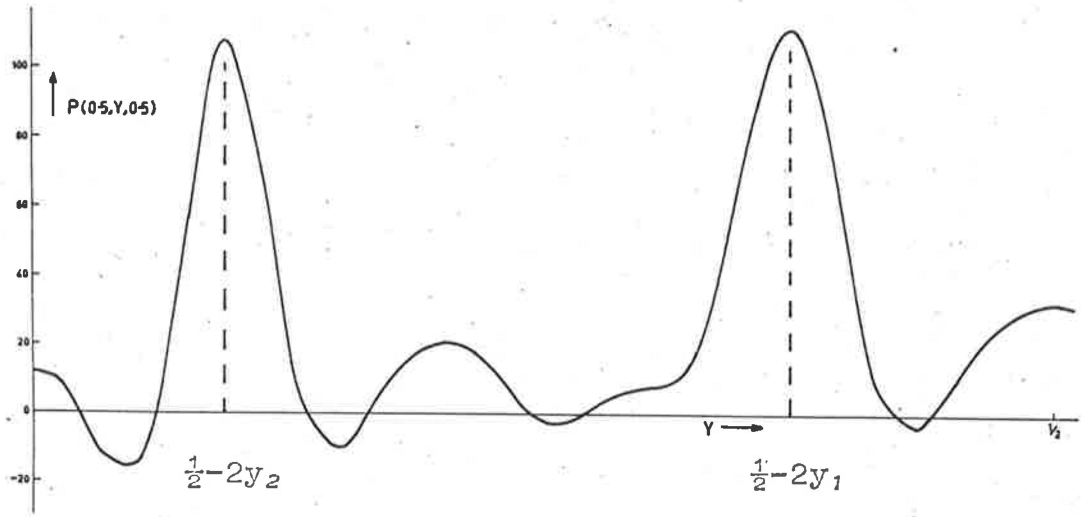
Contours at arbitrary equal intervals.

3.6.3 General Patterson line sections.

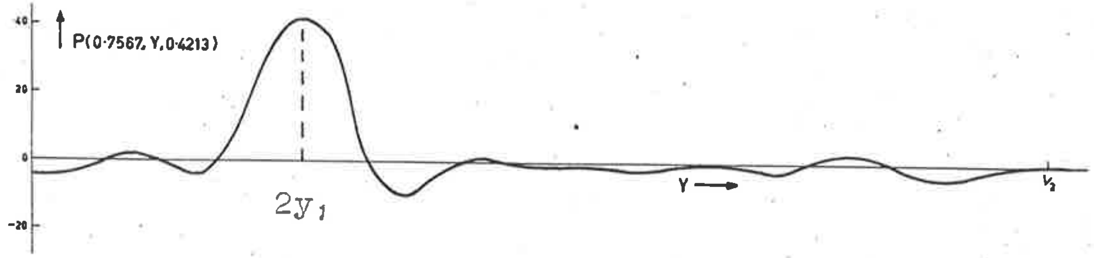
It has been mentioned that heavy atoms at (x_1, y_1, z_1) and equivalent positions in the $P2_1/n$ cell generate Patterson peaks of height $4Z_h.Z_h$ at the special positions ($\frac{1}{2}-2x_1$, $\frac{1}{2}$, $\frac{1}{2}-2z_1$) and ($\frac{1}{2}$, $\frac{1}{2}-2y_1$, $\frac{1}{2}$); in addition, another peak of height $2Z_h.Z_h$ is generated at the general position ($2x_1$, $2y_1$, $2z_1$). Hence if x_1 and z_1, the (x, z) coordinates of a heavy atom, are determined from the Harker section P(x, $\frac{1}{2}$, z), then the value of y_1 can be found by a line section P($2x_1$, y, $2z_1$) through the Patterson function parallel to the b axis. If the heavy-atom peak on this line has y coordinate $2y_1$, then there should be another peak of twice the height occurring at $y = \frac{1}{2}-2y_1$, on the Harker line P($\frac{1}{2}$, y, $\frac{1}{2}$). The first ambiguity mentioned before is thus removed.

The P(x, $\frac{1}{2}$, z) Harker section for B.Br was calculated using the IBM 1620 and is shown in fig. 20: the two Br-Br interactions can readily be seen. From this section the "Br_1-Br_1" and "Br_2-Br_2" vector interactions were found to be at (0.7567, $\frac{1}{2}$, 0.4213) and (0.9903, $\frac{1}{2}$, 0.3500) respectively.

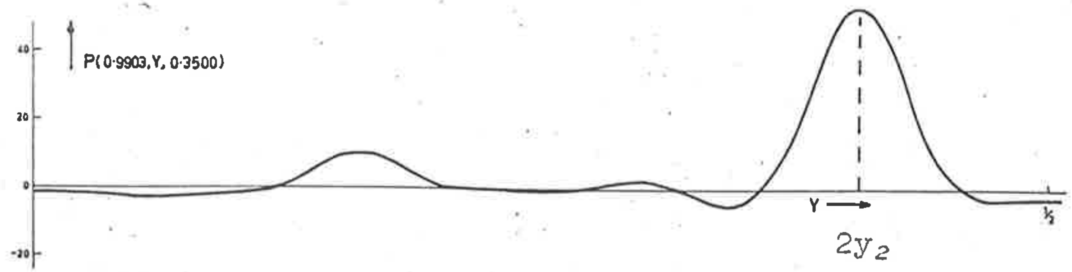
The two Patterson line sections corresponding to these (x, y) values were next calculated on the 1620 computer and are shown in figs. 21b and 21c, along with the Harker line section P($\frac{1}{2}$, y, $\frac{1}{2}$) in fig. 21a. The correlation between


P(0·5,Y,0·5)
100
80
60
40
20
0
-20
$\frac{1}{2}-2y_2$
$\frac{1}{2}-2y_1$
Y →
½

21a


P(0·7567,Y,0·4213)
40
20
0
-20
$2y_1$
Y →
½

21b


P(0·9903,Y,0·3500)
40
20
0
-20
Y →
$2y_2$
½

21c

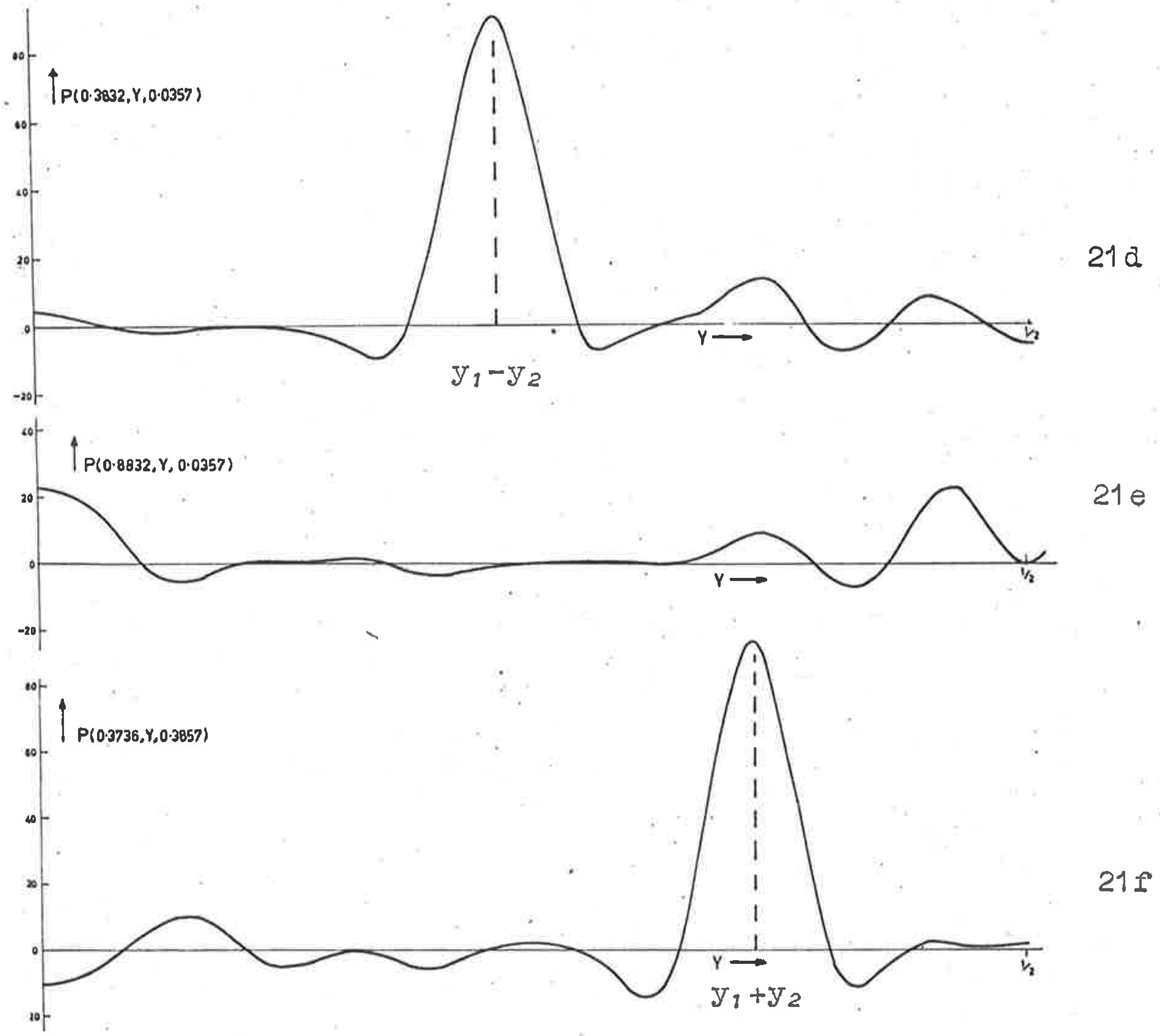


Fig. 21. Patterson line sections

these sections, both with respect to peak height and agreement of the $2y_i$ and $\frac{1}{2}-2y_i$ values can be seen to be very good. (The values of y_1 and y_2 used to determine the position of the vertical lines are those quoted at the end of this section.)

At this stage it was possible to fix the Br_2 coordinates unequivocally as $Br_2(.495, .202, .175)$. However there were still several alternatives for the Br_1 coordinates such as $(.378, \pm .065, .211)$, $(.378+\frac{1}{2}, \pm .065, .211)$ and $(.378, \pm .065+\frac{1}{2}, .211)$.

These alternatives can be resolved by considering vector interactions of the type $Br_1 - Br_2$ which generate Patterson peaks of height $4Z_h.Z_h$ at the positions $(x_1 + x_2, y_1+y_2, z_1+z_2)$ and $(x_1-x_2, y_1-y_2, z_1-z_2)$. We have considered x_2, y_2 and z_2 as fixed; we now also consider z_1 as fixed and evaluate the two Patterson line section $P(x_1-x_2, y, z_1-z_2)$ and $P(x_1-x_2+\frac{1}{2}, y, z_1-z_2)$. One of these should show a heavy atom - heavy atom peak of weight $4Z_h.Z_h$ corresponding to the correct choice of x_1, the other line section should show no such peak. Having thus fixed (x_1, z_1) and (x_2, z_2), the section $P(x_1+x_2, y, z_1+z_2)$ can also be computed both as a final check and also to enable an independent determination of y_1 and y_2. These three line sections calculated for B.Br are shown in figs. 21d, 21e and 21f; once again the verification of the heavy atom positions is quite striking.

The bromine coordinates obtained from Harker and line sections are shown below along with those obtained after final refinement.

		x	y	z
Br_1	Initial	.8784	.4347	.2107
	Final	.8792	.4362	.2111
Br_2	Initial	.4952	.2032	.1750
	Final	.4957	.2031	.1750

3.7 Determination of the light atom positions.

3.7.1 Structure factors.

Before the contribution of the bromine atoms was evaluated the general structure factor expression (2.17) was reduced to the appropriate forms for space group $P2_1/n$. These were found to be identical with (2.18) with the conditions "for h+k even" and "for h+k odd" being replaced by "for h+k+l even" and "for h+k+l odd" respectively.

The reliability index Ra as defined in 2.6.3 was 57% for structure factors calculated from the two bromine atoms.

3.7.2 Fourier syntheses.

As the structure factor expressions for the space group $P2_1/a$ and $P2_1/n$ were found to be closely related, so the expression for the electron density for the space group $P2_1/n$ was found to be identical with (2.22) with the summations over terms with h+k even and odd being replaced by summations over terms with h+k+l even and odd.

For B.Br the ratio of the sum of squares of the atomic numbers of the heavy atoms to that of the light atoms (i.e. $\Sigma(Z_h)^2/\Sigma(Z_l)^2$) was 1.26. Lipson and Cochran (1957, p.207) suggest that a ratio equal to unity is an optimum one for successful use of the "heavy atom" method; also Sim (1960) shows that about 82% of the observed structure amplitudes will be given the correct sign if the signs are taken equal to those of the heavy atom contribution. Although it was therefore reasonable to expect that a "heavy atom" Fourier syntheses based in the usual way (i.e. without weighting) on the signs of the structure factors of the two bromine atoms would lead to the remainder of the structure, it was nevertheless still considered that weighting of each coefficient as in 2.7.2 would help to ensure a correct interpretation of the "heavy atom" synthesis.

Before the Fourier synthesis for B.Br was evaluated, the calculated bromine structure factors (F_h) were subtracted from the observed structure amplitudes (F_o). The resultant electron density is therefore similar to the difference electron density ($\rho_o - \rho_c$) except that the calculated electron density being subtracted is here the density of the heavy atoms only. Woolfson (1956) has shown that in practice this procedure has some superiority in revealing the light atom positions, presumably because it excludes the heavy atoms and the diffraction ripples associated with them. The final expression, analogous to (2.23), for the weighted Fourier coefficients is

$$F(\text{weighted}) = S_h\left[|F_o| . \tanh\left(\frac{|F_oF_h|}{\sum_j (f_j)^2}\right) - |F_h|\right] \qquad (3.4)$$

where S_h is the sign of F_h and the summation over j implies summation over all atoms in the unit cell with the exception of the bromine atoms.

The Fourier synthesis was evaluated, using the 1620 computer, at intervals of about 0.25A in each of the a, b and c directions; this was achieved by using cell divisions of a/36, b/60 and c/96. Total time to sum over the 7100 F's at 56,000 grid points was 28 hours. The program used in this summation was written in three separate sections, each making full use of the symmetry properties of the odd and even cosine and sine functions; a description is included in Appendix 3.

After printing out the final results, a careful inspection revealed that there were nearly fifty prominent density peaks. These peaks were represented by supporting appropriately coloured corks on thin wire stretched parallel to one of the cell axes; Plate 2. shows the completed model. (Although this method is similar to that described by Wood et. al. (1961), it is much cheaper to use because the corks support themselves and it is not necessary to use the specially drilled balls to represent the individual atoms.)

From this model the molecular structure was immediately apparent; the two independent molecules appeared to be very similar and the system of inter-molecular hydrogen bonding could also be seen.

As a final confirmation of the general correctness of the structure (which was unexpected on chemical evidence at this stage) the structure factors were calculated and gave the reliability indices Ra = 33% and R = 28%.

Once again the weighting scheme of Woolfson proved most successful, for, except in the immediate vicinity of

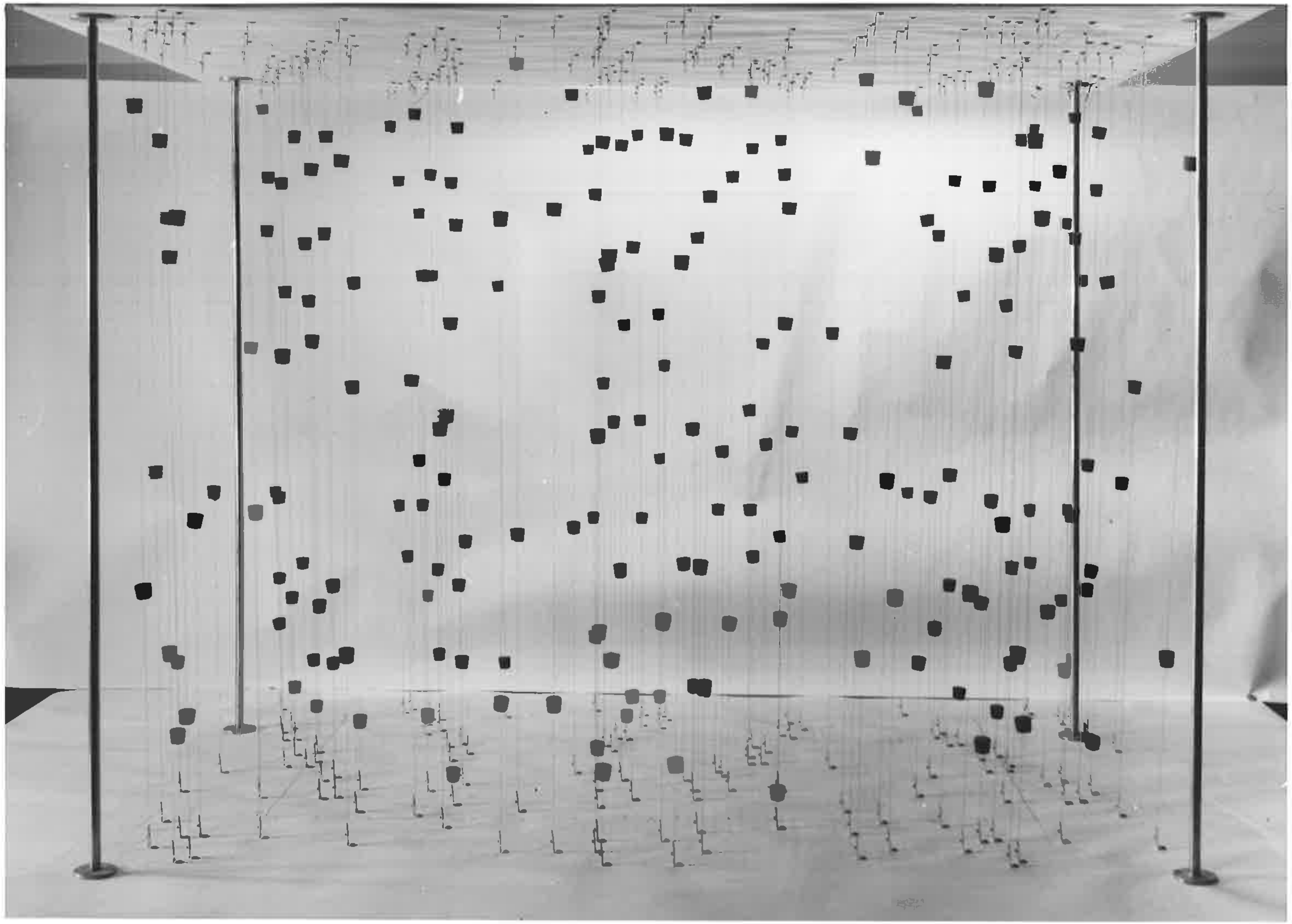


PLATE 2. MODEL OF THE BBr. CRYSTAL STRUCTURE

the bromine positions, the background density only occasionally approached, and nowhere exceeded, the value of 3.6 e/A^3, this being the lowest peak electron density corresponding to a real atom.

To improve the atomic coordinates as known at this stage a second three dimensional Fourier synthesis was calculated using the IBM 1620. In this synthesis the coefficients were not weighted; also the calculated contribution of the bromine atoms was not subtracted from the observed structure amplitudes as done in (3.4). After this synthesis, all the intermolecular bond lengths were compatible with the proposed structure and the residual had been reduced to R = 21%. This synthesis was also used to determine for each atom the parameters A and p of the approximation (4.17); a knowledge of these was necessary for subsequent refinement of the crystal structure.

Fig. 22 illustrates the spatial arrangement of the two molecules comprising the asymmetric unit and also gives the atom numbering which will be used in subsequent discussion.

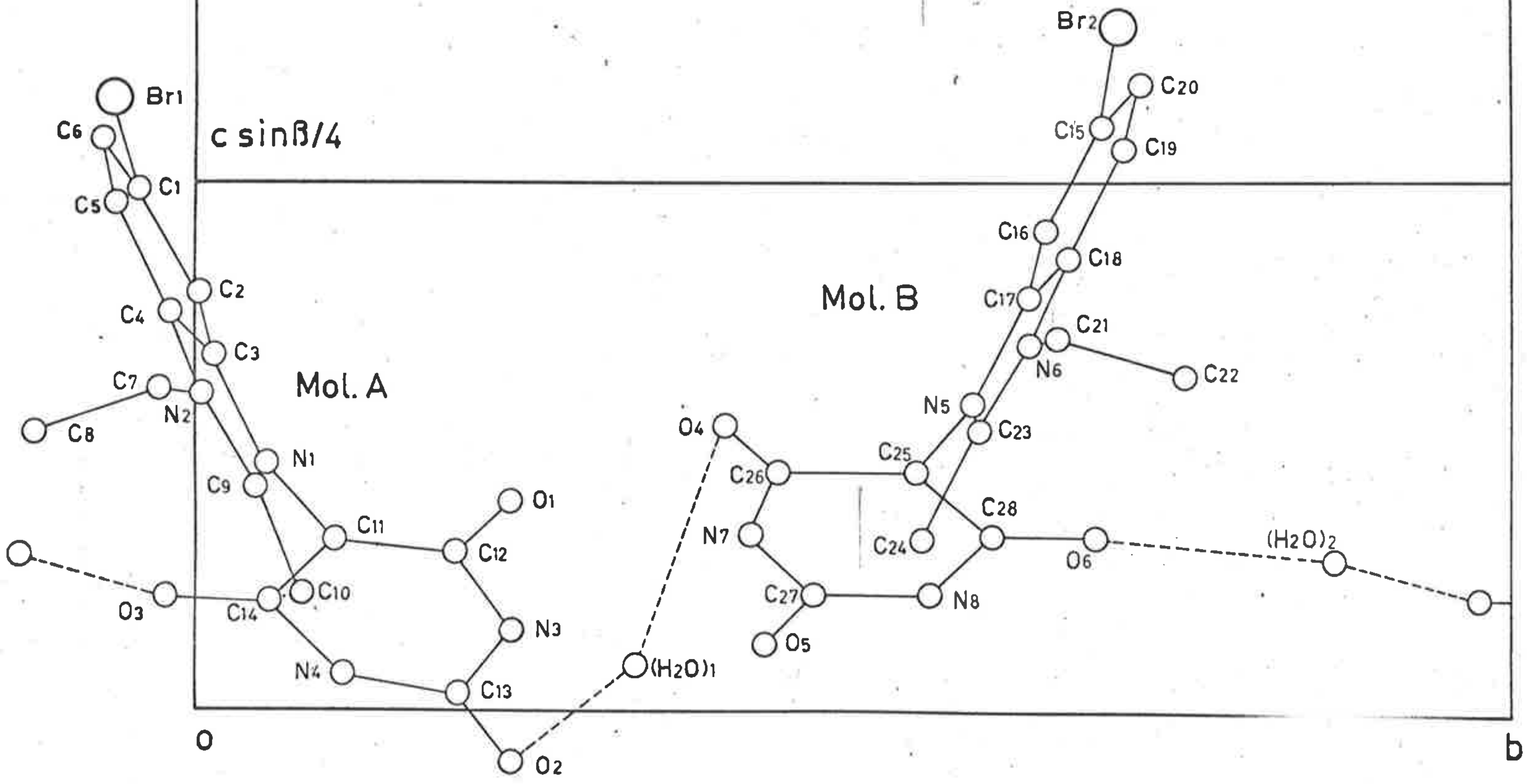

Br1
C6
c sinβ/4
C1
C5
C2
C4
C3
C7
N2
C8
Mol. A
N1
C9
C11
O1
C12
C10
O3
C14
N3
N4
C13
O2
0
(H2O)1
Br2
C20
C15
C19
C16
C18
Mol. B
C17
C21
N6
C22
N5
O4
C23
C25
C26
C28
N7
C24
(H2O)2
O6
C27
N8
O5
b

Fig. 22.

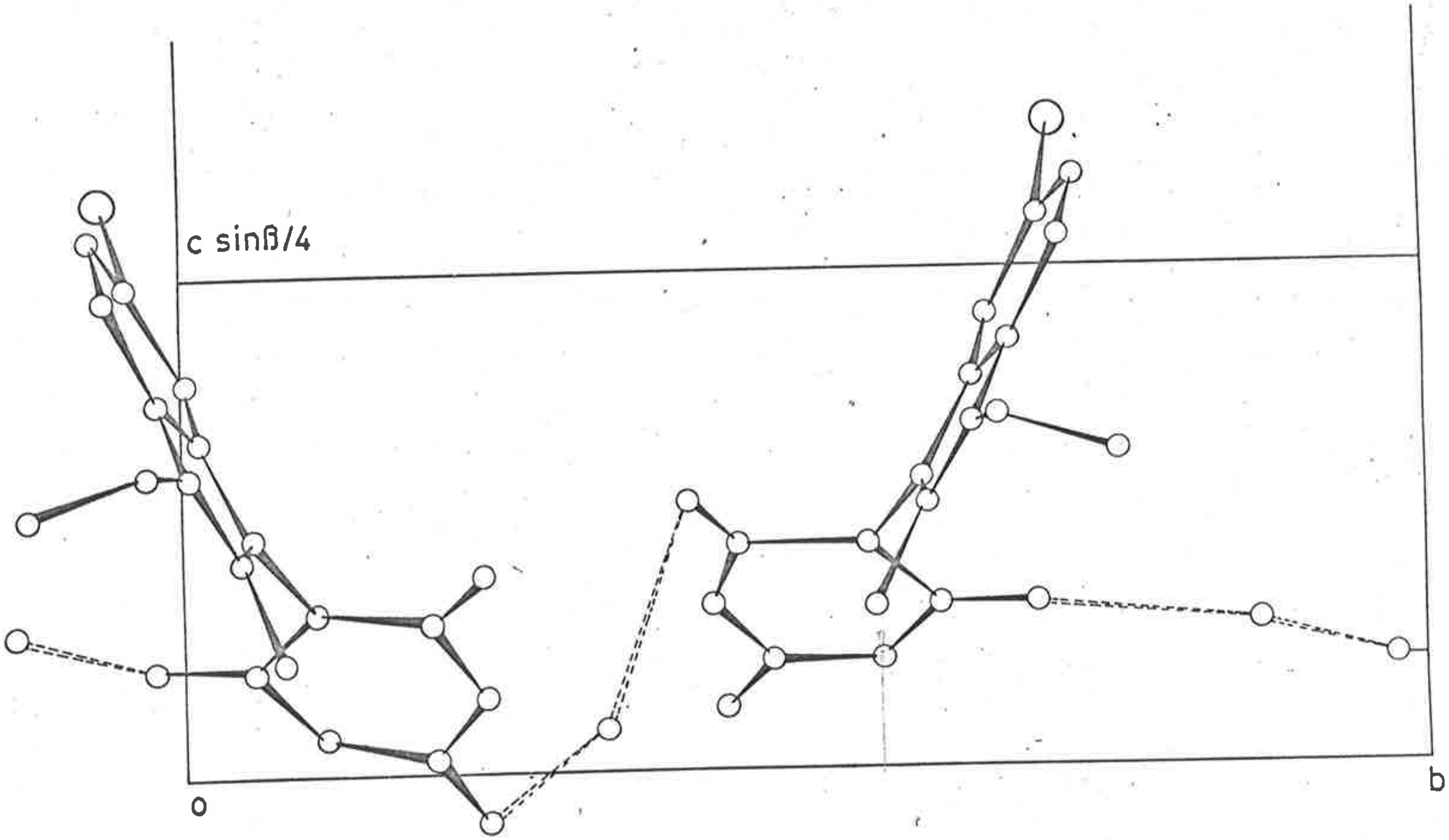


Fig. 22. Spatial arrangement of the B.Br molecules.

3.8 Refinement.

3.8.1 Initial refinement.

Since the observed intensities had probable errors due to absorption, it was decided to use isotropic temperature factors for all subsequent refinement. (The possibility of errors in the thermal parameters due to neglecting absorption was discussed in section 3.5.1.) The necessary theory of the refinement which was by "differential difference" Fourier syntheses is described fully in Chapter 4. In modifying the IBM 7090 structure refinement program which was used for the structure described in Chapter 2, the large number of F's made it necessary to use magnetic tapes to store the observed and calculated structure factors; the program in the form finally used is described in Appendix 3. In all refinement of this crystal structure the coefficients (F_o-F_c) were weighted using the scheme described in 4.3.5; unobserved reflections were treated as described in 4.3.6.

During the initial two cycles of refinement R was reduced to 18.3%. Generally the overall coordinate shifts were not large, averaging about 0.01 A; the greatest shift was 0.09A for C_6, an atom close to a bromine atom.

At this stage all the F_c's were computed (using the 7090) and printed out with the corresponding values of F_o and F_o-F_c. An inspection of these results revealed that there were very few obvious errors in the F_o's.

3.8.2 Extinction.

Using the values of F_o and F_c calculated above, a plot was made as in 2.8.2 to determine the correction for secondary extinction. The value obtained for 2g was 2.8×10^{-6} and this was used to modify the 14 reflections observed to have $F_o > 200$. (The correction for less intense reflections was not significant.)

3.8.3 Final refinement.

Three further cycles of refinement were calculated using the 7090. During these, the maximum shift fell from 0.027A to 0.013A; this shift was for C_1 (adjacent to Br_1) and just exceeded the corresponding coordinate standard deviation of 0.011A. Mean shifts for the x, y and z co-ordinates were 0.0044A, 0.0016A and 0.0026A respectively. The residual R, for spectra included in this refinement, fell from 17.0% to 15.3%; R for all observed reflections was 17.3% (the increase being due to inclusion of the less reliable F_o's near $\sin\theta = 1$).

Instead of giving a detailed list of the 6470 final (non zero) values of F_o and F_c, a summary was made of the relative and absolute values of the differences $\Delta F = ||F_o|-|F_c||$. The 4804 experimentally observed reflections were categorised, firstly according to the value of ΔF, and secondly according to the value of the ratio $r = \frac{\Delta F}{\frac{1}{2}(|F_o|+|F_c|)}$

The results are as follows:

	$0 \leqq r < 0.2$	$0.2 \leqq r < 0.4$	$0.4 \leqq r < 0.6$	$0.6 \leqq r$
$\Delta F < 10$	2508	1009	373	379
$10 \leqq \Delta F < 20$	72	176	88	145
$20 \leqq \Delta F < 30$	9	13	9	12
$30 \leqq \Delta F < 46$	3	4	1	3

(The maximum value of F_o is 356)

The remaining 1666 theoretically observable reflections are summarised as follows:

$\lvert F_c \rvert \leqq 10$	$10 < \lvert F_c \rvert \leqq 20$	$20 < \lvert F_c \rvert < 22$
1496	168	2

(At L.p = 1, the minimum observable value of F_o is 9.0.)

It may be noted that Hanson and Ahmed (1958) use similar categories to summarise the agreement of F_o and F_c, however their final results are more abbreviated than those given above.

The final coordinates with their standard deviations are listed in Table 8 which also gives the final values of the thermal parameters.

Table 8. Final atomic parameters with positional standard deviations.

Atom	x/a	y/b	z/c	$\sigma(x)$ (A)	B (A^2)
Br_1	.6208	-.0638	.2889	.0013	4.7
Br_2	.0043	.7030	.3250	.0012	4.2
O_1	.9362	.2387	.1003	.008	3.9
O_2	.5077	.2414	-.0247	.007	3.6
O_3	.6589	-.0234	.0542	.006	3.1
O_4	.2407	.4049	.1350	.007	3.8
O_5	-.2229	.4318	.0320	.006	3.7
O_6	.0425	.6866	.0811	.008	4.1
$(H_2O)_1$	.2745	.3335	.0215	.013	7.2
$(H_2O)_2$	-.0475	.8657	.0727	.008	4.9
N_1	.9207	.0545	.1164	.007	2.4
N_2	1.1485	.0031	.1499	.007	3.2
N_3	.7204	.2393	.0389	.007	2.9
N_4	.5846	.1104	.0159	.007	2.9
N_5	.2730	.5930	.1438	.007	2.6
N_6	.5065	.6393	.1729	.007	2.9
N_7	.0081	.4210	.0829	.007	2.7
N_8	-.0889	.5590	.0544	.007	3.1
C_1	.7919	-.0408	.2470	.011	3.2
C_2	.7698	.0015	.1960	.008	2.7

Table 8. (cont.)

Atom	x/a	y/b	z/c	$\sigma(x)$ (Å)	B (Å^2)
C_3	.9033	.0141	.1679	.008	2.2
C_4	1.0404	−.0184	.1885	.008	2.9
C_5	1.0653	−.0613	.2404	.010	3.6
C_6	.9366	−.0722	.2691	.010	4.7
C_7	1.3041	−.0295	.1534	.013	4.6
C_8	1.3158	−.1246	.1337	.016	5.7
C_9	1.0679	.0453	.1062	.009	3.2
C_{10}	1.1378	.0784	.0557	.011	4.3
C_{11}	.8077	.1033	.0807	.008	2.7
C_{12}	.8276	.1958	.0755	.008	2.5
C_{13}	.6019	.1997	.0088	.008	2.9
C_{14}	.6857	.0564	.0518	.008	2.3
C_{15}	.1682	.6883	.2776	.009	2.9
C_{16}	.1344	.6461	.2263	.008	2.8
C_{17}	.2678	.6358	.1951	.008	2.4
C_{18}	.4129	.6651	.2137	.008	2.7
C_{19}	.4433	.7068	.2665	.010	3.3
C_{20}	.3133	.7209	.2969	.010	3.4
C_{21}	.6745	.6578	.1764	.010	3.7
C_{22}	.7083	.7513	.1583	.013	5.0
C_{23}	.4258	.5958	.1302	.008	2.8

Table 8. (Cont.)

Atom	x/a	y/b	z/c	$\sigma(x)$ (A)	B (A^2)
C_{24}	.4758	.5552	.0797	.009	3.6
C_{25}	.1487	.5502	.1113	.009	2.5
C_{26}	.1433	.4577	.1121	.008	2.3
C_{27}	-.1063	.4688	.0550	.007	2.5
C_{28}	.0386	.6059	.0823	.008	2.9

3.9 Accuracy.

3.9.1 Standard deviation of coordinates.

As in Chapter 2, use was made of Cruickshank's formula (2.31), however in this case the peak curvatures were evaluated by using (4.19). Standard deviations of the x, y and z coordinates were found to be approximately equal and the quoted deviations are the average of these three.

3.9.2 Standard deviation of bond lengths and angles.

Equality of the s.d.'s for x, y and z result in simpler expressions for the s.d.'s in bond lengths and angles. For bond angles, (2.33) was used with $\sigma(x_1) = \sigma(x_2) = \sigma(x_3)$; for a bond between atoms n and m, (2.32) reduces to

$$\sigma(d_{nm}) = \{ \sigma^2(x_n) + \sigma^2(x_m) \}^{\frac{1}{2}} \tag{3.5}$$

3.10 Discussion of the structure.

3.10.1 Introduction.

In subsequent discussion it will be necessary to refer to specific portions of a particular B.Br molecule; therefore "Molecule A" and "Molecule B" will refer to the two independent molecules as shown in fig. 22. An "imidazole" ring will refer to the five membered ring which has two carbon atoms in common with the benzene ring; the combined double ring will be called a "benzimidazole" system. The remaining six membered ring will be named a "barbituric acid" ring.

3.10.2 The molecular structure.

A summary of the dimensions of the two molecules is given in Tables 9 and 10; these are illustrated diagrammatically in figs. 23 and 24. Generally the two molecules are similar, with the greatest differences being in the vicinity of the imidazole rings. In three cases the individual molecules differ significantly from the "average" molecule. Firstly for the N_1-C_9 (and N_5-C_{23}) bonds the difference is "significant"; secondly for the C_4-N_2-C_9 (and C_{18}-N_6-C_{23}) angles the difference is "possibly significant", and thirdly there is also a "possibly significant" difference for the N_2-C_9-C_{10} (and N_6-C_{23}-C_{24}) angles. (The levels of significance are those suggested by Cruickshank

Table 9. Final bond lengths.

Corresponding bonds from the two molecules are listed side by side.

Bond	Length (A)	σ(l) (A)	Bond	Length (A)	σ(l) (A)
C1 - C2	1.365	.014	C15-C16	1.380	.012
C2 - C3	1.401	.011	C16-C17	1.438	.011
C3 - C4	1.339	.011	C17-C18	1.370	.011
C4 - C5	1.389	.013	C18-C19	1.404	.013
C5 - C6	1.370	.014	C19-C20	1.409	.014
C6 - C1	1.400	.015	C20-C15	1.391	.013
C7 - C8	1.507	.021	C21-C22	1.503	.016
C9 -C10	1.477	.014	C23-C24	1.445	.012
C11-C12	1.405	.011	C25-C26	1.388	.012
C11-C14	1.400	.011	C25-C28	1.403	.012
N1 - C3	1.384	.011	N5 -C17	1.380	.011
N1 - C9	1.330	.011	N5 -C23	1.394	.011
N1 -C11	1.438	.011	N5 -C25	1.423	.011
N2 - C4	1.406	.011	N6 -C18	1.374	.011
N2 - C9	1.355	.011	N6 -C23	1.348	.011
N2 - C7	1.433	.015	N6 -C21	1.481	.012
N3 -C12	1.380	.011	N7 -C26	1.421	.011
N3 -C13	1.339	.011	N7 -C27	1.350	.010
N4 -C13	1.360	.011	N8 -C27	1.361	.010

Table 9. (cont.)

Bond	Length (A)	σ(l) (A)	Bond	Length (A)	σ(l) (A)
N4 -C14	1.421	.011	N8 -C28	1.425	.011
O1 -C12	1.246	.011	O4 -C26	1.248	.011
O2 -C13	1.256	.011	O5 -C27	1.238	.010
O3 -C14	1.221	.010	O6 -C28	1.211	.011
Br1-C1	1.892	.011	Br2-C15	1.904	.009

Table 10. Final bond angles.

Corresponding bond angles from the two molecules are listed side by side.

Atoms	Angle	σ(θ)	Atoms	Angle	σ(θ)
C1 -C2 -C3	115.3°	1.4°	C15-C16-C17	112.6°	1.3°
C2 -C3 -C4	121.6	1.3	C16-C17-C18	124.0	1.3
C3 -C4 -C5	123.7	1.4	C17-C18-C19	121.6	1.4
C4 -C5 -C6	115.2	1.5	C18-C19-C20	115.3	1.5
C5 -C6 -C1	121.2	1.6	C19-C20-C15	121.5	1.6
C6 -C1 -C2	122.6	1.7	C20-C1 -C2	124.5	1.5
C4 -C3 -N1	108.5	1.2	C18-C17-N5	109.4	1.2
C3 -N1 -C9	107.3	1.2	C17-N5 -C23	107.2	1.1
N1 -C9 -N2	110.4	1.3	N5 -C23-N6	106.4	1.2
C9 -N2 -C4	106.0	1.2	C23-N6 -C18	111.4	1.2
N2 -C4 -C3	107.6	1.2	N6 -C18-C17	105.5	1.2
C11-C12-N3	116.1	1.2	C25-C26-N7	114.0	1.2
C12-N3 -C13	124.7	1.2	C26-N7 -C27	125.0	1.2
N3 -C13 -N4	117.3	1.2	N7 -C27-N8	117.0	1.1
C13-N4 -C14	124.4	1.2	C27-N8 -C28	124.6	1.2
N4 -C14-C11	114.1	1.2	N8 -C28-C25	113.7	1.2
C14-C11-C12	123.1	1.3	C28-C25-C26	125.3	1.4
Br1-C1 -C2	119.7	1.3	Br2-C15-C16	117.5	1.1
Br1-C1- C6	117.5	1.4	Br2-C15-C20	117.9	1.2

Atoms	Angle	σ(θ)
C8 -C7 -N2	113.2°	1.9°
C7 -N2 -C4	124.3	1.4
C7 -N2 -C9	128.6	1.4
C10-C9 -N2	123.7	1.4
C10-C9 -N1	125.7	1.5
C11-N1 -C9	124.2	1.2
C11-N1 -C3	128.3	1.2
N1 -C11-C14	118.7	1.2
N1 -C11-C12	118.1	1.2
O1 -C12-C11	124.2	1.4
O1 -C12-N3	119.5	1.3
O2 -C13-N3	122.9	1.3
O2 -C13-N4	119.7	1.3
O3 -C14-N4	118.4	1.3
O3 -C14-C11	127.4	1.2
C22-C21-N6	112.0°	1.5°
C21-N6 -C18	123.3	1.2
C21-N6 -C23	125.2	1.2
C24-C23-N6	130.7	1.3
C24-C23-N5	122.7	1.3
C25-N5 -C17	125.4	1.2
C25-N5 -C23	127.2	1.2
N5 -C25-C28	116.6	1.3
N5 -C25-C26	117.9	1.3
O4 -C26-C25	128.1	1.4
O4 -C26-N7	117.7	1.3
O5 -C27-N7	121.0	1.2
O5 -C27-N8	121.8	1.2
O6 -C28-N8	120.3	1.4
O6 -C28-C25	125.9	1.3

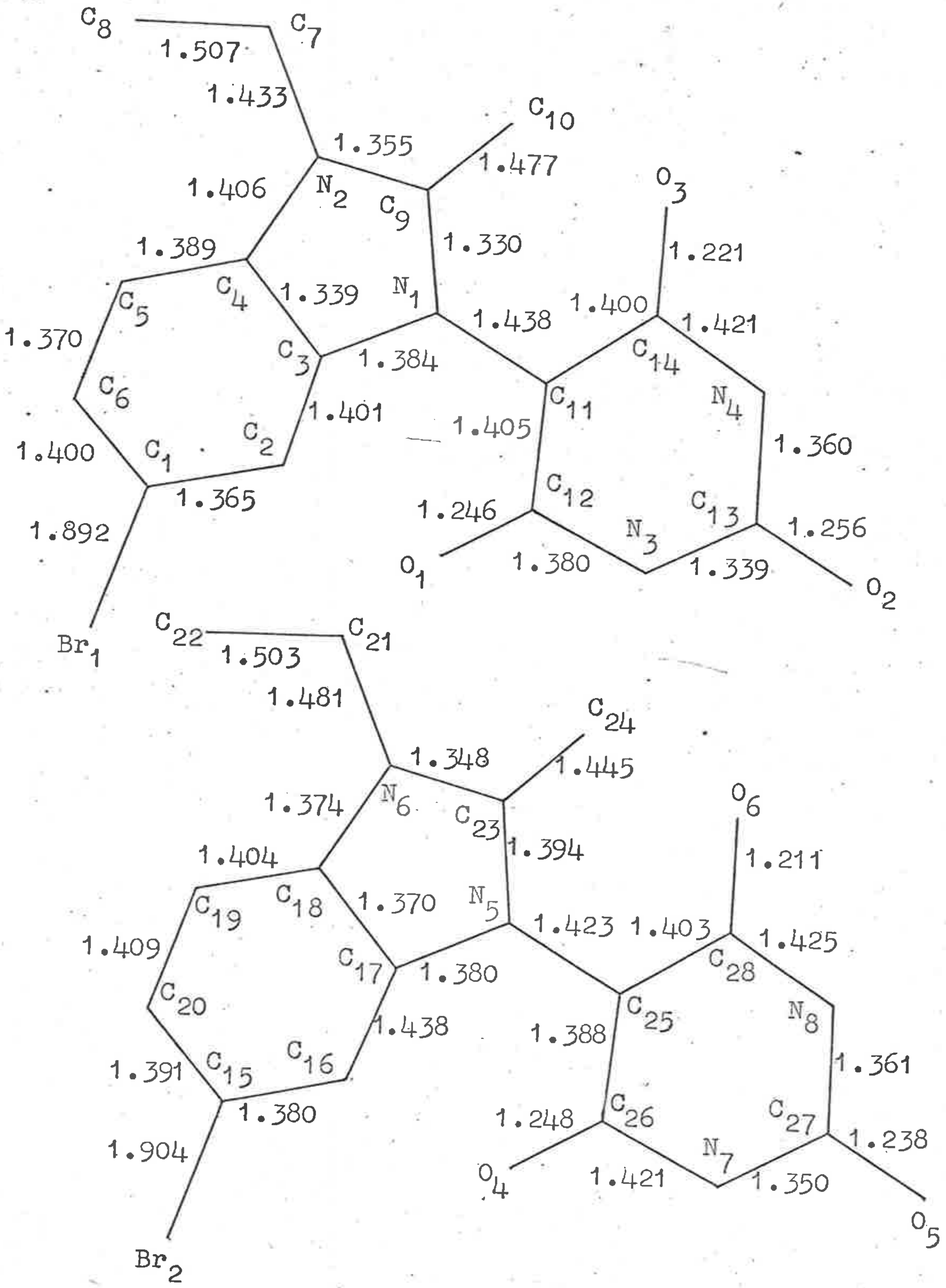


Fig. 23. Intramolecular bond lengths of B.Br.

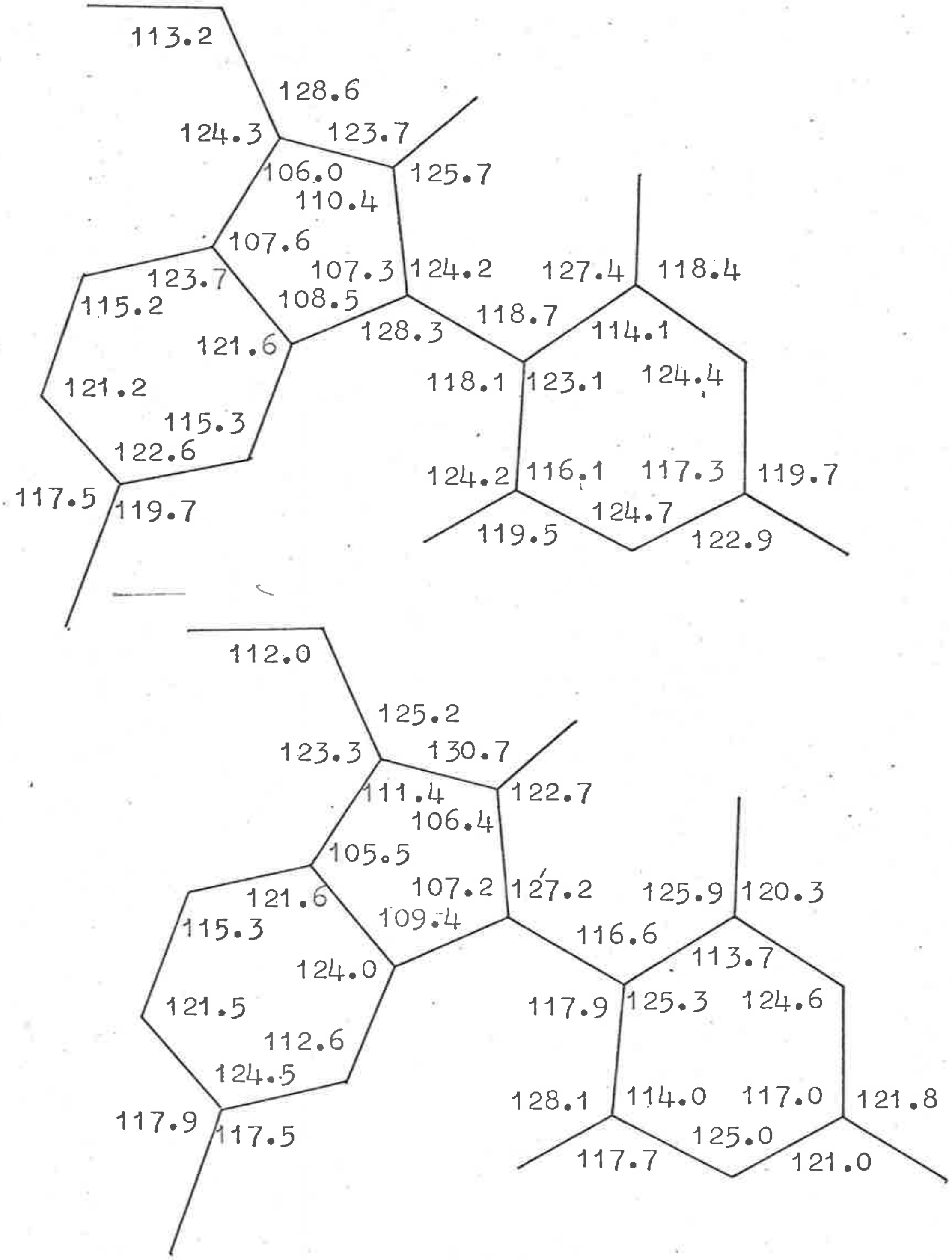


Fig. 24. Intramolecular bond angles of B.Br.

and Robertson (1953) and are discussed in section 2.10.3.) The two instances of significantly different angles mentioned above can be regarded as a consequence of the difference in bond length between N_1-C_9 (1.394A) and N_5-C_{23}(1.330A). The "expected" lengths for carbon-nitrogen single and double bonds are respectively 1.472A and 1.322A, where the "expected" lengths are taken from the International Tables for X-ray Crystallography, (1962), Vol.111, p.276. Since both C-N bonds lie within these limits, the difference between them can be explained by a different double bond character.

To enable a comparison of the observed bond lengths with the "expected" values, an average was taken over chemically equivalent bonds and the results are presented below in tabular form. No individual bond differed significantly from its expected length.

Bond type	Region of molecule	No. of bonds	Average length	Expected length
C-C	Benzene ring	10	1.395 A	1.395 A
C-N	Imidazole ring	8	1.371	1.352 *
C-N	Barbituric acid ring	8	1.382	1.352 *
C=O	"	6	1.237	1.23
C-Br	Benzene ring	2	1.90	1.89

*This length is expected in C_5H_5N, in which the nitrogen has no ring substituent.

The best fit planes through the benzimidazole and barbituric acid rings of each molecule were found by the method of Schomaker et. al. (1959). The plane through the nine benzimidazole atoms of molecule A will be called PA1, that through the six barbituric acid atoms, PA2. Corresponding planes for molecule B will be referred to as PB1 and PB2.

The equations of these four planes are given below, where the constant on the right is the origin to plane distance in Angstroms.

$$\mathrm{PA1} : 1.295x + 13.089y + 10.668z = -3.129$$
$$\mathrm{PB1} : 1.286x - 13.133y + 10.547z = 5.923$$
$$\mathrm{PA2} : 5.545x - 2.410y - 19.138z = -2.677$$
$$\mathrm{PB2} : 4.818x - 0.847y - 20.791z = -2.042$$

The deviations of the ring and ring-substituent atoms from their respective planes are given in Table 11. It can be seen that in each case the atoms are close to coplanar.

For molecule A, the dihedral angle between the benzimidazole and barbituric acid planes is 66.7°, for molecule B this angle is 69.8°.

3.10.3 The molecular arrangement.

The spatial arrangement of the two molecules in the asymmetric unit was shown in fig. 22; the packing of these

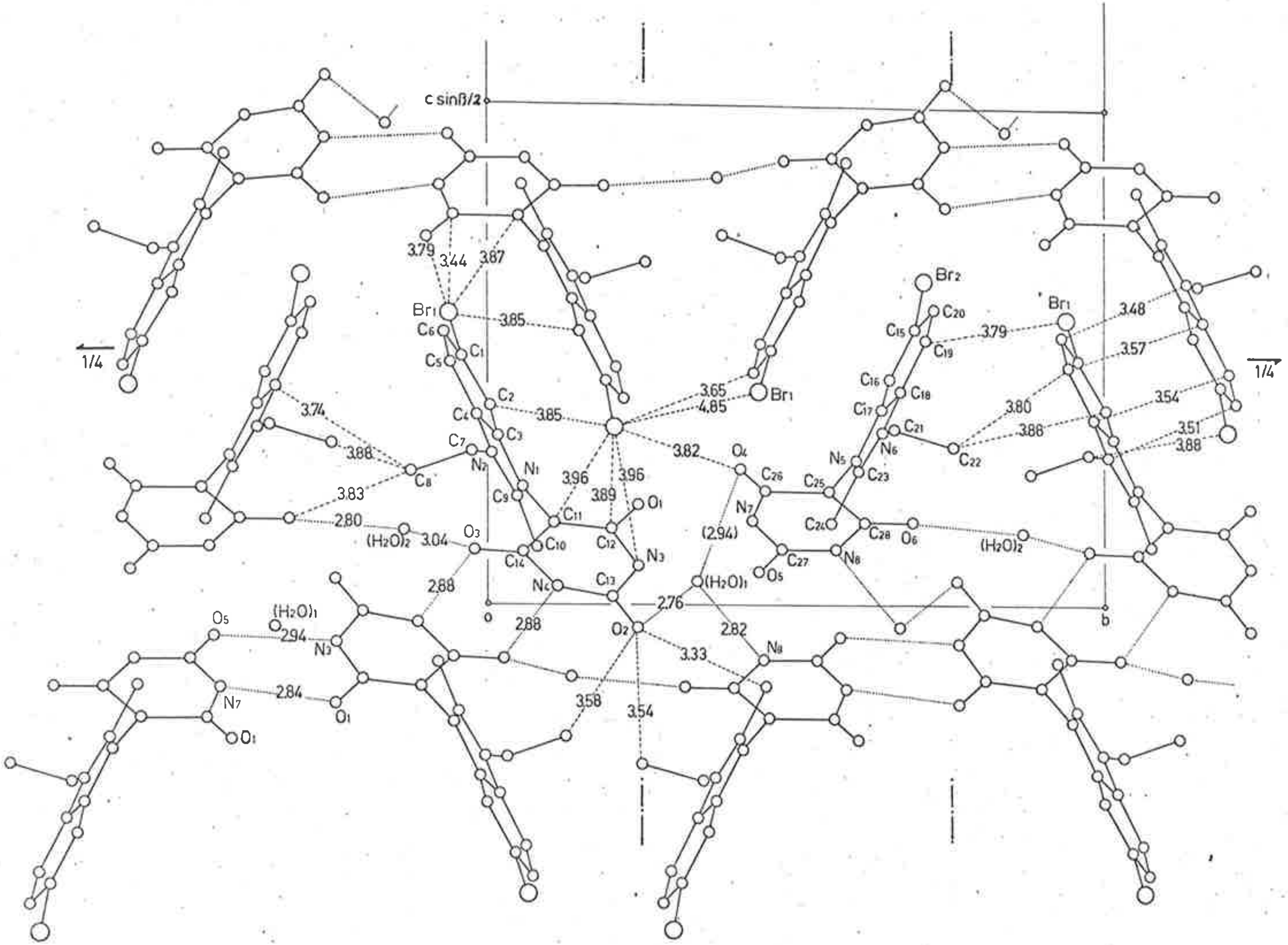


Fig. 25. Intermolecular contacts less than 4.0 A$^{\circ}$.

Table 11. Deviations from planarity.

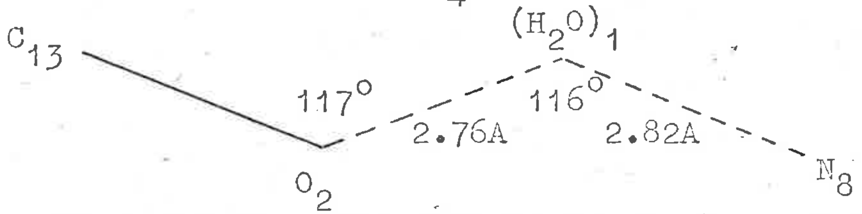
Plane PA1		Plane PB1		Plane PA2		Plane PB2	
Atom	Devn.	Atom	Devn.	Atom	Devn.	Atom	Devn.
C1	-.002 A	C15	.028 A	C11	.008 A	C25	-.022 A
C2	-.022	C16	-.003	C12	-.005	C26	.014
C3	.016	C17	-.025	N3	-.004	N7	.001
N1	.018	N5	.003	C13	.011	C27	-.011
C9	-.020	C23	.019	N4	-.006	N8	.009
N2	-.002	N6	.002	C14	-.002	C28	.004
C4	-.012	C18	-.027				
C5	.013	C19	.021	O1	.019	O4	.052
C6	.009	C20	-.010	O2	.029	O5	-.063
				O3	-.004	O6	-.021
Br1	-.079	Br2	.124				
C11	.130	C25	.062				
C10	-.036	C24	.084				
C7	-.190	C21	.012				

molecules within the crystal is illustrated by fig. 25.

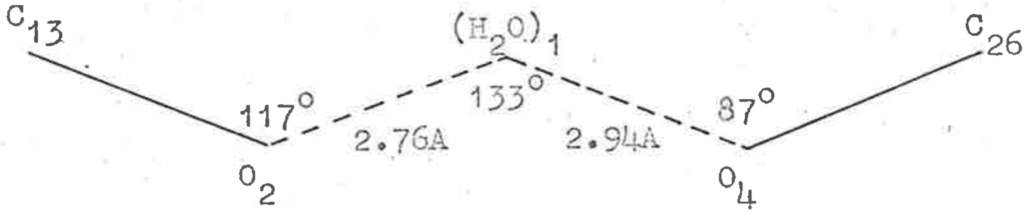
The orientations of the independent molecular planes are somewhat similar, this also being indicated by the similarity of the equations of these planes given in the previous section. The barbituric acid planes of molecules A and B have a dihedral angle of 7.7°; also, after applying the $P2_1/n$ screw operation to molecule B, its benzimidazole plane is only 1.1° from parallel with the corresponding plane of molecule A.

Two hydrogen bonds of the type N-H...O are formed between the independent barbituric acid rings of molecules A and B; the N...O distances are 2.84A and 2.94A. Two similar hydrogen bonds (N...O = 2.88A) are formed across the centre of symmetry.

The only remaining barbituric acid nitrogen atom is N_8 and this is presumably hydrogen bonded to $(H_2O)_1$ (N...O = 2.82A). If this is the case, the proton from N_8 will be associated with O_4 and the bonding of $(H_2O)_1$ will be

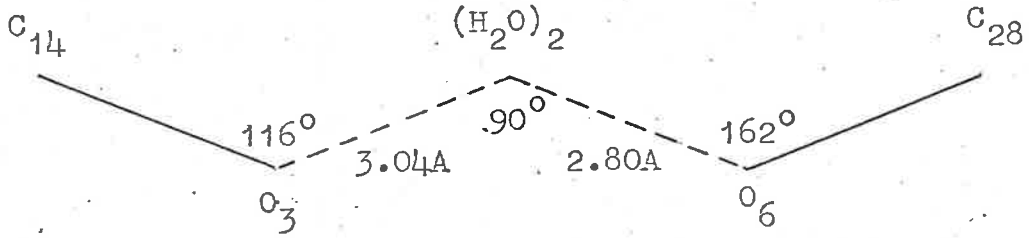


The other alternative would be for O_4 to be hydrogen bonded to $(H_2O)_1$, in which case the bonding would be



The second case does not seem likely, firstly because the angle at the water molecule considerably exceeds its expected value of 90°, secondly because of the acuteness of the angle at O_4.

The second water molecule is hydrogen bonded to O_3 and O_6 as illustrated below.



The hydrogen bonds are shown in fig. 25 as dotted lines; the dashed lines represent the more important (i.e. less than 4.0A) van der Waals contacts.

CHAPTER 4.

THE REFINEMENT OF CRYSTAL STRUCTURES

4.1 Methods of refinement.

Once an approximation to a correct structure has been found it is necessary to improve the approximately known structural parameters until the best possible values have been obtained; this is called the process of refinement.

Although a number of methods of refinement have been proposed (e.g. see Lipson and Cochran, 1957, p.278), only three were considered here; the first was the method of least squares, the second the differential Fourier method and the third the method of difference Fourier syntheses. The first two methods essentially involve iterative numerical calculation and are best used in conjunction with a computer; the third method, although formally similar to the second, is pictorial and is best used as a complement to one of the first two techniques.

4.1.1 Least Squares.

This method, first used by Hughes (1941) is mathematically the most satisfactory for it minimises the residual

$$R(LS) = \sum_{q} w(h,k,l).(|F_o(h,k,l)| - |F_c(h,k,l)|)^2 \qquad (4.1)$$

where $w(h,k,l)$ is the weight given to $|F_o(h,k,l)|^2$ and the summation is over all the independent spectra observed.

For a Gaussian distribution in the errors of the measured F_o's the "best" atomic parameters are those which result in a minimisation of the same residual (Lipson and Cochran, 1957, p.281).

If we let x_{ni} be the i^{th} parameter of atom n, and Δx_{ni} be small changes to the x_{ni}, then for each of the q independent calculated F_c's we can write the relation

$$\Delta F_c = \sum_{m,j} \frac{\partial F_c}{\partial x_{mj}} \Delta x_{mj} \tag{4.2}$$

The values of the shifts Δx_{mj} (say a total of N) are those which most nearly equate ΔF_c to $F_o - F_c$ for all equations where $F_o - F_c$ is known, i.e. for all reflections for which F_o is known.

These "observational equations" can be reduced to the set of N "normal equations" (e.g. see Lipson and Cochran, 1957, p.281) by multiplying each side of (4.2) by $w\frac{\partial F_c}{\partial x_{ni}}$ and adding the q left hand sides and the q right hand sides to give

$$\sum_{m,j} \sum_{q} w . \frac{\partial F_c}{\partial x_{ni}} . \frac{\partial F_c}{\partial x_{mj}} = \sum_{q} w . (F_o - F_c) . \frac{\partial F_c}{\partial x_{ni}} \tag{4.3}$$

The essential problem of the least squares method is to solve these N normal equations to find the N shifts Δx_{mj}.

To retain the mathematical rigour of the method, each of the coefficients of the Δx_{mj} must be included and the complete set of equations solved simultaneously i.e. the complete matrix of coefficients inverted. This has been done by Busing and Levy (1959) although the inversion of such very large matrices involves studies in round-off and truncation error propagation (Eichhorn, 1962).

The more usual and much simpler approach is to appeal to the physical nature of the problem and equate selected off-diagonal matrix elements to zero.

The justification for these simplifications can be seen more clearly by considering the particular example of the refinement of three positional plus one temperature parameter per atom, and putting $x_{n1} = x_n$, $x_{n2} = y_n$, $x_{n3} = z_n$ and $x_{n4} = B_n$. Then, if the atoms are well resolved, terms such as $\Sigma\, w \frac{\partial \underline{F}_c}{\partial x_n} \frac{\partial \underline{F}_c}{\partial x_m}$ and $\Sigma\, w \frac{\partial \underline{F}_c}{\partial x_n} \frac{\partial \underline{F}_c}{\partial B_m}$ are likely to be small. Furthermore, for a given atom, coordinate and temperature factor changes are not likely to be correlated, therefore $\Sigma\, w \frac{\partial \underline{F}_c}{\partial x_n} \frac{\partial \underline{F}_c}{\partial B_n}$ etc. will probably be small. The remaining off-diagonal terms are of the form $\Sigma\, w \frac{\partial \underline{F}_c}{\partial y_n} \frac{\partial \underline{F}_c}{\partial x_n}$ and these can be assumed negligible for orthogonal or near orthogonal axes. Having made these assumptions only the diagonal coefficients remain, and the equations reduce to the linear form

$$\Delta x_{mj} \sum_q w \left(\frac{\partial \underline{F}_c}{\partial x_{mj}} \right)^2 = \sum_q w (F_o - F_c) \frac{\partial \underline{F}_c}{\partial x_{mj}} \qquad (4.4)$$

or for our particular example

$$\Delta x_n = \sum_q w(F_o - F_c)\frac{\partial F_c}{\partial x_n} \Big/ \sum_q w\left(\frac{\partial F_c}{\partial x_n}\right)^2 \qquad (4.5)$$

This is the "diagonal" approximation of the least squares method and is the one used by Hughes.

Some of the approximations made above are worse than others; in a monoclinic system, for example, the assumption of near orthogonal axes may be completely unjustified. In a more sophisticated refinement including scaling factors and anisotropic temperature factor parameters the diagonal approximation becomes increasingly crude and may in fact by invalid (Srinivasan, 1961). If the atomic scattering factor of an atom is modified by a temperature factor of the form

$$T(h,k,l) = \exp\{-[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl]\} \qquad (4.6)$$

then the B_{ij} are not independent; furthermore the interdependence of the scale and temperature factors is common experience. A summary of those interactions which should not be neglected is given by Cruickshank (1959).

A compromise can be made between the diagonal and full matrix methods by including selected off-diagonal interactions which are likely to be important. If, for example, we have n atoms each with ten parameters (3 positional, 6 temperature, 1 scale) then we could include all the interactions between the different parameters of each atom, but ignore all interactions between different atoms. The set of 10n equations in 10n unknowns is then reduced to n sets of 10 equations in 10 unknowns which can be solved more easily. In matrix terminology the 10n x 10n matrix of coefficients of the normal equations is reduced to the n (10x10) sub matrices whose leading diagonals together make up the leading diagonal of the original matrix. This then is one form of the "block diagonal" least squares approximation. An even more simplified form is obtained by neglecting the positional and temperature factor - scale parameter interactions and thereby further reducing each 10x10 ~~matrix~~ to a 3x3 positional plus 7x7 temperature factor - scale matrix.

Sparks (1960) has compared the relative merits of various approximations and recommends the use of a 2x2 block connecting an overall temperature and overall scale factor plus blocks of either 3x3 plus 6x6, or 9x9, for the individual atomic parameters.

The principal advantages of the least squares method are:

a. If the weighting scheme is the correct one (i.e. the weight of an observation proportional to the inverse of its standard deviation) then the "best" atomic parameters are obtained.

b. Allowance can be made for the reliability of the measured intensities.

c. Errors are not introduced through termination of the Fourier series representing the electron density.

d. Parameters of all kinds can be refined.

e. The method is suitable for use on an automatic computer for which output should be at a minimum and with which it is desirable to carry out completely automatic interations.

Two disadvantages are:

a. The need for a choice of weighting function (although Lipson and Cochran (1957, p.283) point out that all reasonable systems of weighting lead to coordinates which differ by amounts small compared with the random errors of the final coordinates).

b. The method is a mathematical one and it is therefore more difficult to follow the course of the refinement and see at a given stage its physical inadequacies. If, for example, isotropic temperature factors are being used, the need for anisotropic parameters is not directly apparent.

4.1.2 Differential syntheses.

Booth (1946a) first showed that shifts to improve atomic coordinates could be found from a knowledge of the slope of the electron density at the approximately correct atomic sites. He later suggested (Booth, 1946b) that "back shifts" to correct for errors introduced by series termination could be found from the slopes of a Fourier synthesis calculated with coefficients equal to the calculated rather than observed structure amplitudes.

An essentially similar but in practice more useful variation of this method was first introduced by Cochran (1951a) and further extended by Cruickshank (1952, 1956) to allow for peak overlap and the refinement of anisotropic temperature factors. They showed that coordinate shifts can be found by using the criteria that the three first derivatives of the difference density $(\rho_o-\rho_c)$ should equal zero at the atomic site and that similar criteria can be applied to the six second derivatives to determine the six anisotropic thermal parameters; furthermore, the overall scaling factor can also be found from the criterion that $(\rho_o-\rho_c)$ should equal zero at the atomic sites.

Since slightly modified versions of this "differential difference" method were used to refine the two structures discussed elsewhere in this thesis, a brief outline of the derivation of the necessary refinement equations for centrosymmetrical space groups will be given here; simplifications and approximations possible for the monoclinic system are discussed in section 4.2.

a. Coordinate refinement.

Let

$$\rho_o(x,y,z) = \frac{1}{V_c} \sum\sum\sum_{hkl} F_o \cos\Theta \tag{4.7}$$

where $$\Theta = 2\pi\left(\frac{hx}{a} + \frac{ky}{b} + \frac{lz}{c}\right), \tag{4.8}$$

and put $D = \rho_o - \rho_c$.

Then the three criteria determining the i^{th} ($x_i = x,y,z$) coordinate of atom n are

$$\left(\frac{\partial D}{\partial x_i}\right)_n = 0$$

or

$$\left(\frac{\partial \rho_o}{\partial x_i}\right)_n = \left(\frac{\partial \rho_c}{\partial x_i}\right)_n \tag{4.9}$$

the derivatives being evaluated at the position of atom n.

By expanding each side of (4.9) in a multivariate Taylor expansion, Cruickshank (1952) derived a set of "modified differential Fourier" equations for the evaluation of coordinate shifts. He also showed that irrespective of whether the atoms overlap, if they have similar scattering factors and $w = 1/f_n$, then these equations are identical with the normal equations (4.3) of the least squares method. This is important to note because it emphasises the essential similarity, yet theoretical difference of the least squares and Fourier methods.

In practice, unless one is restricted to projections of the electron density, peak overlap can be ignored and Cruickshank's refinement equations for the shifts Δx_{nj}

reduce to

$$\left(\frac{\partial D}{\partial x_i}\right)_n = -\sum_j \Delta x_{nj} \left(\frac{\partial^2 \rho_n}{\partial x_i \partial x_j}\right)_n \qquad (4.10)$$

or in full, omitting the subscript n throughout

$$\begin{aligned} -\frac{\partial D}{\partial x} &= \Delta x \frac{\partial^2 \rho}{\partial x^2} + \Delta y \frac{\partial^2 \rho}{\partial x \partial y} + \Delta z \frac{\partial^2 \rho}{\partial x \partial z} \\ -\frac{\partial D}{\partial y} &= \Delta x \frac{\partial^2 \rho}{\partial x \partial y} + \Delta y \frac{\partial^2 \rho}{\partial y^2} + \Delta z \frac{\partial^2 \rho}{\partial y \partial z} \\ -\frac{\partial D}{\partial z} &= \Delta x \frac{\partial^2 \rho}{\partial x \partial z} + \Delta y \frac{\partial^2 \rho}{\partial y \partial z} + \Delta z \frac{\partial^2 \rho}{\partial z^2} \end{aligned} \qquad (4.11)$$

b. Anisotropic thermal refinement.

The six criteria determining the thermal parameters of atom n are

$$\left(\frac{\partial^2 D}{\partial x_k \partial x_l}\right)_n = 0 \qquad (k,l = 1,2,3) \qquad (4.12)$$

Let the temperature factor for atom n be written as in (4.5) with the subscript n implied throughout but omitted for clarity.

Then if $\underline{B} = (B_{11}, B_{12}, \ldots)$, and $\Delta\underline{B} = (\Delta B_{11}, \Delta B_{22}, \ldots)$ be a set of small changes to the B_{ij}, then by the multivariate Taylor expansion

$$\left(\frac{\partial^2 \rho_c}{\partial x_k \partial x_l}\right)_{\underline{B}+\Delta\underline{B}} = \left(\frac{\partial^2 \rho_c}{\partial x_k \partial x_l}\right)_{\underline{B}} + \sum_{i,j} \Delta B_{ij} \frac{\partial}{\partial B_{ij}} \left(\frac{\partial^2 \rho_c}{\partial x_k \partial x_l}\right)_{\underline{B}} \qquad (4.13)$$

The set of B_{ij} which will make the second derivatives of ρ_c equal to the second derivatives of ρ_o can now be found by solving the six simultaneous equations

$$\sum_{i,j} \Delta B_{ij} \frac{\partial}{\partial \overline{B}_{ij}}\left(\frac{\partial^2 \rho_c}{\partial x_k \partial x_l}\right) = \frac{\partial^2 (\rho_o - \rho_c)}{\partial x_k \partial x_l}$$

or in full

$$\begin{aligned}
&\frac{\partial}{\partial \overline{B}_{11}}\left(\frac{\partial^2 \rho_c}{\partial x^2}\right) . \Delta B_{11} + \frac{\partial}{\partial \overline{B}_{12}}\left(\frac{\partial^2 \rho_c}{\partial x^2}\right) . \Delta B_{12} + \cdots \\
&\qquad + \frac{\partial}{\partial \overline{B}_{33}}\left(\frac{\partial^2 \rho_c}{\partial x^2}\right) . \Delta B_{33} = \frac{\partial^2 D}{\partial x^2} \\
&\qquad \ldots\ldots\ldots \qquad\qquad (4.14) \\
&\frac{\partial}{\partial \overline{B}_{11}}\left(\frac{\partial^2 \rho_c}{\partial z^2}\right) . \Delta B_{11} + \frac{\partial}{\partial \overline{B}_{12}}\left(\frac{\partial^2 \rho_c}{\partial z^2}\right) . \Delta B_{12} + \cdots \\
&\qquad \frac{\partial}{\partial \overline{B}_{33}}\left(\frac{\partial^2 \rho_c}{\partial z^2}\right) . \Delta B_{33} = \frac{\partial^2 D}{\partial z^2}
\end{aligned}$$

It may be noted that if equations (4.11) and (4.14) are used for structure refinement then for the case of similar atoms the modified differential Fourier method is exactly equivalent to a 3x3 plus 6x6 block diagonal least squares method with $w = 1/f_n$.

c. Isotropic thermal refinement.

The only criterion necessary is that

$$\frac{1}{3}\left\{\left(\frac{\partial^2 D}{\partial x^2}\right)_n + \left(\frac{\partial^2 D}{\partial y^2}\right)_n + \left(\frac{\partial^2 D}{\partial z^2}\right)_n\right\} = \left(\frac{\partial^2 D}{\partial r^2}\right)_n = 0 \qquad (4.15)$$

If the temperature factor is expressed in the usual way as

$$T = \exp(-B\sin^2\theta/\lambda^2)$$

then application of Taylor's expansion leads to

$$\frac{\partial}{\partial \overline{B}}\left(\frac{\partial^2 \rho_c}{\partial r^2}\right) . \Delta B = \frac{\partial^2 D}{\partial r^2} \qquad (4.16)$$

The subscript n is again implied throughout.

In the approximate forms in which they are generally used the advantages and disadvantages of the modified differential Fourier (DF) and least squares (LS) methods are very similar. Although in the LS method correct weighting leads to the "best" coordinates, weighting of the coefficients (F_o-F_c) can also be used in the DF algorithm. It is worth noting that by using coefficients of the form (F_o-F_c) series termination effects are eliminated; also if any of the F_o's are thought to be unreliable then the corresponding difference can be given a reduced or even zero weight. These features of the DF method are not always recognised; e.g. Buerger (1960, p.612) gives as advantages of the LS method,

> "It is free from the series termination errors which characterize Fourier methods. It is also possible to use less than all the F's in the refining process, which is impossible with any Fourier method."

The general equivalence of the two approaches has been demonstrated in actual examples, e.g. by Jeffrey and Shiono (1959) who found the DF and full matrix LS methods to give final parameters and standard deviations not differing significantly; also by Eichhorn (1956) who found that "The differential method in all cases converges much faster than the least squares one with $w = 1/f_n$."

The final choice of refinement method seems to be largely one of personal taste; this certainly was the case in the author's final selection of DF methods.

There were two advantages of the DF method arising from the form in which it was finally applied.

a. During each refinement cycle the residual electron density $(\rho_o - \rho_c)$ was calculated at each atom site. This gave a useful check on the scaling, temperature factors, and correctness of the scattering factor curves.

b. For "isotropic" refinement, the three principal second derivatives of the difference electron density were evaluated and averaged according to (4.15). The degree of non equality of these three derivatives indicated the need for anisotropic temperature factors directly without recourse to a full difference synthesis.

Within the author's experience DF algorithms have been in all cases successful in refining centrosymmetrical crystal structures. Almost complete convergence of all parameters has generally been attained after two or three refinement cycles, and computer time has not been excessive.

4.1.3 Difference Syntheses.

The use of difference syntheses (Cochran, 1951a) in refining approximately known portions of a crystal structure has been discussed in the previous section. In practice, however, useful information can be obtained by calculating the difference density throughout the unit cell (Cochran, 1951b) rather than evaluating various derivatives of this density at the proposed atomic sites.

Although a three dimensional difference synthesis is not very convenient for the refinement of known parameters it can be most useful in revealing unknown structural features. As such, a difference synthesis can be a powerful tool for structure refinement.

4.2 Refinement expressions for monoclinic space groups.

4.2.1 Coordinate refinement.

To solve the three simultaneous equations (4.11) the coefficients $\left(\frac{\partial^2\rho_n}{\partial x_i \partial x_j}\right)_n$ must be evaluated. Different approximations were used for the cases of isotropic and anisotropic temperature factors.

a. Isotropic.

A useful approximation pointed out by Costain (1941) and developed by Booth (1946b) is that the electron density near the centre of an atom can be approximated by

$$\rho(r) = Z.(p/\pi)^{3/2}\exp(-pr^2)$$

where p is a constant for a given atom.

If we put $Z.(p/\pi)^{3/2} = A$, the density at the centre of the atom, and also take this centre as the coordinate origin, then for the monoclinic system,

$$\rho = A.\exp(-p(x^2+y^2+z^2+2xz.\cos\beta)) \qquad (4.18)$$

Hence by differentiation

$$\left(\frac{\partial^2\rho}{\partial x^2}\right)_o = \left(\frac{\partial^2\rho}{\partial y^2}\right)_o = \left(\frac{\partial^2\rho}{\partial z^2}\right)_o = -2A.p$$

$$\left(\frac{\partial^2\rho}{\partial x\partial y}\right)_o = \left(\frac{\partial^2\rho}{\partial y\partial z}\right)_o = 0 \quad \text{and} \quad \left(\frac{\partial^2\rho}{\partial x\partial z}\right)_o = -2A.p.\cos\beta \qquad (4.19)$$

Substituting in (4.11) and solving, the coordinate shifts are then given by

$$\Delta x = \left(\frac{\partial D}{\partial x} - \cos\beta.\frac{\partial D}{\partial z}\right) / 2A.p(1 - \cos^2\beta)$$

$$\Delta y = \frac{\partial D}{\partial y} / 2A.p \qquad (4,20)$$

$$\Delta z = \left(\frac{\partial D}{\partial z} - \cos\beta.\frac{\partial D}{\partial x}\right) / 2A.p(1 - \cos^2\beta)$$

In using this method the values of A and p for each atom must be predetermined, e.g. from a Fourier synthesis, and read into the computer along with the initial coordinate and other parameters.

b. Anisotropic.

Methods of evaluating derivatives of the electron density with respect to various parameters have been given by Cruickshank (1949, 1956). Approximations based on his suggestions were used both here and in the next section (4.2.2).

It is immaterial whether the coordinates are measured in radians (e.g. $x = 2\pi x'/a$), as fractions (e.g. $x = x'/a$), or in Angstrom units, provided that a consistent system is used throughout; here it was decided to use Angstrom units. The electron density for a centrosymmetrical system is therefore written, using a slightly modified notation, as

$$\rho(x_1,x_2,x_3) = \frac{1}{V_c} \sum_{h_1}\sum_{h_2}\sum_{h_3} F_o(h_1,h_2,h_3)\cos\Theta \qquad (4.21)$$

where

$$\Theta = 2\pi \sum_{i=1}^{3} h_i x_i/a_i$$

By differentiation

$$\frac{\partial^2 \rho}{\partial x_k \partial x_l} = -\frac{4\pi^2}{V_c a_k a_l} \Sigma\Sigma\Sigma\, h_k h_l F_o \cos\Theta \qquad (4.22)$$

Cruickshank shows that the central curvatures of the observed and calculated peaks are the same so that F_o can be replaced by F_c.

For a centrosymmetric system containing N pairs of atoms

$$F_c = 2 \sum_{n=1}^{N} f_n T_n \cos\Theta_n \qquad (4.23)$$

where $T_n = T_n(h_1, h_2, h_3)$ is the temperature factor of atom n. If (4.23) is substituted in (4.22) the cross terms in $\cos\Theta$ can be neglected if peak overlap is ignored. Using the result that the average value of $\cos^2\Theta = \frac{1}{2}$, the curvatures at the centre of atom n are given by

$$\left(\frac{\partial^2 \rho}{\partial x_k \partial x_l}\right)_n = -\frac{4\pi^2}{V_c a_k a_l} \sum_q h_k h_l F_n T_n \qquad (4.24)$$

It is to be remembered that to derive the summation on the right hand side of (4.24) we started with the summation on the right hand side of (4.21). Therefore if for any reason any of the F_o's are omitted from (4.21) (e.g. through being experimentally unobserved) then the term corresponding to this F_o must be omitted from (4.24). Also, if any of the F_o's are given a reduced weight, then the corresponding term in (4.24) must be given the same weight. In a particular example, the summation over q (implying summation over h, k and l) could be written as

$$\left(\frac{\partial^2\rho}{\partial x^2}\right)_n = -\frac{4\pi^2}{V_c a^2}\sum_q w(h,k,l).h^2 f_n T_n \qquad (4.25)$$

where w(h,k,l) is the weight given to $F_o(h,k,l)$ and typically

$$w(h,k,l) = 1$$

$$w(h,0,l) = \tfrac{1}{2} \text{ etc.}$$

It was true for the isotropic case and is a reasonable approximation here that

$$\frac{\partial^2\rho}{\partial x\partial y} = \frac{\partial^2\rho}{\partial y\partial z} = 0$$

and (4.26)

$$\frac{\partial^2\rho}{\partial x\partial z} = \frac{\partial^2\rho}{\partial x^2}.\cos\beta = \frac{\partial^2\rho}{\partial z^2}.\cos\beta$$

Substituting in (4.12) the coordinate shifts are given by

$$\Delta x = \left\{\frac{\partial D}{\partial x}.\left(-\frac{\partial^2\rho}{\partial x^2}\right)^{-1} - \frac{\partial D}{\partial z}.\left(-\frac{\partial^2\rho}{\partial z^2}\right)^{-1}.\cos\beta\right\} \quad \{1 - \cos^2\beta\}$$

$$\Delta y = \frac{\partial D}{\partial y}.\left(-\frac{\partial^2\rho}{\partial y^2}\right)^{-1}$$

Δz: similar to Δx, with x and z interchanged.

These are similar to (4.20) except that the curvatures are determined from (4.24) and the three principal curvatures are not assumed equal.

4.2.2 Isotropic temperature factor refinement.

To solve (4.16) we must evaluate $\frac{\partial}{\partial \bar{B}_n}\left(\frac{\partial^2\rho_c}{\partial r^2}\right)$

where the temperature factor is defined for atom n by

$$T_n = \exp(-B_n \sin^2\theta/\lambda^2) \qquad (4.28)$$

For the isotropic case the electron density peak is assumed spherically symmetrical so that

$$\frac{\partial}{\partial B_n}\left(\frac{\partial^2 \rho c}{\partial r^2}\right) = \frac{\partial}{\partial B_n}\left(\frac{\partial^2 \rho c}{\partial x^2}\right) \text{ etc.} \qquad (4.29)$$

By further differentiating (4.22) and again using (4.23),

$$\frac{\partial}{\partial B_n}\left(\frac{\partial^2 \rho c}{\partial x^2}\right) = \frac{8\pi^2}{V_c a^2} \sum_q \sum_n h^2 f_n T_n.(\sin^2\theta/\lambda^2).\cos\Theta.\cos\Theta_n \qquad (4.30)$$

where summation over q is defined following (4.24).

Once again neglecting cross terms in cosΘ and using the approximation

$$\frac{1}{a^2}\sum_q h^2 .. = \frac{1}{b^2}\sum_q k^2 .. = \frac{1}{c^2}\sum_q l^2 .. = \frac{1}{3}\sum_q (2\sin\theta/\lambda)^2 .. \qquad (4.31)$$

we have

$$\frac{\partial}{\partial B_n}\left(\frac{\partial^2 \rho c}{\partial x^2}\right)_n = \frac{16\pi^2}{3V_c} \sum_q f_n T_n.(\sin\theta/\lambda)^2 \qquad (4.32)$$

Substituting in (4.16), the isotropic temperature factor adjustments are finally given as

$$\Delta B_n = 3V_c\left(\frac{\partial^2 D}{\partial r^2}\right)_n \Big/ 16\pi^2 \sum f_n T_n.(\sin\theta/\lambda)^4 \qquad (4.33)$$

Within the author's knowledge the derivation of (4.33) from (4.16) has not been given elsewhere. The final result is not itself original, for it has since been realised that an equivalent expression, derived from a least squares approach, can be implied from some refinement expressions given by Cochran (1951a), although he does not give (4.33) explicitly.

In practice $\frac{\partial^2 D}{\partial r^2}$ was taken as the mean of the three principal curvatures and with this proviso (4.33) was found most satisfactory in all cases, although an inspection of the ΔB_n from successive cycles revealed that they were generally about 75% of their optimum values.

4.2.3 Anisotropic temperature factor refinement.

The coefficients necessary to solve the six simultaneous equations (4.14) to find the changes to the six thermal exponents B_{ij} defined in (4.5) are of the form

$$\frac{\partial}{\partial B_{ij}}\left(\frac{\partial^2 \rho_c}{\partial x_k \partial x_l}\right) \qquad (i,j,k,l = \text{either } 1,\ 2 \text{ or } 3) \qquad (4.34)$$

From (4.22) and (4.23), and remembering that

$$T_n(h,k,l) = \exp\{-[B_{11}h_1^2+B_{22}h_2^2+B_{33}h_3^2+B_{12}h_1h_2+B_{13}h_1h_3+B_{23}h_2h_3]\} \qquad (4.35)$$

where the subscript n is implied on the right hand side,

$$\frac{\partial}{\partial \bar{B}_{ij}}\left(\frac{\partial^2 \rho_c}{\partial x_k \partial x_l}\right) = \frac{8\pi^2}{V_c}\sum_q \sum_n h_i h_j h_k h'_l f_n T_n . \cos\Theta . \cos\Theta_n \qquad (4.36)$$

Proceeding as before we obtain

$$\frac{\partial}{\partial \bar{B}_{ij}}\left(\frac{\partial^2 \rho_c}{\partial x_k \partial x_l}\right) = \frac{4\pi^2}{V_c}\sum_q h_i h_j h_k h_l f_n T_n \qquad (4.37)$$

Several approximations suggested by Cruickshank for the monoclinic system are

$$\begin{aligned} \Sigma\, k^4 f &= (b^4/a^4)\ \Sigma\, h^4 f \\ \Sigma\, k^2 l^2 f &= (b^2c^2/a^2c^2)\ \Sigma\, h^2 l^2 f \end{aligned} \qquad (4.38)$$

and

$$\Sigma h^2 l^2 f = (\cos^2\beta + \tfrac{1}{3}\sin^2\beta).(a^2c^2/a^4)\ \Sigma h^4 f$$

Furthermore,

$$\Sigma h^2 hkf = \Sigma h^2 klf = 0 \qquad (4.38)$$

By using (4.38) the six equations (4.14) are reduced to two linear equations plus four simultaneous equations. An approximate solution of these equations has been given by Dunitz and Rollett (1956) and is the one finally used.

Two typical refinement expressions are

$$\Delta B_{11} = \frac{\begin{aligned} 3V_c\Big\{\left(\frac{4}{\sin^2\beta}\right)\left(\frac{\partial^2 D}{\partial x^2}\right) - \left(\frac{\partial^2 D}{\partial y^2}\right) - \left(\frac{1-4\cos^2\beta}{\sin^2\beta}\right)\left(\frac{\partial^2 D}{\partial z^2}\right) \\ \left(\frac{8\cos\beta}{\sin^2\beta}\right)\left(\frac{\partial^2 D}{\partial z\partial x}\right)\Big\} \end{aligned}}{40\pi^2 a^2\ \Sigma f_n T_n.(h^4 a^4)}$$

and (4.39)

$$\Delta B_{12} = \frac{V_c \frac{\partial^2 D}{\partial x\partial y}}{40\pi^2\ ab\ \Sigma f_n T_n.(h^2k^2/a^2b^2)}$$

These expressions proved quite satisfactory in practice although during refinement of the NaPTD structure it was found that the calculated shifts were generally too large and had to be reduced to the following percentages of their calculated values

B_{11}(50%), B_{22}(100%), B_{33}(50%), B_{12}(75%), B_{13}(50%), B_{23}(100%).

The need for these "fudge factors" with both DF and LS methods seems to be the rule rather than the exception (e.g. see Cruickshank, 1956, 1960; Sparks, 1960); this is, as Cruickshank remarks, extremely unsatisfactory. In his original paper on the determination of the anisotropic thermal motion of atoms, Cruickshank (1956) shows that the trouble arises from the accidentally absent reflections.

The best procedure in practice seems to be to calculate the first two refinement cycles using damping factors of 50%, and then from an inspection of these results determine the optimum "fudge factor" for each parameter being refined.

4.3 Refinement programs.

Altogether three refinement programs have been written; two were used to refine the NaPTD structure with isotropic and later anisotropic temperature factors, the third to refine the B.Br structure. These programs are largely similar and this section will describe features which are in general common to all three.

A copy of some output from the anisotropic $P2_1/a$ program is given in fig. 8, while a more complete description of the isotropic $P2_1/n$ program is included in Appendix 3.

4.3.1 General description.

Since the refinement programs were written with particular crystal structures very much in mind, they were written only for the appropriate space group. Although other structures of the same symmetry could be refined using these programs this limits the use of the programs. It was realised that this limitation could have been overcome by following the procedure of Sparks et al. (1956) and programming for the space group $P\bar{1}$, thereby making no use of the $P2_1/a$ lattice symmetry, but it was also felt that, if necessary, fairly straightforward changes could be made to the programs themselves to accommodate other space groups. The approach used is therefore similar to that of Lavine and Rollett (1956) who maintain that the increased efficiency of the programs outweighs the additional labour in coding.

In section 4.2 approximations were given for calculation of the various coefficients in the refinement equations; these coefficients were calculated for the first refinement cycle only and thereafter regarded as constant. In practice, refinements were generally carried out in three-cycle runs, so that the coefficients were in effect redetermined every three cycles.

Since a refinement had to proceed without supervision several checking devices were included; a negative result to any of the following tests would terminate the run.

a. Is the initial R value less than a preset value?

b. Has the R value at the end of a cycle decreased by at least a specified (positive or negative) amount?

c. Is any shift greater than a preset (small positive) maximum?

d. Have the stated maximum number of cycles not been completed?

4.3.2 Structure factor part.

The contribution to F_c from those atoms not being refined was calculated only once and then stored; thus only the variable part of F_c needed calculation during each cycle. This feature, which enabled chosen atoms to be refined while the remainder were held constant, was found most useful in a large refinement where a preliminary refinement of a few atoms only could be used to check that the program was running satisfactorily and also to determine the best values of the necessary "fudge factors" without wasting computer time on full refinement cycles.

Before each refinement cycle tables of $\cos 2\pi h_i x_i$ and $\sin 2\pi h_i x_i$ (i = 1,2,3) were evaluated and stored for each atom by calculating $\cos 2\pi x_i$ and $\sin 2\pi x_i$ and then using the recurrence relationships

$$\sin(h\alpha) = 2\sin(h-1)\alpha.\cos\alpha - \sin(h-2)\alpha$$

and (4.40)

$$\cos(h\alpha) = 2\cos(h-1)\alpha.\cos\alpha - \cos(h-2)\alpha$$

These trigonometric tables were then used not only for structure factor calculation but also in evaluating the various derivatives of the difference density.

Although at one stage the atomic scattering factors had been represented by the sixth degree polynomials of Freeman and Smith (1958) it was now realized that economy of storage space was not critical on the 7090 and that a tabular representation of the f-curves was therefore preferable. The latter method can have superior accuracy, is much faster, and permits the use of f-curves for which the polynomial coefficients may not have been determined; it is also a simple matter to allow for differing states of ionization or to extend the $(\sin\theta/\lambda)$ range. Tables of f at intervals of 0.005 in $\sin\theta/\lambda$ were read off from carefully drawn large scale graphs and were used without interpolation. A summary of the maximum errors is given below.

Element	Maximum absolute error in f (electrons)	Maximum percentage error in f (%)
Br	.12	.48
S	.085	.64
Na	.040	.57
O	.045	.74
N	.040	1.0
C	.037	1.0
H	.01	1.1

It may be noted that the percentage error in F_c will be largely independent of the magnitude of F_c because the errors in f for each atom arise from scattering curves of similar shape. To a rough approximation the error $\Delta f_n(h,k,l)$ in each $f_n(h,k,l)$ contributing to a given structure factor equals the same fraction of $f_n(h,k,l)$ for all atoms, so

$$\Sigma \Delta f_n \cos\Theta_n \propto \Sigma f_n \cos\Theta_n \qquad (4.41)$$

The calculated structure factors should therefore be accurate within about 1%.

The atomic scattering factor curves of Berghuis et al. (1955) were used for sodium, oxygen, nitrogen and carbon; that of Dawson (1960) for sulphur; that of McWeeny (1951) for hydrogen and that of Freeman and Watson (1961), modified by the anomalous dispersion correction of Dauben and Templeton

(1955), for bromine.

4.3.3 Fourier part.

The difference electron density $D = \rho_o - \rho_c$ and its various derivatives $\frac{\partial D}{\partial x}$, $\frac{\partial^2 D}{\partial x^2}$ etc. were evaluated by three sets of one-dimensional summations over l, h and k in that order. (This ordering proved convenient for both structures described in this work.) By splitting up the summations in this way a considerable saving of computer time was achieved. If, for example, we perform the summation

$$\sum_{l} F(h,k,l)\cos(2\pi lz/c) = A(h,k) \qquad (4.42)$$

then the coefficients A(h,k) can be used in generating D, $\frac{\partial D}{\partial x}$, $\frac{\partial^2 D}{\partial y^2}$,.. and in fact all the derivatives of D excepting those with respect to z. Similarly the summation

$$-\sum_{l} (2\pi/c).l.F(h,k,l)\sin(2\pi z/c) = A_1(h,k) \qquad (4.43)$$

can be used in generating not only $\frac{\partial D}{\partial z}$, but also $\frac{\partial D}{\partial x \partial y}$ and $\frac{\partial D}{\partial y \partial z}$.

4.3.4 Scaling.

It was decided to scale the observed and calculated structure amplitudes by the criterion that

$$\Sigma\, |F_o| = \Sigma\, |F_c| \qquad (4.44)$$

where the summation was taken over those spectra observed as non zero. Although another possible method of scaling by using a zero difference density criterion has been mentioned (4.1.2), it was found that (4.44) would be most convenient for the layer-by-layer scaling desired for the NaPTD refinement.

In an effort to keep the scale and temperature factor parameters independent, the scale factors were evaluated and applied to the observed F_o's before the other parameter shifts were calculated. The typical procedure was as follows

(i) Calculate F_c for all h,k,l.

(ii) Find the scale factor(s) from $\Sigma |F_c|$.

(iii) Scale F_o.

(iv) Set up the coefficients (F_o-F_c) and evaluate R.

4.3.5 Weighting.

Since the more intense NaPTD reflections had been measured photometrically it was thought that the observed structure amplitudes had in this case an approximately constant absolute uncertainty. Accordingly an "all or nothing" weighting system was used. On the other hand the B.Br data had been entirely estimated by eye estimation and was therefore thought to have nearer a constant percentage uncertainty. In this case a weighting scheme similar to that of Hughes (1941) was used; i.e. the coefficients included were $w(F_o-F_c)$ where

$$\begin{aligned} w &= 1 \quad \text{if } F_o < 4F_m \\ w &= 1/F_o \quad \text{if } F_o > 4F_m \end{aligned} \qquad (4.45)$$

where F_m is the minimum observable value of F_o.

After the coefficients $w(F_o-F_c)$ (with w = 1 for the

NaPTD case) had been formed, two further tests were applied

a. If either $2|F_o| < |F_c|$, or $2|F_c| < |F_o|$, w was put equal to zero. This test was designed to eliminate weak reflections of uncertain sign.

b. If $w|F_o-F_c|$ was greater than some preset value, this coefficient was omitted. Observed F's severely affected by extinction were therefore ignored.

Taken together a. and b. also eliminated obvious errors of measurement or indexing.

4.3.6 Unobserved reflections.

Since about a third of the accessible NaPTD reflections had been experimentally unobserved an effort was made to do better than completely ignore them. From a knowledge of the minimum observable amplitude where the Lorentz-polarization factor was unity, the minimum observable amplitude F_m appropriate to the reflection being considered was calculated. The following procedure was adopted.

a. If $|F_c| < F_m$, ignore.

b. If $F_m < |F_c| < 2F_m$, include the contribution $S_c.(k.F_m - |F_c|)$ where S_c is the sign of F_c and k is a constant discussed below.

c. If $F_c > 2F_m$, ignore.

From the statistical distribution of intensities given by Wilson (1949) it follows that the most probable value of an unobserved structure amplitude is $\frac{1}{2}F_m$ for a centric structure. With this in mind k = ½ was initially used; however, during the final (isotropic) refinement of NaPTD the coordinate shifts began to oscillate and it was found that this could be prevented by using k = 1 which was therefore used for subsequent NaPTD and B.Br refinement. This result is to be expected when it is remembered that instead of all the unobserved spectra, we are considering only a set for which F_c exceeds the maximum possible value of F_o, i.e. a set for which we expect each F_o to be near its threshold value.

When the Weissenberg technique of recording intensities is used, spots with sinθ near unity may either fall in a region of intense back scatter which makes their intensity measurement unreliable, or they may in fact not even be recorded on the film. On the other hand since the Lorentz - polarization factor is here considerable these spots have a very small intensity threshold. To avoid including these unreliable coefficients only those with sinθ less than 0.97 were considered for inclusion in the refinement equations.

4.3.7 Times.

Refinement of 14 atoms of the NaPTD structure (1700 F's) with 6 atoms held constant, all having anisotropic thermal parameters, took 100 sec./cycle. Isotropic parameters made little difference.

For the B.Br structure (7000 F's) refinement of 46 atoms with isotropic temperature factors took 8 mins./cycle.

APPENDIX 1.

OPERATION OF THE SOLUS POWER SUPPLY

To switch the supply on, proceed as follows.

1. Ensure that all switches are off.
2. Water "on" (2-3 l./min.).
3. Close the two wall switches.
4. Close the "manual start" relay.
5. Switch on the power supply (but not the "H.T." switch). Wait 2 mins. for filaments to "warm up".
6. Set the overload control at its maximum. With H.T. selector on "1", close the "H.T." switch.
7. Increase the H.T. voltage and X-ray tube filament current to obtain the desired tube voltage and current. Typical values for copper radiation are

(i)	"H.T.4"	30K.V.	26m.a.
(ii)	"H.T.5"	34K.V.	20m.a.

8. Decrease the overload control to (say) 40 m.a.

To switch off, proceed in reverse order from 7 to 1.

* * *

APPENDIX 2.

Results of refinement of NaPTD using isotropic temperature factors.

The final atomic parameters are listed below along with the residual electron density at the atom sites.

Atom	x/a	y/b	z/c	B ($Å^2$)	$\rho_o-\rho_c$ (e./$Å^3$)
S	.4437	.0928	.1934	4.0	-.23
Na	.1892	.0102	.0236	3.8	-.27
O_1	.2049	.6909	.0797	4.0	-.09
O_2	.9977	.0996	.0984	4.6	.00
N	.1230	.3761	.0805	3.5	.02
C_1	.1309	.5636	.1008	3.4	-.07
C_2	.0290	.2761	.1163	3.5	.03
C_3	.0506	.6248	.1839	4.2	.05
C_4	.1531	.6778	.2724	4.4	-.05
C_5	.2481	.5401	.3202	7.0	-.04
C_6	.3429	.5941	.4013	8.9	-.09
C_7	.3523	.7808	.4287	9.0	.01
C_8	.2670	.9187	.3833	8.9	.00
C_9	.1627	.8683	.3041	6.6	.05
H_1	.479	.734	.159	4.0	
H_2	.243	.396	.297	9.5	
H_3	.412	.489	.437	8.5	

Appendix 2. (cont.)

Atom	x/a	y/b	z/c	B (Å^2)
H_4	.425	.822	.491	8.5
H_5	.272	.065	.406	7.0
H_6	.095	.973	.268	7.0

The overall reliability index R was 10.4% and the values for the individual layers were as follows.

Layer	h0l	h1l	h2l	h3l	h4l	h5l
R(%)	9.0	10.0	10.5	10.6	11.5	12.3

APPENDIX 3.

COMPUTER PROGRAMS

Introduction.

A brief description is given of each program. This is followed by the limitations (e.g. to the size of h, k and l), and a list of the FORTRAN names given to each of the input variables. Then follows a listing of the program.

PROGRAM 1. STRUCTURE FACTORS

An IBM 1620 program for the space group $P2_1/a$.

Description

The program accepts each atom type, coordinates, and individual isotropic temperature factor as initial input. Then one card per reflection containing h, k, l, $F_o(h,k,l)$, $\sin\theta$ and the scattering factors for each atom type appropriate to the reflection is read in. F_c and $F_o - F_c$ are calculated; also the R value for each layer of k.

Input must be strictly in the order

$(k=0, k_{max}(h=0, h_{max}(l=0, l_{max})))$, however control cards can be used to skip calculation for any values of h and k.

Limitations.

$h_{max}, \quad k_{max}, \quad l_{max} \quad < \quad 100$

Maxm. of 25 atoms

Maxm. of 6 atom types.

FORTRAN names.

P(1,I)	Atom type (an integer, 1 to 6)
P(2,I)	x_I

P(3,I)	y_I
P(4,I)	z_I
P(5,I)	B_I
JTRU	h
KTRU	k
LTRU	l
A	$F_o(h,k,l)$
THETA	sinθ
C(6),..,C(1)	Scattering factors. e.g. f_S, f_{Na},..f_H But putting these negative they can be used to skip to the next layer of k (say).

```
C     B W MATTHEWS PHYSICS DEPT 1172
C     STRUCTURE FACTORS   SPACE GROUP P21/A
C     INDIVIDUAL ISOTROPIC TEMPERATURE FACTORS
C     PROGRAM FOR IBM 1620

      DIMENSIONCX(25),SX(25),CY(25),SY(25),CZ(3,25),SZ(3,25)
      DIMENSIONP(5,25),C(6)
      READ3,NMBR
    3 FORMAT(I5)
      P2=6.283
      DO21I=1,NMBR
      READ6,P(1,I),P(2,I),P(3,I),P(4,I),P(5,I)
      PRINT6,P(1,I),P(2,I),P(3,I),P(4,I),P(5,I)
    6 FORMAT(5F10.5)
      CZ(1,I)=COSF(P2*P(4,I))
   21 SZ(1,I)=SINF(P2*P(4,I))
   17 DO290K=1,100
      DK=K-1
      FCSM=0.0
      PDEL=0.0
      DO291I=1,NMBR
      V=P2*DK*P(3,I)
      CY(I)=4.0*COSF(V)
  291 SY(I)=4.0*SINF(V)
      DO190J=1,100
      DJ=J-1
      DO191I=1,NMBR
      V=P2*DJ*P(2,I)
      CX(I)=COSF(V)
  191 SX(I)=SINF(V)
      IDS=K+J
      DO90L=1,100
      DL=L-1
      READ2,JTRU,KTRU,LTRU,A,THETA,C(6),C(5),C(4),C(3),C(2),C(1)
    2 FORMAT(3I3,F6.1,F7.4,F8.2,5F6.2)
      IF(C(6))189,23,23
```

```
23    IF(L-2)25,26,27
25    DO28I=1,NMBR
      CZ(2,I)=1.0
      CZ(3,I)=1.0
      SZ(2,I)=0.0
28    SZ(3,I)=0.0
      GOTO49
26    DO38I=1,NMBR
      CZ(3,I)=CZ(1,I)
38    SZ(3,I)=SZ(1,I)
      GOTO49
27    DO48I=1,NMBR
      Q=CZ(3,I)
      W=SZ(3,I)
      CZ(3,I)=2.0*CZ(3,I)*CZ(1,I)-CZ(2,I)
      SZ(3,I)=2.0*SZ(3,I)*CZ(1,I)-SZ(2,I)
      CZ(2,I)=Q
48    SZ(2,I)=W
49    XA=THETA/3.078
      XC=4.0*XA*XA
      ASUM=0.0
      IF(JTRU)31,32,32
31    B=-1.0
      GOTO35
32    B=1.0
35    DO63I=1,NMBR
      M=P(1,I)
      W=P(5,I)*XC-1.
      T=0.008333+W*(0.001389+W*(0.000198+W*0.0000248))
      T=(1.0+W*(1.0+W*(0.5+W*(0.16667+W*(0.041667+W*T)))))*2.7183
      N=IDS/2-(IDS+1)/2
      IF(N)61,60,60
60    ASUM=ASUM+CY(I)*(CX(I)*CZ(3,I)-B*SX(I)*SZ(3,I))*C(M)/T
      GOTO63
61    ASUM=ASUM-SY(I)*(CX(I)*SZ(3,I)+B*SX(I)*CZ(3,I))*C(M)/T
63    CONTINUE
```

```
 62 SUM=ABSF(ASUM)
    DIFA=ABSF(A-SUM)
    FCSM=FCSM+SUM
    PDEL=PDEL+DIFA
    IF(SENSESWITCH1)46,45
 46 PUNCH7,JTRU,KTRU,LTRU,A,ASUM,DIFA
 45 IF(SENSESWITCH2)44,90
 44 PRINT7,JTRU,KTRU,LTRU,A,ASUM,DIFA
  7 FORMAT(3I3,F8.1,F8.1,F8.1)
 90 CONTINUE
189 IF(C(5))24,190,190
190 CONTINUE
 24 R1=PDEL/(FCSM+0.00001)
    PAUSE
    PRINT8,FCSM,PDEL,R1
  8 FORMAT(F10.1,F9.1,F7.4)
    IF(C(4))289,290,290
290 CONTINUE
289 IF(C(3))288,288,17
288 STOP
    END
```

PROGRAM 2. THREE DIMENSIONAL FOURIER SYNTHESIS

An IBM 1620 program for the space group $P2_1/n$.

Description

The program is run in three stages corresponding to summations over l, h and k. Output from each stage (after sorting into the appropriate order) serves as input for the next stage. The combination of coefficients $(F(\bar{h},k,l) \pm F(h,k,l))$, and sorting into sets of (h+k) even and odd, must both be done prior to the first summation.

Limitations

$h < 20$, $k < 20$, $l < 51$

Any interval of subdivision of z; max. of 130 divisions can be calculated.

Any even interval of subdivision of x; any number of divisions calculated. $\frac{1}{2} - x$ automatically given with x.

Any subdivision of y divisible by 4; any number of divisions calculated. $1-y$, $\frac{1}{2}+y$, $\frac{1}{2}-y$ automatically given with y.

FORTRAN names

First stage (summation over l)

NZDIV	Number of divisions of z (e.g.60)
NCALC	Number of these divisions to be calculated (e.g. 31)
LMAX	Maxm. value of l (e.g. 20)
SCALE	Scaling factor (e.g. 0.1)
J, K, N1, A(L)	h,k, (A(h,k,l-1), l = 1 to N1) where $A(h,k,l) = F(h,k,l) \pm F(\bar{h},k,l)$

Second stage (summation over h)

The coefficients read in are of the form A(h,k,z) where there are a maxm. of 10 coefficients on each card (e.g. $z = \frac{0}{60}$ to $\frac{9}{60}$ for "z range 1", or $z = \frac{10}{60}$ to $\frac{19}{60}$ for "z range 2"). Input is in the order (k = const. ($h = 0, h_{max}$)).

XDIV	Number of divisions of x
NCALC	Number of these divisions to be calculated
IZMIN, IZMAX	Typically equal 1 and 10 to include the 10 coefficients on each card (e.g. $z = \frac{0}{60}$ to $\frac{9}{60}$)
SCALE	Scaling factor
J, I	h, k
I2	z range
M(I)	A(h-1, k-1, z_I).

Third stage (summation over k)

The coefficients read in are of the form A(k,x,z) where, as in stage 2, there are a maxm. of 10 coefficients on each card. Input is in the order (x = const. ($k = 0, k_{max}$)).

YDIV	Number of divisions of y
NCALC	Number of these divisions to be calculated
IZMIN, IZMAX	As in stage 2.
KMAX	k_{max} (this will be the same for all x and z)
SCALE	Scaling factor
ZERO	A constant added to the final electron density
K	k
IX	Integral value of x (e.g. IX = 5 for x = 5/60)
IA	z range : M(I) A(k-1, IX, z_I)

```
C     B W MATTHEWS PHYSICS DEPT 1172
C     3 DIMENSIONAL FOURIER SUMMATION   SPACE GROUP P21/N
C     PROGRAM FOR THE IBM 1620
C     3 DIMENSIONAL FOURIER SUMMATION FIRST STAGE
C     SUM OVER L H+K+L EVEN SIN  , ODD COS
C    COEFFS A(H,K,L) WITH (H+K+L) EVEN ARE SUMMED AS TERMS A.SIN(L.Z)
C     COEFFS WITH (H+K+L) ODD ARE SUMMED AS A.COS(L.Z)

      DIMENSIONA(51),C(51),S(51),M(130),N(130)
      DO50I=1,130
      N(I)=0
   50 M(I)=0
      READ3,NZDIV,NCALC,LMAX,SCALE
    3 FORMAT(3I5,F5.2)
      ZDIV=NZDIV
      Z=6.2832/ZDIV
      MCARD=(NCALC-1)/10+1
      NCARD=LMAX/11+1
      C(1)=1.0
      S(1)=0.0
   10 DO7IL=1,NCARD
      L=11*IL-10
 READ4,J,K,N1,A(L),A(L+1),A(L+2),A(L+3),A(L+4),A(L+5),A(L+6),A(L+7),A(L+8),Q,R
      A(L+9)=Q
    7 A(L+10)=R
    4 FORMAT(2H  ,2I3,3H   ,I3,11F5.0)
      DO20I=1,NCALC
      DI=I-1
      S(2)=SINF(Z*DI)
      C(2)=COSF(Z*DI)
      IF(N1-3)25,26,26
   26 DO27IN=3,N1
      S(IN)=2.0*S(IN-1)*C(2)-S(IN-2)
   27 C(IN)=2.0*C(IN-1)*C(2)-C(IN-2)
   25 SUMC=0.0
      SUMS=0.0
```

```
      DO28IL=1,N1,2
   28 SUMS=SUMS+A(IL)*S(IL)
      DO29IL=2,N1,2
   29 SUMC=SUMC+A(IL)*C(IL)
      M(I)=SUMS*SCALE
   20 N(I)=SUMC*SCALE
      DO40IA=1,MCARD
      L=10*IA-9
      IM1=M(L+1)
      IN2=N(L+1)
      IF(SENSESWITCH1)31,30
31PRINT5,J,K,IA,M(L),IM1,M(L+2),M(L+3),M(L+4),M(L+5),M(L+6),M(L+7),M(L+8),M(L+9)
PRINT6,J,K,IA,N(L),IN2,N(L+2),N(L+3),N(L+4),N(L+5),N(L+6),N(L+7),N(L+8),N(L+9)
    5 FORMAT(2HSE,3I3,1X,10I6)
    6 FORMAT(2HCO,3I3,1X,10I6)
30PUNCH5,J,K,IA,M(L),IM1,M(L+2),M(L+3),M(L+4),M(L+5),M(L+6),M(L+7),M(L+8),M(L+9)
PUNCH6,J,K,IA,N(L),IN2,N(L+2),N(L+3),N(L+4),N(L+5),N(L+6),N(L+7),N(L+8),N(L+9)
   40 CONTINUE
      GOTO10
      END


C     THE APPROPRIATE HALF OF THE COEFFS ARE SUMMED USING THE PROGRAM
C     ABOVE, FOR THE OTHER HALF THE FOLLOWING CHANGES ARE MADE

C     SUM OVER L   H+K+L EVEN COS  , ODD SIN
   28 SUMC=SUMC+A(IL)*C(IL)
   29 SUMS=SUMS+A(IL)*S(IL)
      M(I)=SUMC*SCALE
   20 N(I)=SUMS*SCALE
    5 FORMAT(2HCE,3I3,1X,10I6)
    6 FORMAT(2HSO,3I3,1X,10I6)
```

```
C     FOURIER SUMMATION  SECOND STAGE
C     SUM OVER H  H+K+L ODD
      DIMENSIONC1(20,10),C2(20,10),C(20),S(20),M(20),N(20)
      READ3,XDIV,NCALC,IZMIN,IZMAX,SCALE
    3 FORMAT(F5.0,3I5,F5.2)
      NHALF=XDIV/2.0
      XDIV=6.2832/XDIV
      C(1)=1.0
      S(1)=0.0
      DO60M1=1,20
      N(M1)=0
   60 M(M1)=0
9READ5,J,I,I2,M(1),M(2),M(3),M(4),M(5),M(6),M(7),M(8),M(9),M(10)
      IF(J)8,11,11
   11 NH=J+1
      DO12IZ=IZMIN,IZMAX
   12 C1(NH,IZ)=M(IZ)
      K=I
      IA=I2
      GOTO9
8READ5,J,I,I2,M(1),M(2),M(3),M(4),M(5),M(6),M(7),M(8),M(9),M(10)
      IF(J)19,13,13
   13 NH=J+1
      DO14IZ=IZMIN,IZMAX
   14 C2(NH,IZ)=M(IZ)
    5 FORMAT(2H  ,3I3,1X,10I6)
      GOTO8
   19 DO100IX=1,NCALC
      IX1=IX-1
      DX=IX1
      C(2)=COSF(XDIV*DX)
      S(2)=SINF(XDIV*DX)
      IF(NH-3)25,26,26
   26 DO27IN=3,NH
      C(IN)=2.0*C(IN-1)*C(2)-C(IN-2)
```

```
   27 S(IN)=2.0*S(IN-1)*C(2)-S(IN-2)
   25 DO35IZ=IZMIN,IZMAX
      SUMCO=0.0
      SUMSO=0.0
      SUMCE=0.0
      SUMSE=0.0
      DO28IH=1,NH,2
      SUMCE=SUMCE+C1(IH,IZ)*C(IH)
   28 SUMSE=SUMSE+C2(IH,IZ)*S(IH)
      DO38IH=2,NH,2
      SUMCO=SUMCO+C1(IH,IZ)*C(IH)
   38 SUMSO=SUMSO+C2(IH,IZ)*S(IH)
      M(IZ)=(SUMSE+SUMSO+SUMCE+SUMCO)*SCALE
      IX2=NHALF-IX1
      N(IZ)=(-SUMSE+SUMSO+SUMCE-SUMCO)*SCALE
      IX3=IX1+NHALF
      M(IZ+10)=(SUMSE-SUMSO+SUMCE-SUMCO)*SCALE
      IX4=IX2+NHALF
   35 N(IZ+10)=(-SUMSE-SUMSO+SUMCE+SUMCO)*SCALE
      IF(SENSESWITCH1)31,30
31PRINT6,K,IX1,IA,M(1),M(2),M(3),M(4),M(5),M(6),M(7),M(8),M(9),M(10)
PRINT6,K,IX2,IA,N(1),N(2),N(3),N(4),N(5),N(6),N(7),N(8),N(9),N(10)
PRINT6,K,IX3,IA,M(11),M(12),M(13),M(14),M(15),M(16),M(17),M(18),M(19),M(20)
PRINT6,K,IX4,IA,N(11),N(12),N(13),N(14),N(15),N(16),N(17),N(18),N(19),N(20)
    6 FORMAT(2H0 ,3I3,1X,10I6)
30PUNCH6,K,IX1,IA,M(1),M(2),M(3),M(4),M(5),M(6),M(7),M(8),M(9),M(10)
PUNCH6,K,IX2,IA,N(1),N(2),N(3),N(4),N(5),N(6),N(7),N(8),N(9),N(10)
PUNCH6,K,IX3,IA,M(11),M(12),M(13),M(14),M(15),M(16),M(17),M(18),M(19),M(20)
PUNCH6,K,IX4,IA,N(11),N(12),N(13),N(14),N(15),N(16),N(17),N(18),N(19),N(20)
  100 CONTINUE
      GOTO9
      END

C     SUM OVER H  H+K+L EVEN
      SUMCE=SUMCE+C2(IH,IZ)*C(IH)
   28 SUMSE=SUMSE+C1(IH,IZ)*S(IH)
```

```
      SUMCO=SUMCO+C2(IH,IZ)*C(IH)
   38 SUMSO=SUMSO+C1(IH,IZ)*S(IH)
      M(IZ)=(SUMCE+SUMCO-SUMSE-SUMSO)*SCALE
      N(IZ)=(SUMCE-SUMCO+SUMSE-SUMSO)*SCALE
      M(IZ+10)=(SUMCE-SUMCO-SUMSE+SUMSO)*SCALE
   35 N(IZ+10)=(SUMCE+SUMCO+SUMSE+SUMSO)*SCALE
    6 FORMAT(2HE ,3I3,1X,10I6)


C     FOURIER SUMMATION THIRD STAGE
C     SUM OVER K
      DIMENSIONE(20,10),F(20,10),C(20),S(20),M(20),N(20)
      READ3,YDIV,NCALC,IZMIN,IZMAX,KMAX,SCALE,ZERO
    3 FORMAT(F5.0,4I5,F10.5,F10.5)
      KMA=KMAX
      KMAX=KMAX+1
      NHALF=YDIV/2.0
      YDIV=6.2832/YDIV
      C(1)=1.0
      S(1)=0.0
      DO60M1=1,20
      M(M1)=0
   60 N(M1)=0
    9 DO12IK=1,KMAX
      READ5,K,IX,IA,M(1),M(2),M(3),M(4),M(5),M(6),M(7),M(8),M(9),M(10)
    5 FORMAT(2H  ,3I3,1X,10I6)
      DO12IZ=IZMIN,IZMAX
   12 E(K+1,IZ)=M(IZ)
      DO14IK=1,KMA
      READ5,K,IX,I2,M(1),M(2),M(3),M(4),M(5),M(6),M(7),M(8),M(9),M(10)
      IA=I2
      DO14IZ=IZMIN,IZMAX
   14 F(K+1,IZ)=M(IZ)
      DO100IY=1,NCALC
      IY1=IY-1
      DY=IY1
```

```
      C(2)=COSF(YDIV*DY)
      S(2)=SINF(YDIV*DY)
      DO27IN=3,KMAX
      C(IN)=2.0*C(IN-1)*C(2)-C(IN-2)
   27 S(IN)=2.0*S(IN-1)*C(2)-S(IN-2)
      DO35IZ=IZMIN,IZMAX
      SUMCO=0.0
      SUMSO=0.0
      SUMCE=0.0
      SUMSE=0.0
      DO28IK=1,KMAX,2
      SUMCE=SUMCE+E(IK,IZ)*C(IK)
   28 SUMSE=SUMSE+F(IK,IZ)*S(IK)
      DO38IK=2,KMAX,2
      SUMCO=SUMCO+E(IK,IZ)*C(IK)
   38 SUMSO=SUMSO+F(IK,IZ)*S(IK)
      M(IZ)=(SUMCE+SUMCO-SUMSE-SUMSO)*SCALE+ZERO
      IY2=NHALF-IY1
      N(IZ)=(SUMCE-SUMCO+SUMSE-SUMSO)*SCALE+ZERO
      IY3=IY1+NHALF
      M(IZ+10)=(SUMCE-SUMCO-SUMSE+SUMSO)*SCALE+ZERO
      IY4=IY2+NHALF
   35 N(IZ+10)=(SUMCE+SUMCO+SUMSE+SUMSO)*SCALE+ZERO
      IF(SENSESWITCH1)31,30
   31 PRINT6,IX,IY1,IA,M(1),M(2),M(3),M(4),M(5),M(6),M(7),M(8),M(9),M(10)
      PRINT6,IX,IY2,IA,N(1),N(2),N(3),N(4),N(5),N(6),N(7),N(8),N(9),N(10)
PRINT6,IX,IY3,IA,M(11),M(12),M(13),M(14),M(15),M(16),M(17),M(18),M(19),M(20)
PRINT6,IX,IY4,IA,N(11),N(12),N(13),N(14),N(15),N(16),N(17),N(18),N(19),N(20)
   30 PUNCH6,IX,IY1,IA,M(1),M(2),M(3),M(4),M(5),M(6),M(7),M(8),M(9),M(10)
      PUNCH6,IX,IY2,IA,N(1),N(2),N(3),N(4),N(5),N(6),N(7),N(8),N(9),N(10)
PUNCH6,IX,IY3,IA,M(11),M(12),M(13),M(14),M(15),M(16),M(17),M(18),M(19),M(20)
PUNCH6,IX,IY4,IA,N(11),N(12),N(13),N(14),N(15),N(16),N(17),N(18),N(19),N(20)
    6 FORMAT(1HX,I3,3H  Y,I3,4H  ZR,I2,4H    ,10I4)
  100 CONTINUE
      GOTO9
      END
```

PROGRAM 3. STRUCTURE REFINEMENT.

An IBM 7090 program for the space group $P2_1/n$.

Description

The program operates cyclically, refining approximately known structural parameters by "Differential difference" Fourier syntheses. Descriptions of the method and other features of the program are given in Chapter 4 of this thesis.

Limitations

$h < 10$ $k < 19$ $l < 31$

Maxm. of 46 atoms each with an individual isotropic temperature exponent.

Maxm. of 5 types of atoms.

FORTRAN names

S(N, I)	Scattering factor of atom I at $\sin\theta/\lambda = 0.005N$
AREAL, BREAL, CREAL	a, b, c
BETA	β in radians
JMAX, KMAX, LMAX	h_{max}, k_{max}, l_{max}
SINMX	Maxm. value of $\sin\theta$
WAVEL	Wavelength (in A^o)
K1, J1	k, h
A(J, L)	$F_o(h,k,l) = F_o(J1, K1, L-1)$
B(J, L)	$F_o(\bar{h},k,l) = F_o(J1, K1, L-1)$
A(J, 32)	Number of coefficients $F_o(h,k,l)$ for $h = J1$, $k = K1$
B(J, 32)	Same for $F_o(\bar{h},k,l)$
NMBRC	Number of atoms to be included but not refined.

NMBRV	Number of atoms to be refined
MCYCL	Maxm. number of cycles
FMINO	Minm. F_o observable at L.p = 1
RAB	Maxm. initial R value
DEC	Minm. decrement in R per cycle.
SHFTM	If all coordinate shifts are less than "SHFTM", the program will terminate
FUDGX	Coordinate shift "fudge factor"
FUDGB	Thermal parameter shift "fudge factor"
FK	If $w(F_o-F_c)$ is less than FK, omit this coefficient from the difference synthesis
FMK	If $F_o = 0$ and $2F_{om} \quad F_c \quad F_{om}$, include the coefficient F_c - FMK.F_{om} where F_{om} is the minm. observable value of F_o.
FCK	If FCK.$F_o \quad F_c$ or FCK.$F_c \quad F_o$, omit this coefficient from the difference synthesis. (Typically FCK = 2)
P(1,I)	Atom type
P(2,I), P(3,I), P(4,I)	x_I, y_I, z_I (fractional)
P(5,I)	Temperature exponent B_I
P(6,I)	A_I in the electron density approximation $\rho_I(r) = A_I \exp(-p_I r^2)$
P(7,I)	p_I corresponding to A_I

```
*D5    B W MATTHEWS   UNIVERSITY OF ADELAIDE
C      STRUCTURE REFINEMENT    ISOTROPIC TEMP FACTORS  P21/N
C      PROGRAM FOR IBM 7090

      COMMONA,B,AC,BC,AD,BD,CX,SX,CY,SY,CZ,SZ,S,P,FSUM,AREAL,BREAL,CREAL
     1,CBSTR,SBETA,IJMAX,JMAX,IKMAX,KMAX,ILMAX,LMAX,NMBR,NMBR1,NMBRC,FK,
     2FMK,FCK,SHFTM,WAVEL,MCYCL,FUDGX,FUDGB
      DIMENSIONA(10,32),B(10,32),AC(10,32),BC(10,32),
     1AD(10,19,32),BD(10,19,32),
     2CX(10,46),SX(10,46),CY(19,46),SY(19,46),CZ(31,46),SZ(31,46),
     3S(140,5),P(7,46),FSUM(46),
     4R(19),RFO(19),FOSMA(19),FCSMA(19),PDELA(19),FCOA(19)
      INSF(T)=(T+0.0116)*130.0
      WRITEOUTPUTTAPE3,17
      PRINT17
   17 FORMAT(1H ,44HLOAD UNI TAPE NUMBER 6 (MATTHEWS TAPE) ON B8/1H ,53H
     1THIS PROGRAM ALSO REQUIRES SCRATCH TAPES ON B3 AND A4/1H ,21HPUSH
     2START WHEN READY/////)
      PAUSE
      REWIND18
      REWIND13
      REWIND4
      READINPUTTAPE2,4,S
    4 FORMAT(14F5.2)
      READINPUTTAPE2,1,AREAL,BREAL,CREAL,BETA
    1 FORMAT(4F10.5)
      READINPUTTAPE2,3,JMAX,KMAX,LMAX,SINMX,WAVEL
    3 FORMAT(3I5,2F10.5)
      CBSTR=-COSF(BETA)
      SBETA=SINF(BETA)
      WAVE=WAVEL/2.0
      ASTAR=WAVE/(AREAL*SBETA)
      BSTAR=WAVE/(BREAL)
      CSTAR=WAVE/(CREAL*SBETA)
      BETAS=3.1413-BETA
      CTWO=CSTAR**2
```

```
      ATWO=ASTAR**2
      BTWO=BSTAR**2
      PROD=ASTAR*CSTAR*CBSTR*2.0
      IJMAX=JMAX+1
      IKMAX=KMAX+1
      ILMAX=LMAX+1
      DO10K=1,IKMAX
      DO10J=1,IJMAX
      DO10L=1,32
      AD(J,K,L)=0.0
   10 BD(J,K,L)=0.0
 3001 READTAPE18,K
      IF(K+1)3001,3002,3001
 3002 DO3301K=1,IKMAX
      DO3301J=1,IJMAX
 3302 READTAPE18,K1,J1,(A(J,L),L=1,32),(B(J,L),L=1,32)
      IF(J1-J)3302,3605,3302
 3605 AD(J,K,32)=A(J,32)
 3301 BD(J,K,32)=B(J,32)
      REWIND18
   21 READINPUTTAPE2,503,NMBRC,NMBRV,MCYCL,FMINO,RAB,DEC,SHFTM
  503 FORMAT(3I5,4F10.5)
      NMBR=NMBRC+NMBRV
      NMBR1=NMBRC+1
      FMIN4=FMINO*4.
      READINPUTTAPE2,1000,FUDGX,FUDGB,FK,FMK,FCK
 1000 FORMAT(5F10.5)
      DO139I=1,NMBR
  139 READINPUTTAPE2,8,(P(JA,I),JA=1,7)
    8 FORMAT(7F10.5)
      DO504I=1,NMBR
      SX(1,I)=0.0
      CX(1,I)=1.0
      SY(1,I)=0.0
      CY(1,I)=1.0
      SZ(1,I)=0.0
```

```
504 CZ(1,I)=1.0
    IF(NMBRC)291,291,509
509 DO508I=1,NMBRC
    SX(2,I)=SINF(6.283*P(2,I))
    CX(2,I)=COSF(6.283*P(2,I))
    SY(2,I)=SINF(6.283*P(3,I))
    CY(2,I)=COSF(6.283*P(3,I))
    SZ(2,I)=SINF(6.283*P(4,I))
    CZ(2,I)=COSF(6.283*P(4,I))
    DO505J=3,IJMAX
    CX(J,I)=2.0*CX(J-1,I)*CX(2,I)-CX(J-2,I)
505 SX(J,I)=2.0*SX(J-1,I)*CX(2,I)-SX(J-2,I)
    DO506K=3,IKMAX
    CY(K,I)=2.0*CY(K-1,I)*CY(2,I)-CY(K-2,I)
506 SY(K,I)=2.0*SY(K-1,I)*CY(2,I)-SY(K-2,I)
    DO507L=3,ILMAX
    CZ(L,I)=2.0*CZ(L-1,I)*CZ(2,I)-CZ(L-2,I)
507 SZ(L,I)=2.0*SZ(L-1,I)*CZ(2,I)-SZ(L-2,I)
    DO508K=1,IKMAX
    CY(K,I)=4.0*CY(K,I)
508 SY(K,I)=4.0*SY(K,I)
291 N5=0
    K1=-1
    WRITETAPE13,K1
    DO290K=1,IKMAX
    DK=K-1
    DK2=DK*DK*BTWO
    DO14J=1,IJMAX
    DO14L=1,ILMAX
    AC(J,L)=0.
 14 BC(J,L)=0.
    DO190J=1,IJMAX
    DJ=J-1
    DJ2=DJ*DJ*ATWO
    ILM=BD(J,K,32)
    IF(ILM)3005,3005,3006
```

```
3006 DO90L=1,ILM
     DL=L-1
     AB=DL*DL*CTWO+DK2+DJ2
     AP=PROD*DJ*DL
     THETA=SQRTF(AB+AP)
     THETB=SQRTF(AB-AP)
     IF(THETA-SINMX)510,511,511
 511 AD(J,K,L)=0.0
     TEMPA=0.0
     GOTO514
 510 AD(J,K,L)=THETA
     N5=N5+1
     TEMPA=1.0
 514 IF(THETB-SINMX)513,91,91
  91 BD(J,K,L)=0.0
     TEMPB=0.0
     GOTO515
 513 BD(J,K,L)=THETB
     N5=N5+1
     TEMPB=1.0
 515 IF(TEMPA+TEMPB-0.9)3390,422,422
3390 BD(J,K,32)=L-1
     GOTO3005
 422 IF(NMBRC)90,90,512
 512 IDS=K+J+L+1
     ISA=INSF(THETA)
     ISB=INSF(THETB)
     THOL2=(THETA/WAVEL)*(THETA/WAVEL)
     THOL3=(THETB/WAVEL)*(THETB/WAVEL)
     IF(IDS/2-(IDS+1)/2)36,35,35
  35 DO60I=1,NMBRC
     M=P(1,I)
     CC=CX(J,I)*CZ(L,I)
     SS=SX(J,I)*SZ(L,I)
     AC(J,L)=AC(J,L)+(CY(K,I)*(CC-SS)*S(ISA,M))/EXPF(P(5,I)*THOL2)
  60 BC(J,L)=BC(J,L)+(CY(K,I)*(CC+SS)*S(ISB,M))/EXPF(P(5,I)*THOL3)
```

```
      GOTO90
   36 DO61I=1,NMBRC
      M=P(1,I)
      SC=SX(J,I)*CZ(L,I)
      CS=CX(J,I)*SZ(L,I)
      AC(J,L)=AC(J,L)-(SY(K,I)*(SC+CS)*S(ISA,M))/EXPF(P(5,I)*THOL2)
   61 BC(J,L)=BC(J,L)+(SY(K,I)*(SC-CS)*S(ISB,M))/EXPF(P(5,I)*THOL3)
   90 CONTINUE
 3005 WRITETAPE13,K,J,(AC(J,L),L=1,ILMAX),(BC(J,L),L=1,ILMAX)
  190 CONTINUE
  290 CONTINUE
      REWIND13
      WRITEOUTPUTTAPE3,1290
 1290 FORMAT(1H ,30HCONSTANT PART OF FC CALCULATED)
      DK=KMAX
      DJ=JMAX
      DL=LMAX
 2001 READTAPE18,K
      IF(K+1)2001,2002,2001
 2002 DO2003K=1,IKMAX
      DO2003J=1,IJMAX
 2303 READTAPE18,K1,J1,(A(J,L),L=1,32),(B(J,L),L=1,32)
      IF(J1-J)2303,3505,2303
 3505 DO2005L=1,ILMAX
      IF(A(J,L))2005,2007,2005
 2007 AD(J,K,L)=0.0
 2005 CONTINUE
 2003 CONTINUE
      REWIND18
      DO901I=NMBR1,NMBR
      F1=0.0
      F11=0.0
      F111=0.0
      M=P(1,I).
      DO902J=1,IJMAX
      IF(AD(J,1,1))902,902,907
```

```
  907 ISA=INSF(AD(J,1,1))
      F1=F1+(AD(J,1,1)**4)*S(ISA,M)/EXPF(P(5,I)*(AD(J,1,1)/WAVEL)*(AD(J,
     11,1)/WAVEL))
  902 CONTINUE
      DO903K=2,IKMAX
      DO903L=2,ILMAX
      IF(AD(1,K,L))903,903,904
  904 ISA=INSF(AD(1,K,L))
      F11=F11+(AD(1,K,L)**4)*S(ISA,M)/EXPF(P(5,I)*(AD(1,K,L)/WAVEL)*(AD(
     11,K,L)/WAVEL))
  903 CONTINUE
      DO1905K=2,IKMAX
      DO1905J=2,IJMAX
      ILM=BD(J,K,32)
      IF(ILM)1905,1905,3008
 3008 DO905L=2,ILM
      IF(AD(J,K,L))905,905,906
  906 ISA=INSF(AD(J,K,L))
      F111=F111+(AD(J,K,L)**4)*S(ISA,M)/EXPF(P(5,I)*(AD(J,K,L)/WAVEL)*(A
     1D(J,K,L)/WAVEL))
  905 CONTINUE
 1905 CONTINUE
  901 FSUM(I)=2.0*F1*(1.0+DK/DJ+DL/DJ)+4.0*F11*(1.0+DJ/DK+DJ/DL)+12.57*F
     1111/BETAS
      NCYCL=-1
  293 NCYCL=NCYCL+1
      K=-1
      WRITETAPE 4,K
      N1=0
      N2=0
      N3=0
      N4=0
      DO604I=NMBR1,NMBR
      SX(2,I)=SINF(6.283*P(2,I))
      CX(2,I)=COSF(6.283*P(2,I))
      SY(2,I)=SINF(6.283*P(3,I))
```

```
      CY(2,I)=COSF(6.283*P(3,I))
      SZ(2,I)=SINF(6.283*P(4,I))
      CZ(2,I)=COSF(6.283*P(4,I))
      DO605J=3,IJMAX
      CX(J,I)=2.0*CX(J-1,I)*CX(2,I)-CX(J-2,I)
  605 SX(J,I)=2.0*SX(J-1,I)*CX(2,I)-SX(J-2,I)
      DO606K=3,IKMAX
      CY(K,I)=2.0*CY(K-1,I)*CY(2,I)-CY(K-2,I)
  606 SY(K,I)=2.0*SY(K-1,I)*CY(2,I)-SY(K-2,I)
      DO607L=3,ILMAX
      CZ(L,I)=2.0*CZ(L-1,I)*CZ(2,I)-CZ(L-2,I)
  607 SZ(L,I)=2.0*SZ(L-1,I)*CZ(2,I)-SZ(L-2,I)
      DO608K=1,IKMAX
      CY(K,I)=4.0*CY(K,I)
  608 SY(K,I)=4.0*SY(K,I)
  604 CONTINUE
      FOSMB=0.0
      FCSMB=0.0
      PDELB=0.0
      FCOB=0.0
      D2HH=0.
      D2KK=0.
      D2LL=0.
      SCOFF=0.0
      SCOF2=0.0
 2008 READTAPE13,K1
      IF(K1+1)2008,2009,2008
 2009 CONTINUE
 2010 READTAPE18,K1
      IF(K1+1)2010,2011,2010
 2011 CONTINUE
      DO790K=1,IKMAX
      DK=K-1
      DK2=DK*DK*BTWO
 1100 FOSMA(K)=0.
      FCSMA(K)=0.
```

```
      PDELA(K)=0.
      FCOA(K)=0.
      DO690J=1,IJMAX
      DJ=J-1
      DJ2=DJ*DJ*ATWO
      READTAPE13,K1,J1,(AC(J1,L),L=1,ILMAX),(BC(J1,L),L=1,ILMAX)
 2012 READTAPE18,K1,J1,(A(J,L),L=1,32),(B(J,L),L=1,32)
      IF(J1-J)2012,2013,2012
 2013 CONTINUE
      ILM=BD(J,K,32)
      IF(ILM)3009,3009,3010
 3010 DO590L=1,ILM
      DL=L-1
      AB=DL*DL*CTWO+DJ2+DK2
      AP=PROD*DJ*DL
      THETA=SQRTF(AB+AP)
      THETB=SQRTF(AB-AP)
      IF(THETA-SINMX)22,121,121
  121 TEMPA=0.0
      THETA=0.0
      GOTO23
   22 TEMPA=1.0
   23 IF(THETB-SINMX)25,24,24
   24 TEMPB=0.0
      THETB=0.0
      GOTO26
   25 TEMPB=1.0
   26 IF(TEMPA+TEMPB-0.9)3009,27,27
   27 IDS=K+J+L+1
      ISA=INSF(THETA)
      ISB=INSF(THETB)
      THOL2=(THETA/WAVEL)*(THETA/WAVEL)
      THOL3=(THETB/WAVEL)*(THETB/WAVEL)
      ASUM=0.0
      BSUM=0.0
      IF(IDS/2-(IDS+1)/2)536,535,535
```

```
535 DO560I=NMBR1,NMBR
    M=P(1,I)
    CC=CX(J,I)*CZ(L,I)
    SS=SX(J,I)*SZ(L,I)
    ASUM=ASUM+(CY(K,I)*(CC-SS)*S(ISA,M))/EXPF(P(5,I)*THOL2)
560 BSUM=BSUM+(CY(K,I)*(CC+SS)*S(ISB,M))/EXPF(P(5,I)*THOL3)
    GOTO562
536 DO561I=NMBR1,NMBR
    M=P(1,I)
    SC=SX(J,I)*CZ(L,I)
    CS=CX(J,I)*SZ(L,I)
    ASUM=ASUM-(SY(K,I)*(SC+CS)*S(ISA,M))/EXPF(P(5,I)*THOL2)
561 BSUM=BSUM+(SY(K,I)*(SC-CS)*S(ISB,M))/EXPF(P(5,I)*THOL3)
562 AD(J,K,L)=(AC(J,L)+ASUM)*TEMPA
    BD(J,K,L)=(BC(J,L)+BSUM)*TEMPB
    PCALA=ABSF(AD(J,K,L))
    PCALB=ABSF(BD(J,K,L))
    IF(A(J,L))108,108,109
108 FCOA(K)=FCOA(K)+PCALA
    SSA=(THETA**2)-(THETA**2)**2
    TIL=SQRTF(SSA*(1.0-((DK/(2.0*BREAL))**2)/THOL2))/(1.0-2.0*SSA)
    FMIN=FMINO*SQRTF(TIL)
    IF(PCALA-FMIN)115,115,356
356 IF(PCALA-2.0*FMIN)491,491,492
492 N3=N3+1
    GOTO115
491 A(J,L)=-PCALA+FMIN*FMK
    GOTO115
109 FOSMA(K)=FOSMA(K)+A(J,L)
    FCSMA(K)=FCSMA(K)+PCALA
    N4=N4+1
115 IF(B(J,L))112,112,114
112 FCOA(K)=FCOA(K)+PCALB
    SSB=(THETB**2)-(THETB**2)**2
    TIL=SQRTF(SSB*(1.0-((DK/(2.0*BREAL))**2)/THOL3))/(1.0-2.0*SSB)
    FMIN=FMINO*SQRTF(TIL)
```

```
      IF(PCALB-FMIN)590,590,357
 357  IF(PCALB-2.0*FMIN)493,493,594
 594  N3=N3+1
      GOTO590
 493  B(J,L)=-PCALB+FMIN*FMK
      GOTO590
 114  FOSMA(K)=FOSMA(K)+B(J,L)
      FCSMA(K)=FCSMA(K)+PCALB
      N4=N4+1
 590  CONTINUE
3009  WRITETAPE 4,K,J,(A(J,L),L=1,32),(B(J,L),L=1,32)
 690  CONTINUE
      FOSMB=FOSMB+FOSMA(K)
      FCSMB=FCSMB+FCSMA(K)
      FCOB=FCOB+FCOA(K)
 790  CONTINUE
      REWIND18
      REWIND4
      REWIND13
      SCALE=FCSMB/FOSMB
2014  READTAPE 4,K1
      IF(K1+1)2014,2015,2014
2015  CONTINUE
      DO791K=1,IKMAX
      DK2=(K-1)*(K-1)
      DO691J=1,IJMAX
      DJ2=(J-1)*(J-1)
      READTAPE 4,K1,J1,(A(J1,L),L=1,32),(B(J1,L),L=1,32)
      ILM=BD(J,K,32)
      IF(ILM)691,691,3012
3012  DO591L=1,ILM
      DL2=(L-1)*(L-1)
      IF(A(J,L))350,350,351
 351  ASK=A(J,L)*SCALE
      GOTO352
 350  ASK=0.0
```

```
 352 IF(B(J,L))353,353,354
 354 BSK=B(J,L)*SCALE
     GOTO355
 353 BSK=0.0
 355 IF(AD(J,K,L))408,410,410
 408 PCALA=-AD(J,K,L)
     SIGNA=-1.0
     GOTO409
 410 PCALA=AD(J,K,L)
     SIGNA=1.0
 409 PDELA(K)=PDELA(K)+ABSF(ASK-PCALA)
     IF((FCK*ASK-PCALA)*(FCK*PCALA-ASK)-0.0001)411,1412,1412
1412 IF(ASK-FMIN4)3411,3411,3412
3411 ASKP=ASK-PCALA
     A11=ASKP*ASKP
     GOTO3413
3412 ASKP=(ASK-PCALA)*FMIN4/ASK
     A11=(ASK-PCALA)*(ASK-PCALA)
3413 IF(ABSF(ASKP)-FK)412,411,411
 411 AD(J,K,L)=0.
     A11=0.
     GOTO413
 412 AD(J,K,L)=SIGNA*ASKP
     N1=N1+1
 413 IF(A(J,L))358,371,371
 358 AD(J,K,L)=SIGNA*A(J,L)
     N2=N2+1
 371 IF(BD(J,K,L))414,416,416
 414 PCALB=-BD(J,K,L)
     SIGNB=-1.0
     GOTO417
 416 PCALB=BD(J,K,L)
     SIGNB=1.0
 417 PDELA(K)=PDELA(K)+ABSF(BSK-PCALB)
     IF((FCK*BSK-PCALB)*(FCK*PCALB-BSK)-0.0001)418,1419,1419
1419 IF(BSK-FMIN4)3418,3419,3419
```

```
3418 BSKP=BSK-PCALB
     B11=BSKP*BSKP
     GOTO3420
3419 BSKP=(BSK-PCALB)*FMIN4/BSK
     B11=(BSK-PCALB)*(BSK-PCALB)
3420 IF(ABSF(BSKP)-FK)419,418,418
 418 BD(J,K,L)=0.0
     B11=0.
     GOTO0372
 419 BD(J,K,L)=SIGNB*BSKP
     N1=N1+1
 372 IF(B(J,L))359,1591,1591
 359 BD(J,K,L)=SIGNB*B(J,L)
     N2=N2+1
1591 SCOFF=SCOFF+ABSF(AD(J,K,L))+ABSF(BD(J,K,L))
     SCOF2=SCOF2+AD(J,K,L)*AD(J,K,L)+BD(J,K,L)*BD(J,K,L)
     ADB=A11+B11
     MM=(J-1)*(K-1)*(L-1)
     IF(MM)1593,1592,1593
1592 ADB=0.5*ADB
     MM=(J-1)*(K-1)+(J-1)*(L-1)+(K-1)*(L-1)
     IF(MM)1593,1595,1593
1595 ADB=0.5*ADB
1593 D2HH=D2HH+ADB*DJ2
     D2KK=D2KK+ADB*DK2
     D2LL=D2LL+ADB*DL2
 591 CONTINUE
 691 CONTINUE
     PDELB=PDELB+PDELA(K)
     R(K)=PDELA(K)/FCSMA(K)
     RFO(K)=(PDELA(K)-FCOA(K))/FCSMA(K)
 791 CONTINUE
     D2HH=4.*D2HH
     D2KK=4.*D2KK
     D2LL=4.*D2LL
     REWIND4
```

```
      TDEL=PDELB-FCOB
      RA=TDEL/FOSMB
      TFC=FCSMB+FCOB
      REL=PDELB/FOSMB
      IF(NMBRC)2281,2281,2282
 2282 WRITEOUTPUTTAPE3,281
  281 FORMAT(1H1,11HFIXED ATOMS,//)
      DO167I=1,NMBRC
      WRITEOUTPUTTAPE3,168,(P(J,I),J=1,7)
  167 PUNCH8,(P(J,I),J=1,7)
  168 FORMAT(1H ,4HTYPE,F3.0,4H X= ,F6.4,4H Y= ,F6.4,4H Z= ,F6.4,5H  B=
     1,F6.3,5H  D= ,F6.2,5H  P= ,F6.3)
 2281 IF(NCYCL)277,277,278
  278 WRITEOUTPUTTAPE3,282
  282 FORMAT(1H //14H REFINED ATOMS//)
      GOTO280
  277 WRITEOUTPUTTAPE3,279
  279 FORMAT(1H //33H INITIAL PARAMETERS TO BE REFINED//)
  280 DO567I=NMBR1,NMBR
      WRITEOUTPUTTAPE3,168,(P(J,I),J=1,7)
  567 PUNCH8,(P(J,I),J=1,7)
      WRITEOUTPUTTAPE3,169
  169 FORMAT(1H ///63H LAYER                   H0L   H1L   H2L   H3L   H4L
     1H5L   ...ETC.)
      WRITEOUTPUTTAPE3,171,(R(K),K=1,IKMAX)
  171 FORMAT(1H ,17HR (INC. FO = 0) =,10F6.3)
      WRITEOUTPUTTAPE3,172,(RFO(K),K=1,IKMAX)
  172 FORMAT(1H ,17HR (EXC. FO = 0) =,10F6.3)
      WRITEOUTPUTTAPE3,93,FOSMB
   93 FORMAT(1H /16H SUM OF F OBS  =,F10.1//)
      WRITEOUTPUTTAPE3,170,SCALE
  170 FORMAT(1H /16H SCALE FACTOR = ,F8.4//)
      WRITEOUTPUTTAPE3,97
   97 FORMAT(1H ,19HINCLUDING F OBS = 0)
      WRITEOUTPUTTAPE3,173,TFC
  173 FORMAT(1H ,15HSUM OF F CALC =,F10.1)
```

```
      WRITEOUTPUTTAPE3,174,PDELB
  174 FORMAT(1H ,16HSUM OF FO - FC =,F9.1)
      WRITEOUTPUTTAPE3,175,REL
  175 FORMAT(1H ,21HRELIABILITY INDEX R =,F6.4//)
      PRINT175,REL
      WRITEOUTPUTTAPE3,176
  176 FORMAT(1H ,19HEXCLUDING F OBS = 0)
      WRITEOUTPUTTAPE3,173,FCSMB
      WRITEOUTPUTTAPE3,174,TDEL
      WRITEOUTPUTTAPE3,175,RA
      PRINT175,RA
      WRITEOUTPUTTAPE3,484,N5
  484 FORMAT(1H ,37H TOTAL NUMBER OF SPECTRA CALCULATED =,I6)
      WRITEOUTPUTTAPE3,485,N4
  485 FORMAT(1H ,44H TOTAL NUMBER OF OBSERVED NON ZERO SPECTRA =,I6)
      WRITEOUTPUTTAPE3,483,N3
  483 FORMAT(1H ,59H NUMBER OF F CALC GREATER THAN TWICE THE MIN F OBSER
     1VABLE =,I4)
      WRITEOUTPUTTAPE3,1597
 1597 FORMAT(1H //61H SUMMATIONS FOR CALCULATION OF COORDINATE STANDARD
     1DEVIATIONS)
      WRITEOUTPUTTAPE3,1598,D2HH,D2KK,D2LL
 1598 FORMAT(1H ,20H SUM OF H2(FO-FC)2 =,F11.1/1H ,20H SUM OF K2(FO-FC)2
     1 =,F11.1/1H ,20H SUM OF L2(FO-FC)2 =,F11.1)
      WRITEOUTPUTTAPE3,482
  482 FORMAT(1H //19H FOR THE NEXT CYCLE)
      WRITEOUTPUTTAPE3,481,N1
  481 FORMAT(1H ,56H NUMBER OF COEFFS WITH F NOT OBSERVED AS ZERO INCLUD
     1ED =,I6)
      WRITEOUTPUTTAPE3,340,N2
  340 FORMAT(1H ,74H NUMBER OF COEFFS WITH F CALC GREATER THAN THE MIN F
     1 OBSERVABLE INCLUDED =,I5)
      WRITEOUTPUTTAPE3,1481,SCOFF
 1481 FORMAT(1H ,29H SUM OF ALL COEFFS INCLUDED =,F9.1)
      WRITEOUTPUTTAPE3,1482,SCOF2
 1482 FORMAT(1H ,40H SUM OF SQUARES OF ALL COEFFS INCLUDED =,F10.1)
```

```
      WRITEOUTPUTTAPE3,381,NCYCL
      PRINT381,NCYCL
  381 FORMAT(1H ///13H END OF CYCLE,I3)
      IF(MCYCL-NCYCL)999,999,100
  100 IF(RAB-RA)999,79,79
   79 RAB=RA-DEC
      CALLFRED
      GOTO293
  999 PRINT1999
 1999 FORMAT(1H ,32HREMOVE UNI TAPE NUMBER 6 FROM B8/1H ,15HJOB IS FINIS
     1HED/////)
      CALLEXIT
      END



      SUBROUTINEFRED
      COMMONA,B,AC,BC,AD,BD,CX,SX,CY,SY,CZ,SZ,S,P,FSUM,AREAL,BREAL,CREAL
     1,CBSTR,SBETA,IJMAX,JMAX,IKMAX,KMAX,ILMAX,LMAX,NMBR,NMBR1,NMBRC,FK,
     2FMK,FCK,SHFTM,WAVEL,MCYCL,FUDGX,FUDGB
      DIMENSIONA(10,32),B(10,32),AC(10,32),BC(10,32),
     1AD(10,19,32),BD(10,19,32),
     2CX(10,46),SX(10,46),CY(19,46),SY(19,46),CZ(31,46),SZ(31,46),
     3S(140,5),P(7,46),FSUM(46),
     4R(19),RFO(19),FOSMA(19),FCSMA(19),PDELA(19),FCOA(19),
     5C1(10,19),C1Z(10,19),C1ZZ(10,19),D1(10,19),D1Z(10,19),D1ZZ(10,19),
     6C2(10,19),C2Z(10,19),C2ZZ(10,19),D2(10,19),D2Z(10,19),D2ZZ(10,19),
     7E(19),EZ(19),EZZ(19),F(19),FZ(19),FZZ(19),
     8EX(19),EXX(19),FX(19),FXX(19)
      CB1=1.0-CBSTR**2
      VOL=AREAL*BREAL*CREAL*SBETA
      DX1=0.0
      DXSUM=0.0
      DYSUM=0.0
      DZSUM=0.0
      WRITEOUTPUTTAPE3,183
```

```
183 FORMAT(1H1,115HCOORDINATE SHIFTS IN ANGSTROMS,  CHANGE IN TEMPERAT
   1URE EXPONENT B,  AND DENSITY IN ELECTRONS PER CUBIC ANGSTROM OF ,/
   268H THE DIFFERENCE SYNTHESIS SIGMA(FO-FC) AT THE ATOMIC POSITION X
   3,Y,Z.////)
    WRITEOUTPUTTAPE3,997
997 FORMAT(1H ,34H         COORDINATE SHIFTS         ,14H   B CHANGE
   1,45HSECOND DERIVATIVES OF THE DIFFERENCE DENSITY ,20H  DIFFERENCE
   2DENSITY///)
    DO200K=1,IKMAX
    DO200L=1,ILMAX
    DO200J=1,IJMAX
    FA=AD(J,K,L)
    FB=BD(J,K,L)
    AD(J,K,L)=FA+FB
200 BD(J,K,L)=FA-FB
    AD(1,1,1)=0.0
    DO201K=1,IKMAX
    DO201L=1,ILMAX
    AD(1,K,L)=0.5*AD(1,K,L)
201 BD(1,K,L)=0.5*BD(1,K,L)
    DO202K=1,IKMAX
    DO202J=1,IJMAX
    AD(J,K,1)=0.5*AD(J,K,1)
202 BD(J,K,1)=0.5*BD(J,K,1)
    DO203L=1,ILMAX
    DO203J=1,IJMAX
    AD(J,1,L)=0.5*AD(J,1,L)
203 BD(J,1,L)=0.5*BD(J,1,L)
    DO299I=NMBR1,NMBR
    DO995K=1,IKMAX
    CY(K,I)=0.25*CY(K,I)
995 SY(K,I)=0.25*SY(K,I)
    DO622J=1,IJMAX
    DO622K=1,IKMAX
    C1(J,K)=0.0
    C1Z(J,K)=0.0
```

```
      C1ZZ(J,K)=0.0
      C2(J,K)=0.0
      C2Z(J,K)=0.0
      C2ZZ(J,K)=0.0
      D2(J,K)=0.0
      D2Z(J,K)=0.0
      D2ZZ(J,K)=0.0
      D1(J,K)=0.0
      D1Z(J,K)=0.0
  622 D1ZZ(J,K)=0.0
      DO623J=1,IJMAX,2
      J1=J+1
      DO623K=1,IKMAX,2
      K1=K+1
      ML=BD(J,K,32)
      IF(ML)623,623,1623
 1623 DO2623L=1,ML,2
      DL=L-1
      DL1=L
      L1=L+1
      C1(J,K)=C1(J,K)+AD(J,K,L)*CZ(L,I)
      C1Z(J,K)=C1Z(J,K)-AD(J,K,L)*DL*SZ(L,I)
      C1ZZ(J,K)=C1ZZ(J,K)-AD(J,K,L)*DL*DL*CZ(L,I)
      D1(J,K)=D1(J,K)+BD(J,K,L)*SZ(L,I)
      D1Z(J,K)=D1Z(J,K)+BD(J,K,L)*DL*CZ(L,I)
      D1ZZ(J,K)=D1ZZ(J,K)-BD(J,K,L)*DL*DL*SZ(L,I)
      C2(J,K)=C2(J,K)+AD(J,K,L1)*SZ(L1,I)
      C2Z(J,K)=C2Z(J,K)+AD(J,K,L1)*DL1*CZ(L1,I)
      C2ZZ(J,K)=C2ZZ(J,K)-AD(J,K,L1)*DL1*DL1*SZ(L1,I)
      D2(J,K)=D2(J,K)+BD(J,K,L1)*CZ(L1,I)
      D2Z(J,K)=D2Z(J,K)-BD(J,K,L1)*DL1*SZ(L1,I)
      D2ZZ(J,K)=D2ZZ(J,K)-BD(J,K,L1)*DL1*DL1*CZ(L1,I)
      C1(J1,K1)=C1(J1,K1)+AD(J1,K1,L)*CZ(L,I)
      C1Z(J1,K1)=C1Z(J1,K1)-AD(J1,K1,L)*DL*SZ(L,I)
      C1ZZ(J1,K1)=C1ZZ(J1,K1)-AD(J1,K1,L)*DL*DL*CZ(L,I)
      D1(J1,K1)=D1(J1,K1)+BD(J1,K1,L)*SZ(L,I)
```

```
      D1Z(J1,K1)=D1Z(J1,K1)+BD(J1,K1,L)*DL*CZ(L,I)
      D1ZZ(J1,K1)=D1ZZ(J1,K1)-BD(J1,K1,L)*DL*DL*SZ(L,I)
      C2(J1,K1)=C2(J1,K1)+AD(J1,K1,L1)*SZ(L1,I)
      C2Z(J1,K1)=C2Z(J1,K1)+AD(J1,K1,L1)*DL1*CZ(L1,I)
      C2ZZ(J1,K1)=C2ZZ(J1,K1)-AD(J1,K1,L1)*DL1*DL1*SZ(L1,I)
      D2(J1,K1)=D2(J1,K1)+BD(J1,K1,L1)*CZ(L1,I)
      D2Z(J1,K1)=D2Z(J1,K1)-BD(J1,K1,L1)*DL1*SZ(L1,I)
      D2ZZ(J1,K1)=D2ZZ(J1,K1)-BD(J1,K1,L1)*DL1*DL1*CZ(L1,I)
      C1(J1,K)=C1(J1,K)+AD(J1,K,L1)*CZ(L1,I)
      C1Z(J1,K)=C1Z(J1,K)-AD(J1,K,L1)*DL1*SZ(L1,I)
      C1ZZ(J1,K)=C1ZZ(J1,K)-AD(J1,K,L1)*DL1*DL1*CZ(L1,I)
      D1(J1,K)=D1(J1,K)+BD(J1,K,L1)*SZ(L1,I)
      D1Z(J1,K)=D1Z(J1,K)+BD(J1,K,L1)*DL1*CZ(L1,I)
      D1ZZ(J1,K)=D1ZZ(J1,K)-BD(J1,K,L1)*DL1*DL1*SZ(L1,I)
      C2(J1,K)=C2(J1,K)+AD(J1,K,L)*SZ(L,I)
      C2Z(J1,K)=C2Z(J1,K)+AD(J1,K,L)*DL*CZ(L,I)
      C2ZZ(J1,K)=C2ZZ(J1,K)-AD(J1,K,L)*DL*DL*SZ(L,I)
      D2(J1,K)=D2(J1,K)+BD(J1,K,L)*CZ(L,I)
      D2Z(J1,K)=D2Z(J1,K)-BD(J1,K,L)*DL*SZ(L,I)
      D2ZZ(J1,K)=D2ZZ(J1,K)-BD(J1,K,L)*DL*DL*CZ(L,I)
      C1(J,K1)=C1(J,K1)+AD(J,K1,L1)*CZ(L1,I)
      C1Z(J,K1)=C1Z(J,K1)-AD(J,K1,L1)*DL1*SZ(L1,I)
      C1ZZ(J,K1)=C1ZZ(J,K1)-AD(J,K1,L1)*DL1*DL1*CZ(L1,I)
      D1(J,K1)=D1(J,K1)+BD(J,K1,L1)*SZ(L1,I)
      D1Z(J,K1)=D1Z(J,K1)+BD(J,K1,L1)*DL1*CZ(L1,I)
      D1ZZ(J,K1)=D1ZZ(J,K1)-BD(J,K1,L1)*DL1*DL1*SZ(L1,I)
      C2(J,K1)=C2(J,K1)+AD(J,K1,L)*SZ(L,I)
      C2Z(J,K1)=C2Z(J,K1)+AD(J,K1,L)*DL*CZ(L,I)
      C2ZZ(J,K1)=C2ZZ(J,K1)-AD(J,K1,L)*DL*DL*SZ(L,I)
      D2(J,K1)=D2(J,K1)+BD(J,K1,L)*CZ(L,I)
      D2Z(J,K1)=D2Z(J,K1)-BD(J,K1,L)*DL*SZ(L,I)
 2623 D2ZZ(J,K1)=D2ZZ(J,K1)-BD(J,K1,L)*DL*DL*CZ(L,I)
  623 CONTINUE
      DO920K=1,IKMAX
      E(K)=0.0
      EZ(K)=0.0
```

```
      EZZ(K)=0.0
      F(K)=0.0
      FZ(K)=0.0
      FZZ(K)=0.0
      EX(K)=0.0
      EXX(K)=0.0
      FX(K)=0.0
  920 FXX(K)=0.0
      DO632K=1,IKMAX
      DO632J=1,IJMAX
      DJ=J-1
      E(K)=E(K)+C1(J,K)*CX(J,I)-D1(J,K)*SX(J,I)
      EZ(K)=EZ(K)+C1Z(J,K)*CX(J,I)-D1Z(J,K)*SX(J,I)
      EZZ(K)=EZZ(K)+C1ZZ(J,K)*CX(J,I)-D1ZZ(J,K)*SX(J,I)
      EX(K)=EX(K)-C1(J,K)*DJ*SX(J,I)-D1(J,K)*DJ*CX(J,I)
      EXX(K)=EXX(K)-C1(J,K)*DJ*DJ*CX(J,I)+D1(J,K)*DJ*DJ*SX(J,I)
      F(K)=F(K)-C2(J,K)*CX(J,I)-D2(J,K)*SX(J,I)
      FZ(K)=FZ(K)-C2Z(J,K)*CX(J,I)-D2Z(J,K)*SX(J,I)
      FZZ(K)=FZZ(K)-C2ZZ(J,K)*CX(J,I)-D2ZZ(J,K)*SX(J,I)
      FX(K)=FX(K)+C2(J,K)*DJ*SX(J,I)-D2(J,K)*DJ*CX(J,I)
  632 FXX(K)=FXX(K)+C2(J,K)*DJ*DJ*CX(J,I)+D2(J,K)*DJ*DJ*SX(J,I)
      DENS=0.0
      DX=0.0
      DXX=0.0
      DY=0.0
      DYY=0.0
      DZ=0.0
      DZZ=0.0
      DO635K=1,IKMAX
      DK=K-1
      DENS=DENS+E(K)*CY(K,I)+F(K)*SY(K,I)
      DX=DX+EX(K)*CY(K,I)+FX(K)*SY(K,I)
      DXX=DXX+EXX(K)*CY(K,I)+FXX(K)*SY(K,I)
      DZ=DZ+EZ(K)*CY(K,I)+FZ(K)*SY(K,I)
      DZZ=DZZ+EZZ(K)*CY(K,I)+FZZ(K)*SY(K,I)
      DY=DY-E(K)*DK*SY(K,I)+F(K)*DK*CY(K,I)
```

```
 635 DYY=DYY-E(K)*DK*DK*CY(K,I)-F(K)*DK*DK*SY(K,I)
     DEN=12.57*FUDGX/(VOL*P(6,I)*P(7,I))
     DX=(DX*DEN)/AREAL
     SHFTY=DY*DEN/BREAL
     DZ=DZ*DEN/CREAL
     SHFTX=(DX-CBSTR*DZ)/CB1
     SHFTZ=(DZ-CBSTR*DX)/CB1
     DENS=4.0*DENS/VOL
     DDX=DXX/(AREAL**2)
     DDY=DYY/(BREAL**2)
     DDZ=DZZ/(CREAL**2)
     SHFTB=(DDX+DDY+DDZ)*(WAVEL**4)*FUDGB/(0.75*FSUM(I))
     WRITEOUTPUTTAPE3,636,SHFTX,SHFTY,SHFTZ,SHFTB,DDX,DDY,DDZ,DENS
 636 FORMAT(1H ,5H DX= ,F6.3,5H DY= ,F6.3,5H DZ= ,F6.3,6H  DB= ,F6.3,9H
    1     DDX= ,F9.2,6H DDY= ,F9.2,6H DDZ= ,F9.2,12H  DENSITY = ,F7.3)
     DX2=ABSF(SHFTX)
     DY2=ABSF(SHFTY)
     DZ2=ABSF(SHFTZ)
     DXSUM=DXSUM+DX2
     DYSUM=DYSUM+DY2
     DZSUM=DZSUM+DZ2
     IF(DX1-DX2)1005,1006,1006
1005 DX1=DX2
1006 IF(DX1-DY2)1007,1008,1008
1007 DX1=DY2
1008 IF(DX1-DZ2)1009,1010,1010
1009 DX1=DZ2
1010 CONTINUE
     P(2,I)=P(2,I)+SHFTX/AREAL
     P(3,I)=P(3,I)+SHFTY/BREAL
     P(4,I)=P(4,I)+SHFTZ/CREAL
 299 P(5,I)=P(5,I)+SHFTB
     ANMBV=NMBR-NMBRC
     AVX=DXSUM/ANMBV
     AVY=DYSUM/ANMBV
     AVZ=DZSUM/ANMBV
```

```
      IF(SHFTM-DX1)1011,1011,1012
 1012 MCYCL=0
 1011 WRITEOUTPUTTAPE3,1013,AVX,AVY,AVZ,DX1
      PRINT1013,AVX,AVY,AVZ,DX1
 1013 FORMAT(1H //12H MEAN SHIFTS/5H DX= ,F7.4,5H DY= ,F7.4,5H DZ= ,F7.4
     1,20H   GREATEST SHIFT = ,F7.4,9H ANGSTROM)
      RETURN
      END
```

APPENDIX 4.

Observed and calculated structure factors for NaPTD

The structure factors are listed in sets of constant h and k, with l increasing. Reading from the left the three columns give the values of l, $10|F_o|$, and $10.F_c$.

For those F_o's experimentally unobserved, the threshold value is given and marked with an asterisk.

```
l    Fo    Fc
    0 0 l
 1   800   974
 2    50    46-
 3    45    50-
 4   486   520-
 5    69    55-
 6   290   265-
 7   107    93-
 8   311   299-
 9    64    59
10   534   521
11   275   275
12    63*    7-
13   165   144-
14   113   121-
15    60*   20
16    55*   42
17    52    44-
18    43    59-
    2 0 l
 0    99    98-
 1   130   126
 2  1068  1052-
 3  1402  1281-
 4  1230  1186-
 5   142   143-
 6   284   300
 7   130   108-
 8    91    60-
 9    56*   46-
10   148   140
11   109   112
12   107   103-
13   240   218-
14   144   132-
15    55*   19-
16    40*   50
17    41    44
   -2 0 l
 1   769   758
 2   111   156
 3  1018  1044-
 4   911   896
 5   349   370
 6   183   213-
 7   296   309-
 8   104   105-
 9   234   218
10   182   153
11   227   214
12    62*   33-
13   106   115-
14    71    66
15   118   113
16    62    73
17    50*   35
18    40*    9
    4 0 l
 0    93    78
 1   525   521
 2   260   276
 3   150   149-
 4    47*   85
 5   176   175
 6   373   357
 7   182   179
 8    60*    6
 9    62*    5
10    64*   28
11   122   104
12   102    94
13    58*   20
14    52*   29-
15    43*   29
16    69    71
   -4 0 l
 1   229   239-
 2   406   422-
 3    40*   38
 4   376   379-
 5   213   242-
 6   163   156-
 7   439   447-
 8    52*   40-
 9   200   175
10    78    91
11   220   197-
12   217   205-
13    71    56-
14    63*   48-
15    60*   50-
16    91    83-
17    75    83-
18    39*   10-
    6 0 l
 0   206   217
 1   288   268
 2   286   263
 3    57*   15-
 4   130   136-
 5   178   192-
 6   147   142-
 7    87    95
 8    64*   28
 9    87    73-
10    87    60-
11    56*   14
12    50*   15
13    42*   36-
14    57    34-
   -6 0 l
 1    52*   53
 2   183   198
 3   373   379
 4   169   181
 5   123    91-
 6   176   158-
 7   233   203
 8   340   350
 9   271   279
10   111   120
11    71    57-
12    64*   35-
13    77    75
14    95   102
15    56*   21-
16    98    91-
17    41*   22-
18    57    50
    8 0 l
 0   146   144-
 1   113   116-
 2    64*   32
 3    78    88
 4   186   186-
 5   225   218-
 6    67    67-
 7    59*   38
 8    61    54
 9    50*    8
10    43*   19-
11    34*   47-
   -8 0 l
 1    85    93-
 2    63*   37
 3    63*    4
 4   185   177-
 5   418   405-
 6   345   347-
 7    64*   16-
 8   227   205
 9   132   129
10    63*   54-
11    62*   35-
12    85    72
13   108    93
14    51*    9
15    87    78-
16    73    81-
   10 0 l
 0    71    61-
 1    57*    4-
 2    61    71
 3    57    51
 4    58*   12
 5    46*   29-
 6    41*   14-
 7    33*   39
  -10 0 l
 1   132   134
 2   257   272
 3   164   173
 4    60*   28-
 5   138   134-
 6    87    95-
 7    58*   23-
 8    56*    7
 9    58    55-
10    93   109-
11    48*   47-
12    61    68
13    57    84
14    26*   15-
   12 0 l
 0    37    60-
  -12 0 l
 1    32*   14-
 2    34*   43
 3    37    52
 4    35*    8-
 5    35*    2-
 6    51    79
 7    73   107
 8    26*   38
    0 1 l
 0     0*    0-
 1   269   295
 2   720   752-
 3    41    22
 4    92    94
 5   161   187
 6   133   119-
 7    44*   21-
 8   237   233
 9    52*   32-
10    78    65-
11   123   114-
12    89    82-
13    64*    2-
14    55    48
15    59*   25
16    54*    2-
17    45*   12-
18    33*    3-
    1 1 l
 0   364   418-
 1    84    93-
 2   553   588
 3   646   725
 4   216   229
 5   307   334-
 6   457   467-
 7    51    48-
 8    50*   18-
 9   149   139-
10   197   203-
11   284   293-
12    82    66-
13   108    97
14    62*   34-
15    89    84-
16    84    81-
17    41*   43-
18    25*   10
   -1 1 l
 1   297   319-
 2   321   368
 3   503   499
 4   212   187-
 5   180   167-
 6   246   244
 7   499   531
 8   542   525
 9   256   275
10    55*    7-
11    51    33
12   141   140
13   135   126
14    55    51
15    82    69-
16    62    58-
17    48*   30
18    37*   33
    2 1 l
 0   206   215
 1   335   332-
 2   740   804-
 3   408   431-
 4    37*   13
 5   137   124-
 6   200   215
 7   132   128
 8    73    62
 9   117   114
10    98   101
11    62*   14
12    99    84-
13    51    53-
14    60*    3-
15    54*   32
16    46*    2
17    35*   10-
   -2 1 l
 1   780   816-
 2   211   228
 3   324   332-
 4   404   399-
 5    36*   14
 6    79    73-
 7   228   223
 8   285   268
 9   268   262
10    70    54-
11   192   205-
12    62*   20-
13    73    56
14    56    44
15    61*   18-
16    64    47-
17    49*   19-
18    39*   16
    3 1 l
 0   167   182-
 1   127   132-
 2    58    43
 3   212   215
 4   206   199-
 5   427   427-
 6   366   372-
 7   299   306-
 8   155   172
 9   223   229
10    62*   18-
11    68    73
12    75    69
13    58    65
14    89    88
15    49*   10
16    40*   34-
   -3 1 l
 1   196   180
 2    57    47
 3   600   610-
 4   562   603-
 5   753   759-
 6   460   452-
 7   103    83
 8    37    30-
 9   163   141-
10    88   102-
11    64    84
12   114    97
13    64*   13
14    64    53-
15    64    55-
16    56*    2-
17    48*   46
18    39*   44
    4 1 l
 0    40*   23
 1   291   292-
 2   120   102-
 3   197   208-
 4   101    94
 5   373   384
 6   303   305
 7    76    61
 8   136   143-
 9    62*   29-
```

```
10     63*    33-
11     62     51-
12     76     79-
13     51     50-
14     50*     7
15     42*    38
16     62     45

   -4  1  ℓ

 1     61     67-
 2    163    161
 3    240    230
 4     42*     1
 5    493    500-
 6     44     25-
 7    169    156
 8    120     95
 9     55*    14-
10    175    172-
11    146    148-
12     55     49-
13    114    103
14    106     98
15     39*     8
16     34*     6-
17     47*    28
18     37*    42

    5  1  ℓ

 0    376    389
 1    176    161
 2     51     57
 3     56     49
 4    239    237
 5     43     49
 6     82     80-
 7    119    112
 8     95     78
 9    146    143
10    163    158
11     61*    15-
12     51     45-
13     50*    13-
14     42*    19
15     29*    20-

   -5  1  ℓ

 1    525    553
 2    373    383
 3    117    110
 4    176    166-
 5     49*    26
 6    189    171
 7     79     73-
 8     92     84-
 9     79     91-
10     61*    27-
11    141    124
12     88     77
13     91     87-
14    161    159-
15     73     73-
16     52*     9
17     44*     5-
18     33*    35-

    6  1  ℓ

 0    201    188
 1    170    172
 2     94     79-
 3    173    174-
 4     60     68-
 5    148    146
 6     62*     3-
 7     85     86-
 8    106    108-
 9     85     79-
10     60*    12
11     50     44
12     50     49
13     41*     6
14     28*     5

   -6  1  ℓ

 1     52*    18-
 2     81     85-
 3     52*     4-
 4     68     46-
 5     71     50-
 6     73     56
 7    280    282
```

```
 8    311    308
 9     61*     8-
10    150    137-
11    129    110-
12     56     48-
13     54     46-
14     79     60-
15     53     36-
16     48*     2-
17     39*    43

    7  1  ℓ

 0    102    115
 1    129    135-
 2    218    224-
 3    163    159-
 4    119    113-
 5     63*    30
 6     64*    36-
 7    173    177-
 8     96     88-
 9     57*    18-
10     53*     1
11     46*    22-
12     38*    27-

   -7  1  ℓ

 1    109    115
 2     59     62-
 3    149    159-
 4     59*    14-
 5    184    180
 6    176    180
 7     61*    32
 8    143    136-
 9     63*    38-
10    175    186
11    188    181
12     76     79
13     59*     2
14     55*     8-
15     64     56
16     76     89
17     32*    40

    8  1  ℓ

 0     63*     2-
 1     63*     7-
 2    128    126-
 3     88     78-
 4     63*    27-
 5     62*     4
 6     75     69
 7     56     41
 8     54*     7
 9     48*    17-
10     41*    26
11     58     44

   -8  1  ℓ

 1     64     58
 2     67     56
 3    116    115-
 4    207    210-
 5     87     88-
 6     63*     5
 7     68     63
 8     88     67
 9     62     52
10     62*    19
11     61*    35
12     76     62
13     54*     9
14     60     52-
15     51     47-
16     33*     3

    9  1  ℓ

 0     73     75
 1     84     79
 2     66     55-
 3     67     62-
 4     54     58
 5     76     79
 6     47     46
 7     48*     7-
 8     42*    29-
 9     33*     5

   -9  1  ℓ
```

```
 1     64     55-
 2    185    188-
 3    208    200-
 4     56     56-
 5     73     67
 6     63*    28
 7    102    105-
 8    146    145-
 9     64     57-
10     58*    26
11     55*     7
12    100    101-
13    129    134-
14     41     42-
15     31*    34

   10  1  ℓ

 0     54     46-
 1     56*    14-
 2     49     48
 3     52*    19
 4     49*     5-
 5     44*     0-
 6     39*    31
 7     31*    18

  -10  1  ℓ

 1     59*    27
 2     59*    20
 3     59*    26-
 4     59*    49-
 5     59*     8-
 6     58*    60
 7     57*    26
 8     67     57-
 9     46     48-
10     50*    10
11     46*    25
12     41*     8-
13     35*    27-

   11  1  ℓ

 0    115    132
 1     93    115
 2     49     53
 3     37*     9-
 4     31*    21-

  -11  1  ℓ

 1     51     52
 2     42     45-
 3     50*    28-
 4     43     49
 5     50     63
 6     48*    11
 7     47*    20-
 8     44*    25
 9     86     93
10     88    104
11     31*    39

  -12  1  ℓ

 1     29*    31
 2     34     38-
 3     54     53-
 4     33*    12-
 5     33*    17
 6     31*    19
 7     28*     4


    0  2  ℓ

 0    370    408
 1    186    218
 2     71     73
 3    271    307
 4    136    139
 5    363    395
 6    317    343
 7     45*     9-
 8     49*    24
 9     53     52
10    133    128
11     60*     2-
12     62     44-
13     62*    41-
14    105     93-
15     56*    23-
16     50*    14-
17     41*    28-
```

```
18     25*    26-

    1  2  ℓ

 0    244    241-
 1     63     79-
 2     45     45
 3     72     50-
 4    239    252-
 5    121    122-
 6    214    220
 7    229    211
 8     32     31
 9    142    145-
10     79     85-
11     61*     2-
12     62*    30-
13     62*    35
14     42     20-
15     52     48-
16     48     46
17     43     52

   -1  2  ℓ

 1    356    387
 2    195    175-
 3    372    420-
 4    176    178-
 5     59     65
 6    262    272
 7    178    167
 8     55     34-
 9    153    143-
10     56*    16
11    130    133
12     62*    22-
13    168    152-
14     85     94-
15     57*    26
16     49     52
17     49     58
18     31*    15

    2  2  ℓ

 0    165    184-
 1    100    105
 2    121    142-
 3    449    476-
 4    103     97-
 5    170    167-
 6    219    208-
 7    243    243-
 8    238    245-
 9    178    192-
10    144    132-
11     66     60
12     36      3-
13     60*    28-
14     56*     7-
15     50*     5
16     42*    21
17     28*     2

   -2  2  ℓ

 1    134    154-
 2    221    226-
 3    133    126-
 4     51     54
 5     37*    13
 6    183    189-
 7    111    101-
 8    115     95-
 9     95     78
10    207    219
11    170    171
12    108    103
13     51     62
14    125    124
15     56     59
16     52*     7-
17     44*    11-
18     33*    17-

    3  2  ℓ

 0    223    236-
 1     87     78
 2    342    365
 3    151    152
 4    172    159-
 5    323    309-
 6    120    106-
 7     95     99
```

```
 2   248   253
 3   305   328
 4   143   136
 5    39*   13-
 6   285   266-
 7    79    67-
 8   187   204
 9    89   101
10    69    62-
11   131   138-
12    34    41
13   114   110
14    75    73
15    52*   21
16    87    83-
17    47    45-

     3  3  ℓ

 0   284   298-
 1   283   290-
 2   218   191-
 3   126   121-
 4   114   112-
 5    56    51
 6   155   165
 7    54*    5-
 8    57*   16-
 9    63    51
10    53    47
11    59*   13-
12    57*   15-
13    52*    5-
14    46*    8-
15    37*   19

    -3  3  ℓ

 1   222   228-
 2   348   359-
 3   307   308-
 4   175   154-
 5    99   103-
 6    39    26
 7    55    42-
 8    78    65-
 9    55*    6-
10    57*    9-
11   118   106-
12    88    82-
13    59*   15-
14    47    51-
15    52*   22-
16    45*   39
17    34    38

     4  3  ℓ

 0   402   387
 1   136   137
 2   258   219-
 3   217   206-
 4    39    36-
 5   206   226
 6   104    91
 7    41    41-
 8    55    57-
 9    68*    1-
10   103    99
11    29    18
12    28    45-
13    94    86-
14    39    32-
15    25*   34

    -4  3  ℓ

 1   218   203-
 2    42*    6-
 3   209   184
 4    44*    1-
 5   225   206-
 6    56    38-
 7   186   198
 8   223   226
 9    77    74
10   173   166-
11   185   175-
12    60*    5-
13    90    93
14    32    46
15    71    56-
16    31    28-
17    34*   30

     5  3  ℓ
```

```
 0   173   182
 1   198   199
 2   131   144
 3    78    56
 4   127   124
 5   118   127
 6    71    61
 7    59    62
 8    76    65
 9    39*   34
10    56*    3-
11    52*    1-
12    47*    6-
13    39*    6-
14    26*   13-

    -5  3  ℓ

 1   134   147
 2   123   193
 3   147   168
 4    58*   24
 5    51*    6
 6    53*   26-
 7    55*    8
 8    57*    8
 9    58*   16-
10    68*   14
11    60*    3-
12    59*   32-
13    57*   20-
14    53*    2-
15    54    48-
16    68    64-
17    38*   17-

     6  3  ℓ

 0   157   162
 1   110   122
 2   114   112-
 3   206   207-
 4    98    95-
 5    65    66
 6   102    96
 7    59*   37-
 8    67    64-
 9    63    51-
10    31    43
11    76    66
12    37*    5-

    -6  3  ℓ

 1    57    21-
 2   184   193
 3   108   103
 4   143   146-
 5   193   202-
 6    28    28-
 7   178   162
 8   144   130
 9    60*   34-
10   113   109-
11    39    40-
12    44    44
13    43    47
14    36    40-
15    94    89-
16    45    45-

     7  3  ℓ

 0   105    99-
 1   131   129-
 2   113   100-
 3    60*   31-
 4    48    46-
 5    55    51-
 6    47    32-
 7    56*    6-
 8    52*   19-
 9    68    52-
10    69    65-
11    43    39-

    -7  3  ℓ

 1    88    66-
 2    58*   13-
 3    50    43
 4    87    81
 5    59*    5
 6    59*    5
 7   108    87
```

```
 8   108    97
 9    65    35
10    59*   10
11    28    35
12    67    56
13    56    44
14    39    38
15    38*   26
16    26*    3

     8  3  ℓ

 0   106   103
 1   138   137
 2    59*   21
 3   106   101-
 4   112    99-
 5    48    46-
 6    46    48
 7    26    35
 8    43*   14-
 9    36*   12
10    24*   40

    -8  3  ℓ

 1    37    32
 2    84    68
 3    60*    3-
 4    54    56-
 5    34    22-
 6    99    90
 7   123   119
 8    58*   24
 9    83    79-
10    44    47-
11    59    57
12    93    82
13    44*   17
14    37*   47-
15    27*   44-

     9  3  ℓ

 0    55    47-
 1    55*    5-
 2    45    42
 3    50    46
 4    49*   14
 5    46*    8-
 6    41*    8
 7    35*   19
 8    25*    5

    -9  3  ℓ

 1    57*   15-
 2    57*    3
 3    58*   27-
 4    72    71-
 5    94    88-
 6   103    94-
 7    82    83-
 8    28    28-
 9    26    27-
10    64    60-
11    55    47-
12    40*    1
13    34*   17

    10  3  ℓ

 0    48*    1-
 1    46*   24
 2    44*   17
 3    58    54-
 4    84    82-
 5    30*   27-

   -10  3  ℓ

 1    49*   10
 2    28    31-
 3   101    85-
 4    72    65-
 5    28    33
 6    90    78
 7    47*   19
 8    63    61-
 9    86    70-
10    38*    7-
11    33*   50
12    24*   41

    11  3  ℓ
```

```
 0    34*    2
 1    30*    4

   -11  3  ℓ

 1    36*   27
 2    78    68
 3    83    84
 4    47    52
 5    37*   32
 6    36*   38
 7    34*   35
 8    30*   13
 9    24*    3

     0  4  ℓ

 0   213   210-
 1    16    21
 2   268   299
 3   236   252
 4   133   157
 5    30    42
 6    83    79
 7   182   202
 8   207   219
 9    92    97
10   147   149-
11   111   111-
12    55*   12-
13    31     5-
14    28     4-
15    23    38-
16    31*   31-

     1  4  ℓ

 0    49    43-
 1   110   101
 2    38    50-
 3   120   127-
 4   156   171-
 5    54    61-
 6    30    35
 7    76    81
 8    78    68
 9   167   171-
10   133   124-
11    56*   33
12    59    45
13    51*   27
14    45*    4
15    38*   22
16    24*   24

    -1  4  ℓ

 1   100    90
 2    60    66-
 3   219   227-
 4   176   167-
 5   125   118
 6   264   295
 7   202   209
 8    50*    1
 9    53*   12-
10    58    46-
11    70    63-
12    56*   13-
13    89    79-
14    93    93-
15    43*   14-
16    45    55

     2  4  ℓ

 0   286   281-
 1   218   221-
 2    61    68-
 3    53    31
 4    42*    6
 5   148   149-
 6   223   242-
 7    52*   11
 8    31    38
 9   103    97-
10   119   130-
11   152   156-
12    66    69-
13    21    15
14    52    47
15    32*    7

    -2  4  ℓ
```

```
     -2  4  l
  1   228   225-
  2    31*    4-
  3    34    18
  4   182   177-
  5   189   185-
  6    54    54
  7   147   156
  8   158   165
  9    55    54
 10    56*    1-
 11    56*   15
 12    51    55
 13    66    66
 14    50*    8
 15    44*   13-
 16    35*   17

      3  4  l
  0   206   200-
  1   155   153-
  2    38    43
  3    62    59
  4    46*   11-
  5   125   137-
  6   100   107
  7   196   196
  8    45    46
  9    37    25
 10    37    30-
 11    53*    7-
 12    49*   29
 13    44*   28
 14    36*    5

     -3  4  l
  1    82    60
  2    45    28-
  3   278   254-
  4   208   212-
  5    44*   14
  6    90    97
  7    49*   18
  8    65    50-
  9    54*   25
 10   148   149
 11   131   138
 12    55*    1-
 13    37    43-
 14    49*   27-
 15    43*    7-
 16    35*   21

      4  4  l
  0    53    45
  1    59    74-
  2    47*   26-
  3   163   171
  4    89    90
  5    53*    2
  6    71    59
  7    32    35
  8    84    84
  9    83    81
 10    39    28
 11    50*   29-
 12    44*    9
 13    62    67
 14    36    47

     -4  4  l
  1   121   128
  2    53    57
  3    78    50-
  4   132   144-
  5   173   176-
  6    98    81-
  7    34    25-
  8   116   118-
  9   152   155-
 10    70    67-
 11    56*   11-
 12    55*    0-
 13    34    37-
 14    48    53-
 15    41*   31-
 16    33*    4-

      5  4  l
  0   101    96-
  1    51    48-
  2   144   148

  3   119   105
  4    32    30-
  5    56*   15-
  6    75    83-
  7    56*    8-
  8    55    44
  9    53*    2
 10    49*   38-
 11    64    58-
 12    37*    9-
 13    24*   19

     -5  4  l
  1    49*    4
  2   168   177-
  3    58    56-
  4   116   118
  5   108   105
  6    54    51
  7    88    75-
  8   120   122-
  9    52    57-
 10    56*   13
 11    55*    4
 12    61    57-
 13    68    70-
 14    45*    8
 15    61    66
 16    26*   34

      6  4  l
  0    81    83
  1    48    39-
  2    62    69-
  3   101    90-
  4    56*   17
  5    71    62
  6    55*   17
  7    54*   22-
  8    51*    7
  9    47*   11
 10    42*   25-
 11    34*   23-

     -6  4  l
  1   199   195
  2   135   145
  3    63    56
  4   118   110
  5   206   202
  6   158   149
  7    36    42
  8    56*   32-
  9    32    35-
 10    32    36
 11    92    92
 12    50*   44
 13    46*   26-
 14    41*   15-
 15    33*   31

      7  4  l
  0    52    48-
  1   107    94-
  2   128   120-
  3    56*   15-
  4    55*    4
  5    49    47-
  6    58    39-
  7    48*    1
  8    78    69
  9    62    52
 10     5*   29-

     -7  4  l
  1    81    74-
  2   156   157-
  3   105    97-
  4    33    37
  5   129   122
  6    56*   16
  7    56*   17-
  8    65    67
  9   100    99
 10    34    52
 11    58*   33-
 12    59    72-
 13    47    50-
 14    34*    0-

      8  4  l

  0    55*   22-
  1    73    82-
  2   156   156-
  3   107   109-
  4    50*    3
  5    51    55
  6    41    41
  7    38*    9
  8    27    29-

     -8  4  l
  1    86    71-
  2   126   110-
  3   126   105-
  4    39    33-
  5    32    63
  6    73    60
  7    53    54-
  8   116   108-
  9    35    31-
 10    38    38
 11    44*   32
 12    39*   20-
 13    38    54-

      9  4  l
  0    38    29-
  1    81    86-
  2    48    42-
  3    48    34
  4    82    83
  5    49    44
  6    29*    9

     -9  4  l
  1    44    42-
  2    50*   22-
  3    50*    5
  4    50*    7
  5    50*   31-
  6    66    51-
  7    39    36-
  8    45*   18
  9    76    77
 10    35    37
 11    36    40-
 12    21    44-

     10  4  l
  0    57    63
  1    33    37
  2    33*    3-
  3    28*    4-

    -10  4  l
  1    28    26
  2    33    37-
  3    41    26-
  4    33    37
  5    54    54
  6    39*   12
  7    39    41-
  8    38    49-

  9    30*    4-

      0  5  l
  0     0*    0-
  1    49    65-
  2    50    45-
  3    72    87
  4    30    40
  5    40*    9-
  6    44*   30-
  7    79    83-
  8    67    65-
  9    51*    2-
 10    51*    1
 11    29    39-
 12    34    34-
 13    42*    5
 14    36*   22
 15    25*    9

      1  5  l
  0   101   113
  1   144   154
  2   103   103-

  3   170   179-
  4    63    64
  5   181   178
  6   118   115
  7   110   110-
  8   174   179-
  9   117   119-
 10    45    41-
 11    49*   19
 12    31    40-
 13    56    62-
 14    33*   34-

     -1  5  l
  1    17    21-
  2    81    92-
  3    31    24-
  4   136   142
  5   304   313
  6   193   180
  7    37    34-
  8    53    57-
  9    63    55
 10   127   138
 11    66    71
 12    48*    5
 13    44*   10-
 14    38*   24
 15    38    52

      2  5  l
  0    32*    5-
  1    22    17-
  2    36*    3-
  3    74    64-
  4    42*    9-
  5    58    41
  6    25    37-
  7    50    53-
  8    35    34
  9    40    44
 10    50*   17
 11    47*    2-
 12    43*    2
 13    36*    2-
 14    26*   13

     -2  5  l
  1   104   110-
  2    45    44-
  3    61    64
  4   137   133
  5   112    98
  6    42    47
  7    72    74
  8    38    29
  9    51*    0-
 10    51*   18-
 11    43    42-
 12    48*   35-
 13    44*    7-
 14    38*   25
 15    30*   27

      3  5  l
  0    45    36-
  1    86    75-
  2   150   136-
  3   204   195-
  4    79    76-
  5    61    54
  6    78    72
  7    57    58
  8    87    83-
  9    64    68-
 10    47*   27
 11    68    72
 12    59    54
 13    30*   13-

     -3  5  l
  1   245   227-
  2   267   254-
  3    40*   27
  4   163   168
  5    81    78
  6    72    68-
  7   166   160-
  8   175   167-
  9    72    77-
 10    30    32-
```

```
 11     56     59-
 12     64     67-
 13     43*     1
 14     58     72
 15     42     66

     4  5  ℓ

  0     64     61
  1     45*     0-
  2    101    105-
  3     49     45-
  4     46     38
  5     23      0-
  6     51*    27
  7     53     50
  8     31     19
  9     47*     5-
 10     44*     1-
 11     38*     2-
 12     31*    22-

    -4  5  ℓ

  1     39     37-
  2    122    118-
  3    165    153-
  4     76     69-
  5     33     29-
  6     49*    10
  7     54     53
  8     85     89
  9     52     45
 10     50*    12-
 11     49*     9-
 12     46*    17-
 13     42*    14-
 14     36*     6-
 15     26*     1

     5  5  ℓ

  0     76     77-
  1     69     64
  2    141    128
  3    156    146
```

```
  4     52     50
  5    104    108
  6    153    153
  7     82     81
  8     46*     1
  9     68     60-
 10     37*    18-
 11     38*     6

    -5  5  ℓ

  1    162    154-
  2     68     63-
  3     64     55
  4    215    203
  5    168    150
  6     51*    20
  7     39     41
  8    118    103
  9     66     56
 10     52     58-
 11    101    115-
 12     84     83-
 13     39*    14-
 14     32*    21

     6  5  ℓ

  0     78     81-
  1    104     98-
  2     51*    17-
  3     51*     2
  4     58*    11-
  5     34     34
  6     39     47
  7     44*    15
  8     40*    25-
  9     35*    29-
 10     26*    30-

    -6  5  ℓ

  1     71     64
  2     73     69
  3     51*    15-
  4    118    114-
  5     69     74-
  6     51*    11-
  7     51*    11-
  8     50*     6-
```

```
  9     49*     4
 10     47*     3
 11     44*     2-
 12     40*    12
 13     34*     1
 14     24*    23-

     7  5  ℓ

  0    111    104-
  1     50*    29
  2     98     94
  3     48*    25
  4     35     43-
  5     83     84-
  6     46     50-
  7     35     39-
  8     30*    30-

    -7  5  ℓ

  1     77     80-
  2     51*     1
  3     68     58
  4     50*     2-
  5     79     73-
  6     61     44-
  7     28     22
  8     96     96
  9     79     81
 10     42*     7-
 11     34     36-
 12     33*    31
 13     46     91

     8  5  ℓ

  0     24     28-
  1     50     48
  2     53     54
  3     41*    30
  4     38*    14
```

```
  5     35*    13
  6     29*     8

    -8  5  ℓ

  1     55     61
  2     47*    36
  3     47*    29
  4     47*     9
  5     46*     7-
  6     45*    18
  7     39     36
  8     42*     5-
  9     28     30-
 10     35*     1-
 11     30*    22

     9  5  ℓ

  0     68     74-
  1     48     48-
  2     33*    12
  3     29*    28

    -9  5  ℓ

  1     39     43-
  2     45     48
  3     64     71
  4     39*    11-
  5     64     70-
  6     45     46-
  7     35*    18
  8     32*    10
  9     40     60-

   -10  5  ℓ

  1      0*     0-
  2     24*     6-
  3     25*    30-
  4     25*    19-
  5     23*     7
```

TABLES

PLATES

FIGURES

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