THE PHYSICAL STRUCTURE OF TWO PARABANIC ACID COMPLEXES AND AN INVESTIGATION OF SHORT INTERMOLECULAR CARBON-OXYGEN CONTACTS

by

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A thesis submitted for the
degree of Doctor of Philosophy
in the University of Adelaide

July 1969.

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SUMMARY

This thesis describes the structure determination of two complexes of parabanic acid, and the nature of intermolecular contacts found in each compound.

Urea parabanate (UPBA) was studied in the search for further examples of carbon-oxygen contacts of the type previously found in parabanic acid and four other organic solids. The absence of a heavy atom in this structure led to the investigation and determination of the structure of thiourea parabanate (TUPBA) from its Patterson function. Although the two structures are not isomorphous, sufficient information was available from the second to determine the UPBA structure from its Patterson function. Both structures were refined by least squares methods.

Carbon-oxygen contacts have been found in UPBA. The contact length and angle are not in accord either with previous data or with suggested mechanisms for the contact. A re-evaluation of the data has suggested an alternative mechanism which explains both the spread in contact angles and the lack of correlation between contact length and angle.

A second type of contact has been found in TUPBA. Here the contact is between sulphur and carbon atoms, and the contact angle (at the sulphur atom) is near 90°. A mechanism for this violation of the Van der Waals' packing is also suggested.

DECLARATION

The work described in this thesis was carried out in the Department of Physics between February 1966 and July 1969. Except where otherwise stated, it is the personal work of the author.

Only that material contained in section 1.1.1 has been submitted for the award of another degree in this or any other University; that section is included for completeness.

P. M. Colman

ACKNOWLEDGEMENTS

I would like to thank my supervisor, Dr. E. H. Medlin, for his guidance throughout this project.

The facilities of the Physics Department were generously provided by Professors J. H. Carver and K. G. McCracken.

I am also grateful to Messrs. M. T. Schubert, R. E. Dingle and D. W. Field for helpful discussions, to Mr. D. W. Field for reading the manuscript, and to Miss H. Barrow for her assistance with hand calculations and drawings.

I would also like to thank Drs. M. Snow (Physical and Inorganic Chemistry Department (Adelaide)) and M. Taylor (School of Physical Sciences (Flinders)) for their assistance with computing problems and for the use of some of their programs. Dr. E. W. Radoslovich (C.S.I.R.O. Adelaide) kindly made available a Fourier program in the early part of the project.

I am grateful for the award of a Commonwealth Post Graduate Scholarship (1966-1969).

CHAPTER ONE

THE CARBON-OXYGEN CONTACT AND AN INVESTIGATION OF THE STRUCTURE OF UREA PARABANATE

1.1 Introduction

Since the statement of Bragg's law, X-ray and neutron diffraction methods have been employed in the determination of many crystal structures. The data which has thus been accumulated include the spatial arrangement of atoms within the unit cell, and as such may be useful in three main ways.

(i) Comparison of theoretical with empirical bond lengths and angles has provided a means for testing various conceptions of atomic structure.

(ii) Specific predictions about the interaction of certain classes of atoms may be made. For example, the dimensions and planarity of the benzene ring, and many hetero-cyclic compounds, are well known.

(iii) General forecasts may be made about systems for which there is no explicit data. Such a prediction may concern the possibility of hydrogen bonding between molecules in a solid, the basis for this being the prevalence of this kind of intermolecular bonding in those organic crystals which

have been studied.

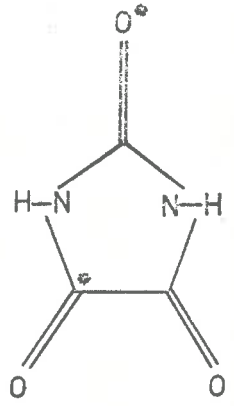
Although there are inherent dangers in making dogmatic statements on such a basis, much insight on the crystal structure may be gained by this approach. Examples of the use of this technique include the Watson-Crick base-pairing in their model for D.N.A. (Watson and Crick (1953)) and the discovery of the α-helix (Pauling, Corey and Branson (1951)). With regard to the latter, proteins were known to be polymers of amino acids linked together in polypeptide chains and X-ray diffraction photographs had shown some of these chains to be helical. Of two sterically reasonable helices (the α and γ forms) the α-helix requires less bending of the N-H....O hydrogen bonds and was therefore selected. Subsequent structure analyses have verified the α-helical structure of proteins.

On the other hand, the recent discovery of another intermolecular bonding mechanism in a certain class of organic solids has shown that its influence must also be considered when making general predictions about the crystal structure.

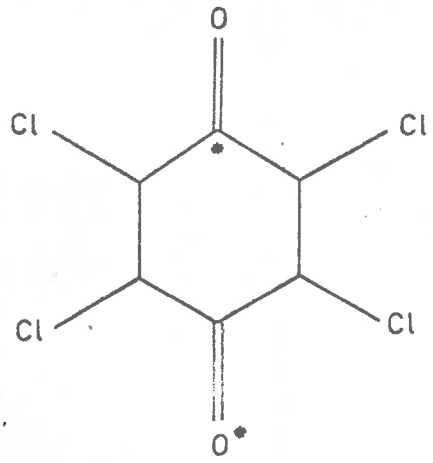
Until 1966 only five examples of this new mechanism had been observed. They were in parabanic acid (Medlin (1955) and Davies and Blum (1955)), chloranil (Chu,

Jeffrey and Sakurai (1962)), anhydrous barbituric acid (Bolton (1963)), alloxan (Bolton (1964(a))) and triketoindane (Bolton (1965)). Figure 1.1 shows the most stable valence bond structure for these compounds and the intermolecular contact data in each case. The contact is always between a carbonyl oxygen atom and a ring carbon atom and it results in a significant shortening of the sum of the Van der Waals' contact radii for carbon and oxygen atoms (3·1Å). Further, in each case there is a deficiency of acidic protons for complete hydrogen bonding of all the electronegative atoms in the crystal. These consistencies in the data enabled Bolton (1964(b)) to predict the existence of contacts in alloxan and triketoindane. In fact in these two structures no hydrogen bonding occurs, despite the presence of two N-H groups in alloxan.

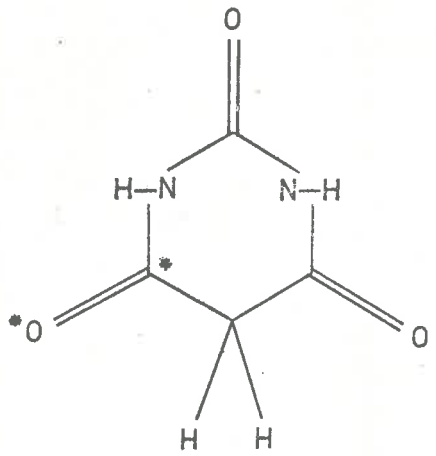
Bolton (1964(b)) has formulated two empirical criteria for the formation of carbon-oxygen contacts. The requirements are the existence of several carbonyl groups associated with a ring molecule and the deficiency of protons outlined above. The significance of the second condition has yet to be verified. The implication that facilities for hydrogen bonding will be utilized in preference to those for contact formation is contradicted by



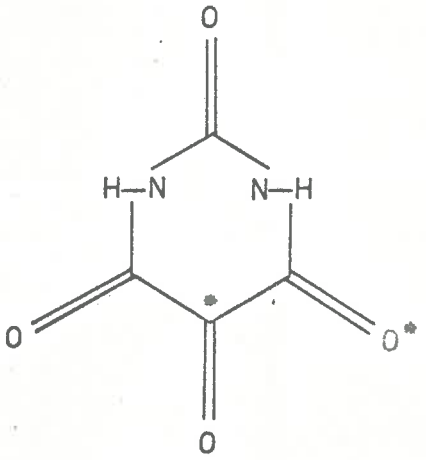
Parabanic acid
(2.77 Å , 157.4°)



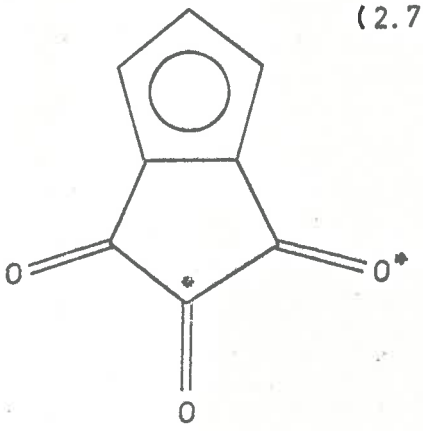
Chloranil
(2.85 Å , 161.0°)



Barbituric acid
(2.90 Å , 162.5°)



Alloxan
(2.79 Å , 154.7°)



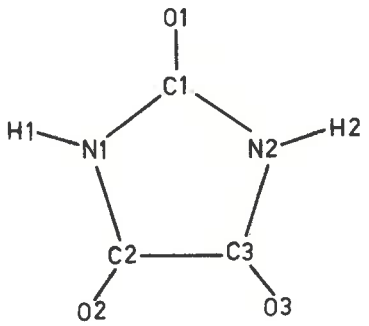
Triketoindane
(2.85 Å , 150.7°)

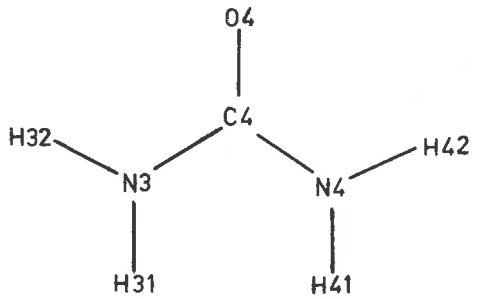
Fig. 1.1 Previously observed contacts. The dimensions are those of the O----C' contact length and the C=O----C' contact angle. The contact atoms are starred.

the alloxan structure.

Two other points of interest are in context in this introduction. The approximate collinearity of C = O .. .. C′ atoms and the direction of the contact relative to the p_z orbital of C′ support the view of Bolton (1964(b)), whereby the interaction is similar to hydrogen bonding, a dipole attracting a charge. Also, there is no adequate explanation for the fact that the oxygen atom involved in the contact is not involved in a hydrogen bond (i.e. apart from the fact that in some cases no protons are available), since there is no geometrical reason why the two mechanisms may not act simultaneously. It is well known, for example, that a given oxygen atom may be active in multiple hydrogen bonding (Vaughan and Donohue (1952)).

The study of a compound with excess protons for hydrogen bonding, but which still might be expected to be stabilized by the contacts, was considered. Urea parabanate (UPBA), a complex of urea and parabanic acid, is such a compound.





There are six protons in the structure ($CO(NH_2)_2$ - $(CO)_3(NH)_2$) and all four carbonyl oxygen atoms may therefore be hydrogen bonded. Since the parabanic acid crystal structure is stabilized by a contact, knowledge of the UPBA structure should provide interesting information on the way in which the two bonding mechanisms compete. To the author's knowledge, this is the first complex of any of the five compounds in question to be studied.

The study of this compound is related to other work in this laboratory. During the synthesis of parabanic acid, Medlin (1955) observed two unknown compounds which have since been identified as urea oxalate and urea parabanate. The structure of the first of these was determined by Gurr (1961).

1.1.1 Preliminary Investigation of UPBA

Preliminary work on the structure of UPBA was done in 1965 as part of the B.Sc. Honours course in Physics. In brief, the report of that work contains the following relevant information.

(a) Crystals of UPBA were grown by saturating a warm solution of parabanic acid with urea. The crystal habit is tabular prismatic, elongated in

the b-direction with the (101) face well developed.

(b) The crystals melt at 183°C and the clear melt decomposes at approximately 220°C.

(c) The results of micro-analysis give the relative proportions of the elements as $C_2O_2N_2H_3$, suggesting that the complex has formed with urea and parabanic acid in the ratio 1:1 (M.W. = 174).

(d) The density (δ) was found by flotation to be 1·61 grms/cc.

(e) Rotation and Weissenberg data about the b-axis give the approximate unit cell as

$$a = 9{\cdot}05\text{Å}$$
$$b = 5{\cdot}56\text{Å}$$
$$c = 14{\cdot}8\text{Å}$$
$$\beta = 107^\circ$$

Using the relationship

$$\delta = \frac{mn}{N_0 V}$$

where m = molecular weight

N_0 = Avagadro's number

and V = unit cell volume,

n, the number of asymmetric units per unit cell, is four. This value gives agreement with the measured density to within 1%.

(f) Extinction along reciprocal lattice rows defined by (h,o,2n+1) is a necessary but not sufficient condition for space group $P2_1/c$. (The space group was subsequently determined unequivocally when a-axis photographs revealed extinction of (0,2n+1,0) reflections).

(g) The angle between the optic axes (2V) is close to 90°, implying therefore at least that the structure is not planar.

(h) There are no well defined cleavage planes but two were found which are apparently related by the screw axis. (Later, these planes were found to be close to (211) and $2\bar{1}1$)). A less well defined cleavage was subsequently indexed as $(\bar{1}01)$.

(i) Infra-red spectra of urea, parabanic acid and UPBA were recorded (in potassium bromide discs) for 'finger printing' purposes only. Considering the method of preparation of the complex it was not surprising that no new high energy (covalent) groups were evident.

(j) This work ended at this stage with collection of three dimensional b-axis data by the Weissenberg method. Multiple (4) film packs were used. Four layers of unintegrated intensities were recorded on a three day exposure from a crystal which had been etched into a cylinder of radius ·1 mms. This was done to minimise absorption effects (see section 1.2.1).

1.1.2 Equipment

For most of the work described in this thesis a modified Solus Medical X-ray Unit was used (Matthews (1963)). Typical tube ratings for Cu Kα radiation were 30 kV (full wave rectified) and 20 mA. The only modification to this unit as described by Matthews was the replacement of the vacuum diodes by solid state rectifiers, this alteration being made for the work described in chapter two. Several of the alignment photographs for the work in chapter two were taken on a Hilger X-ray Diffraction Unit.

1.2 Intensity Data

Of the 1600 independent reflections within the limiting sphere for Cu Kα radiation, 956 were estimated by eye from the b-axis setting. A well shaped, low angle

reflection was used in the preparation of a calibration strip with linear range from 1 to 30. On this basis 879 of the reflections were assigned non-zero intensity. In addition to the three day exposure taken earlier, six day and three hour exposures were also recorded. The former enabled more accurate determination of weak reflections whilst the latter was necessary for those orders of diffraction which were otherwise outside the linear density range of the film. Film factors were calculated by hand and all intensities were scaled to the top film of the six day exposure. Intensities in the range 1 to 40000 (on some arbitrary scale) could be estimated (F(000) = 360).

1.2.1 Physical and Geometrical Corrections

Corrections for contraction and elongation of upper level Weissenberg data were made according to Phillips (1954). These corrections were made by hand by measuring the distortion in length of the reflections in question. For contracted reflections the correction is

$$I_c = I_o \left(\frac{L-\Delta L}{L}\right) \qquad (a)$$

and for elongated reflections

$$I_c = I_o \left(\frac{L+\Delta L}{L}\right) \qquad (b)$$

where ΔL is the distortion from the mean length L and I_o is the intensity estimated from the film. When the contraction was severe (b) was used alone.

Equivalent reflections were then averaged according to the rules for space group symmetry $P2_1/c$, viz.

$$I(hk\ell) = I(h\bar{k}\ell)$$

and $$I(\bar{h}k\ell) = I(hk\bar{\ell})$$

and the mean value was used for subsequent calculations.

The C.S.I.R.O's CIRRUS 3200 computer was available to students of the University and this was programmed to make Lorents-polarisation corrections. Unitary and normalised structure amplitudes, which at this stage were unscaled and uncorrelated from layer to layer, were also calculated. These quantities are defined as

$$U_h = \frac{F_h}{\Sigma f_{jh}} \quad \text{(sum over atoms)}$$

and $$E_h = \left(\frac{|F_h|^2}{\epsilon \Sigma f_j^2}\right)^{\frac{1}{2}}$$

respectively, where the value of ϵ depends on the space group and the value of h.

Since $\mu = 13{\cdot}0\ cm^{-1}$ for UPBA, the optimum thickness is ·15 cms. The crystal diameter is therefore approximately $\cdot 2/\mu$ and absorption effects were considered to be negligible.

Multiple diffraction was considered and rejected as insignificant. Although this effect is probably present on (hKℓ) sections when $K \neq 0$ (since $c \approx 15\text{Å}$) it will not effect a structure analysis in which accuracy of ·01Å is required. Panke and Wolfel (1969) have recently shown that in Mg_2Si the errors introduced by multiple diffraction are of the order of $0{\cdot}1\ e/A^3$ in the final electron density distribution.

1.2.2 a-axis Photographs

Several of the faces in the [010] zone were indexed from the zero layer Weissenberg film and it was therefore possible to align the crystal for a-axis photographs. However, the morphology of the crystal made it difficult to obtain a crystal suitable for X-ray work. The c-axis was also unsatisfactory in this respect and it was decided to work on the b-axis data alone. The main implications of such a decision are the failure to record certain principal axis data (in this case (020), (040) etc) and the lack of information for correlation of intensities

measured from parallel reciprocal lattice sections. The principal axis data is of most importance when there is a molecular plane perpendicular to this axis and in this case the cleavage information left little doubt that U(oko) would not be significantly large. Furthermore, since all the b-axis data had been scaled to the six day exposure (and fluctuations in the X-ray flux over six days should average themselves out) it was considered that the interlayer scaling constants required to correlate the separate layers would be close to unity.

1.2.3 The Double-Slit Weissenberg Method

As a check on these constants, a modified version of Stadler's (1950) double slit Weissenberg method was used to record simultaneously the zeroth and nth b-axis layers. A pair of compatible layer line screens were constructed for the purpose of recording each layer on separate halves of the film. (See appendix A). This eliminates the need for the ring of variable width as required by Stadler. Rotation of the screens through 180°, followed by a second photograph, provides the necessary data for making the Phillips correction.

Whilst the correction for the Lorentz factor is a function of $\cos\nu$, the polarisation correction varies with

$\sin\nu$. $(Lp)^{-1}$ is therefore different for data collected in the equi- and anti-equi-inclination positions. In the double slit method, the zero layer cone intersects the film in the anti-equi-inclination position. Martha (1952) has drawn contours of $(Lp)^{-1}$ (for anti-equi-inclination) as a function of the inclination setting and these were used to make the corrections for zero layers from this set of data.

For a given film, approximately twenty reflections of each type, (hoℓ) and hKℓ), were estimated visually and corrected in the way outlined above. The ratio of the final intensity to the intensity of the same reflection from the b-axis film packs was then found. The constants are all close to unity. If

$$\left(\frac{\overline{I(hK\ell)}_{\text{double slits}}}{I(hK\ell)_{\text{b-axis data}}}\right)=C_K\left(\frac{\overline{I(ho\ell)}_{\text{double slits}}}{I(ho\ell)_{\text{b-axis data}}}\right)$$

then $C_1 = 1{\cdot}01$

$C_2 = {\cdot}94$

$C_3 = 1{\cdot}19$

From the data, these values are reckoned to be accurate to within 10%.

1.2.4 The Wilson Plot

Least squares fitting of the data to a Wilson plot (Wilson (1942)) showed that it was almost on an absolute scale. The best fit parameters (see Fig. 1.2) were

$$k = 1{\cdot}01$$

$$B = 2{\cdot}3$$

where $kI_{obs} = I_{abs}$

and B is the temperature factor constant in the expression $f = f_o \exp(-BS^2)$.

1.3 Unit Cell Data

After a satisfactory trial structure had been determined, the unit cell constants were redetermined with greater accuracy than before. This was necessary in order that sufficient accuracy in the bond length and angle data might be obtained, especially when it was apparent that close carbon-oxygen contacts were present in the structure.

The Weissenberg film was calibrated with sodium chloride lines in the following way. Crystals mounted for both b and a axis photographs were dipped several times into a cold concentrated solution of sodium chloride (ANALAR). Powder lines are produced on the Weissenberg

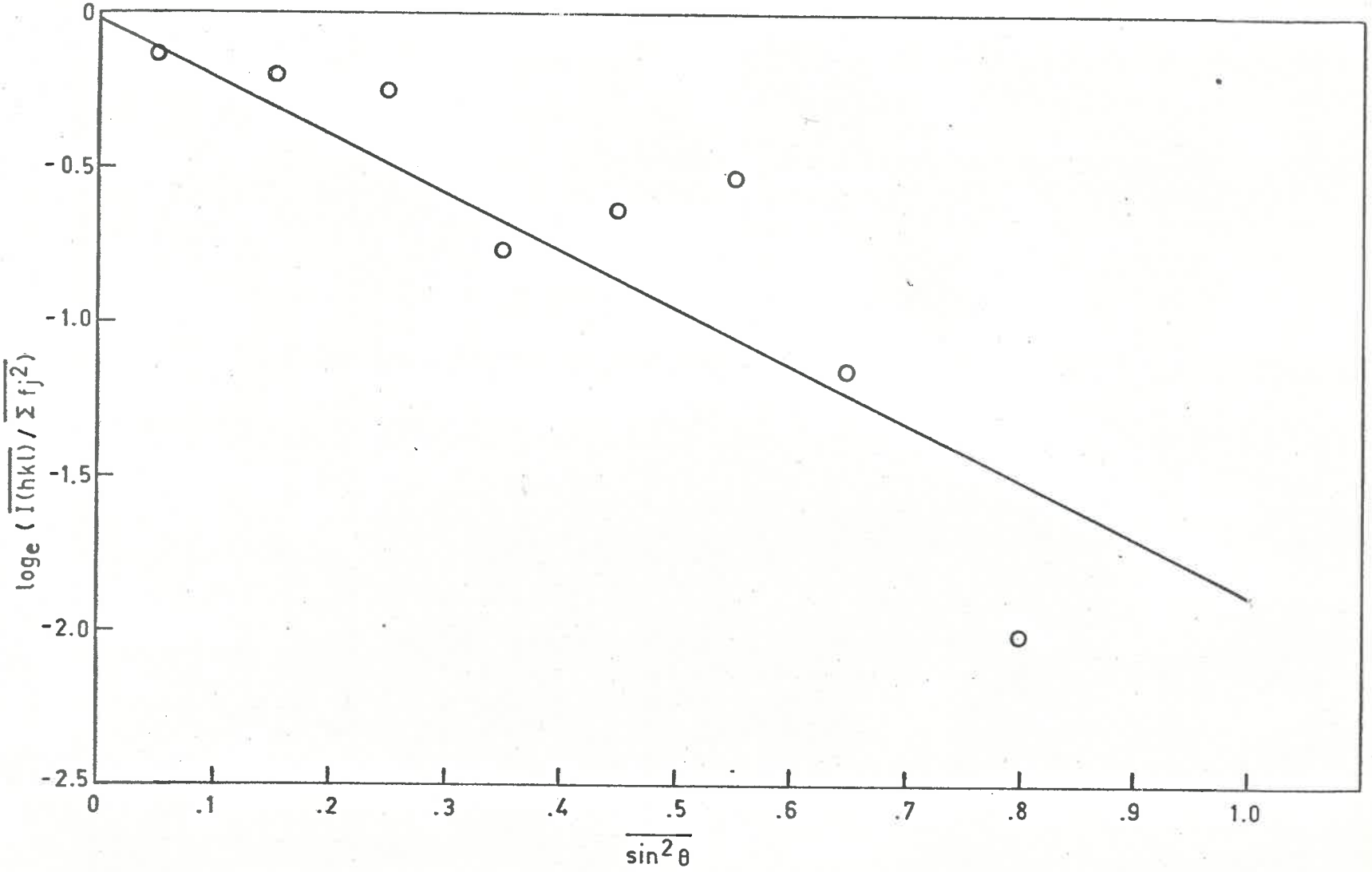


Fig. 1.2 Wilson plot UPBA.

film. For a body-centred cubic reciprocal lattice (NaCℓ being f.c.c.) the extinction conditions are such that, if zero is considered an even number, the indices of reflections with non-zero intensity are either all odd or all even. The cell constant for NaCℓ is 5·6274Å. The reciprocal lattice coordinates of the powder lines were determined by $dd^* = \lambda$. From the (hoℓ) and (okℓ) sections of data

$$a^* = \cdot1786 \pm \cdot0003$$

$$b^* = \cdot2742 \pm \cdot0002$$

$$c^* = \cdot1087 \pm \cdot0003$$

The angle of the cell was determined by measuring accurately the angle between three well developed faces of the crystal, all of which were in the [010] zone. These faces were (101), (001) and $(\bar{1}01)$ and the angles, as determined from measurements made on a one-circle Unicam S.25 goniometer, were accurate to one minute of arc. Several measurements from two separate crystals were made. The values for two independent angles can be used to get two values of β^* by using the geometry of the (hoℓ) reciprocal lattice section. The final unit cell parameters are

$$a = 9\cdot137 \pm \cdot014\text{Å}$$

$$b = 5\cdot623 \pm \cdot003\text{Å}$$

$$c = 15\cdot013 \pm \cdot045\text{Å}$$

$$\beta = 109^\circ 08' \pm 02'$$

This technique of determining the cell constants is recommended by its simplicity, even though the accuracy obtained is somewhat less than that obtainable by other methods (e.g. Farquhar and Lipson (1946)). The uncertainty in the length of a 1Å bond in the c-direction is approximately ·003Å and it was expected that this would be significantly less than the standard deviation of bond lengths as determined by the least squares procedure.

1.4 The Phase Problem

The well known Fourier transform relationship between an object (e.g. crystal structure) and its diffraction amplitudes has been discussed by Lipson and Cochran (1966). The three dimensional periodicity of the unit cell in the crystal structure requires sampling of the unit cell transform at points on a reciprocal lattice, the geometry of which is inversely related to that of the real lattice.

Three important properties of the Fourier transform which are relevant to crystal structure work are:

(a) repetition in one space gives sampling in the other,

(b) multiplication in one space gives convolution in the other, and

(c) a section in one space gives a projection in the other.

The operations of addition and subtraction are preserved by the transform provided proper account is taken of the phase. The property (c) was must useful before the advent of high speed electronic computers, since knowledge of two 2-dimensional projections of a structure suffices to locate the scatterers in 3-dimensions (provided overlap is not too severe).

If $\rho(xyz)$ is the density distribution in a cell of volume V and $\underline{F}(hk\ell)$ is the complex diffraction amplitude of order $(hk\ell)$ we may write

$$\rho(xyz) = \frac{1}{V} \sum_{-\infty}^{\infty} \sum \sum \underline{F}(hk\ell) \exp[-2\pi i(hx+ky+\ell z)]$$

From intensity measurements of the diffraction data only the real part of the complex amplitudes are known and determination of $\rho(xyz)$ cannot proceed directly.

The structure factor equations are

$$\underline{F}(\underline{S}) = \sum_{j=1}^{N} f_j \exp 2\pi i(\underline{r}_j \cdot \underline{S})$$

where f_j is the atomic scattering factor of the jth atom

at the coordinate $\underline{r}_j$ and $\underline{S}$ is the reciprocal lattice vector to the point (hkℓ). There are 3N unknowns in such an equation and it might be expected that the observation of 3N orders of diffraction would be different for a unique solution. However, each new observation introduces a new unknown, viz. the phase of that structure factor, and for m equations there are 3N + m unknowns.

There are two ways of approaching the phase problem.

(1) What information about the structure is carried by the intensities?

(2) What information about the phases is carried by the amplitudes?

The inherent equivalence of the two approaches is masked by the way each is expressed.

(1) Patterson (1935) has defined a function

$$P(\underline{u}) = V\int_0'\int_0'\int_0' \rho(\underline{x})\,\rho(\underline{x}+\underline{u})\,dx$$

which can be shown to reduce to

$$P(\underline{u}) = \frac{1}{V}\sum_{\underline{S}} |F(S)|^2 \exp 2\pi i(\underline{u}.\underline{S})$$

The Patterson function is, by definition, the autocorrelation function of the unit cell contents and for

computational purposes is the Fourier transform of the intensities. The autocorrelation function of a set of N points is the vector set of the fundamental set and contains N images of this set at the origin. The finite size of the atoms and the crowding of N^2-N peaks into the Patterson cell (of the same volume as the real cell) causes overlap of peaks, and the function, for large N, is often insoluble.

(2) The fact that the phaseless intensity data can be transformed into a function directly related to the scattering density implies that phase information is stored in the diffraction amplitudes. However, the existence of homometric sets (i.e. two real sets with the same vector set) suggests that this phase information will not always be unique. If it can be extracted, the Fourier transform relation can be used to find the scattering distribution.

In a structure of two atoms (space group P1) the structure factor equations can be solved to find the coordinates as follows.

$$\underline{F}(S) = f_1 \exp 2\pi i(\underline{r}_1.\underline{S}) + f_2 \exp 2\pi i(\underline{r}_2.\underline{S})$$

$$|F(S)| = [(f_1 \cos 2\pi(\underline{r}_1.\underline{S}) + f_2 \cos 2\pi(\underline{r}_2.\underline{S}))^2 + (f_1 \sin 2\pi(\underline{r}_1.\underline{S}) + f_2 \sin 2\pi(\underline{r}_2.\underline{S}))^2]^{\frac{1}{2}}$$

$$\therefore |F(S)|^2 = f_1^2 + f_2^2 + 2f_1f_2 \cos 2\pi\underline{S}.(\underline{r}_1-\underline{r}_2)$$

Without loss of generality, atom 1 may be put at the origin. The solution of the equations

$$|F(100)|^2 = f_1^2 + f_2^2 + 2f_1f_2 \cos 2\pi(x_2)$$
$$|F(010)|^2 = f_1^2 + f_2^2 + 2f_1f_2 \cos 2\pi(y_2)$$
$$|F(001)|^2 = f_1^2 + f_2^2 + 2f_1f_2 \cos 2\pi(z_2)$$

will yield $|x_2|$, $|y_2|$ and $|z_2|$.

Likewise

$$F(110) = f_1^2 + f_2^2 + 2f_1f_2 \cos 2\pi(x_2+y_2)$$

will yield $|x_2+y_2|$, and the relative signs of x_2 and y_2, and similarly of x_2 and z_2, may be determined. Measurement of five orders of diffraction is sufficient to solve this system.

When there are three scatterers in the cell, higher order diffraction amplitudes must be considered and polynomial equations are generated. Geometrically the problem with N>2 is that the shape of a three sided figure (N=2) is determined by the length of its sides, but this is not so for a four sided figure.

Karle and Hauptman (1953) have used probability methods to determine the signs of structure amplitudes of centrosymmetric crystals and the literature illustrates the growing use of this and similar methods of phase

determination. Recently Karle and Karle (1966) have given a procedure for noncentrosymmetric space groups.

Other methods of phase determination include the heavy atom method (Carlisle and Crowfoot (1945)) and the method of ismorphous replacement (Cork (1927)).

The underlying importance of phase determination in all crystal structure work has stimulated the following speculations on possible solutions.

(a) Consider the following pairs of functions which are Fourier mates (i.e. one is the Fourier transform of the other and vice versa).

$$\begin{aligned} \rho(r) &\leftrightarrow \underline{F}(S) \\ P(u) &\leftrightarrow |F(S)|^2 \\ p(r) &\leftrightarrow |\underline{F}(S)| \end{aligned} \qquad (1)$$

Here ρ, P and F have their usual meaning and p(r) is defined on the unit cell of $\rho(r)$ to be that distribution of scattering material which has a purely real diffraction pattern $|F(S)|$. In one dimension

$$p(x) \simeq \sum_{h=-\infty}^{\infty} |F(h)| \exp 2\pi i h x \qquad (2)$$

$$= \sum_{h=-\infty}^{\infty} |F(h)| (\cos 2\pi h x + i \sin 2\pi h x)$$

$$= \sum_{h=0}^{\infty} \left\{ |F(h)| \begin{matrix} (\cos 2\pi h x + i \sin 2\pi h x) \\ (\cos 2\pi h x - i \sin 2\pi h x) \end{matrix} \right\} + |F(-h)|$$

$$= 2 \sum_{h=0}^{\infty} |F(h)| \cos 2\pi hx \qquad (3)$$

since $|F(h)| = |F(-h)|$ (Friedel's Law) $\therefore$ $p(x)$ is real. The logic in this result is

$$\rho(x) \text{ real} \rightarrow \text{Friedel's Law} \rightarrow p(x) \text{ real.}$$

(It should be noted that Friedel's Law only holds for non-anomalous scattering). However $\rho(x)$ is strictly positive (in reality) whereas $p(x)$ may assume negative values. The physical meaning of these negative regions in $p(x)$ is that a phase change of π occurs when radiation is scattered from them. (Bragg scattering occurs without change of phase). Equation (3) implies that

$$p(x) = p(-x)$$

and $p(x)$ is therefore centrosymmetric, regardless of symmetry elements in $\rho(x)$.

An interesting property of $p(x)$ is that it has the same autocorrelation function as $\rho(x)$. If $*$ represents an operation by which a function is convoluted with its inverse, then

$$P(u) = \rho(r) * \rho(r) = p(r) * p(r)$$

(The inverse function here is defined as the centrosymmetrically related function). The existence of homometric

sets has been mentioned earlier in this section. If distributions which scatter with a phase change are considered, then every set has an infinite number of homometric sets; each corresponds to the transform of the amplitudes with a particular combination of phase angles. In general, only two of these sets are real, viz. p and ρ, since Friedel's law states

$$\underline{F}(h) = \underline{F}^*(-h)$$

and the result (3) does not necessarily follow from (2) when the Fourier coefficients are complex.

Two possible uses for p(r) are

(i) improving the resolution of P(u) as defined by p(r)*p(r) rather than by the Fourier transform method, and

(ii) direct determination of ρ(r) from p(r).

(i) The following argument may be used against the first proposition. Although p(r) will be sharper than P(u) (Fourier transform of a broader distribution is involved) this resolution will be lost when the autocorrelation operation is performed. All that is known about p(r) is that it is real and centrosymmetric. Whether or not it

is a continuous distribution (unlike $\rho(r)$ which is concentrated around well defined points in the cell) is open to speculation. If $p(r)$ does have the same character as $\rho(r)$ then we can define a function $p'(r)$ which is the point set corresponding to $p(r)$, each point having a certain weight and a phase angle of 0 or π. A geometrical autocorrelation of $p'(r)$ will then give a point vector set which can then be solved for $\rho(r)$ on the basis that $\rho(r)$ is always positive. The approximation of

$$P(u) = p(r)*p(r)$$

to

$$P'(u) = p'(r)*p'(r)$$

is obviously critical.

In some geophysical work, the scattering medium (e.g. the ionosphere) is a continuous distribution and $p(r)$ may well be such a function. However since $p(r)$ does have some of the properties of $\rho(r)$ (e.g. it is real), the character of the $\rho(r)$ distribution may also be found in $p(r)$.

(ii) From the above discussion it is seen that $p(r)$ and $\rho(r)$ are apparently unique as real solutions to the Patterson function $P(u)$. One way of looking at $p(r)$ is

to say that the phase information carried by the amplitudes has been converted into the phase information in the function p(r). It is interesting that phase angles carried by amplitudes from a noncentrosymmetric structure convert into phase angles of 0 or π in p(r).

(b) Another approach to the problem was by consideration of Fourier series whose amplitudes were $\underline{F}^{1/n}$ where n is integral. The error in approximating these coefficients by $|\underline{F}|^{1/n}$ is smaller for large n. Thus if

$$\rho \leftrightarrow \underline{F}$$

$$p \leftrightarrow |F|$$

$$\rho^{1/n} \leftrightarrow F^{1/n}$$

$$p^{1/n} \leftrightarrow |\underline{F}|^{1/n}$$

then $$\lim_{n\to\infty} \rho^{1/n} = p^{1/n}$$

The function $\rho^{1/n}$ may be complex but approaches the real function $p^{1/n}$ in the limit. If n is even then

$$p^{2/n} = p^{1/n} * p^{1/n} \text{ and } \rho^{2/n} = \rho^{1/n} *' \rho^{1/n}$$

(*' represents self-convolution, not autocorrelation). For large n, $p^{1/n}$ is very sharp since the coefficients $|\underline{F}|^{1/n}$ are quite flat. It is likely that errors in

measurement of $|F|^2$ will be magnified when the nth root of $|F|$ is used as coefficient in the Fourier expansion. The function $p^{1/n}$ is always centrosymmetric and therefore the operation of successive self convolutions will always regenerate p and not ρ.

The foregoing discussion contains some of the author's ideas on the phase problem. The function p(r) has not been calculated for either of the structures determined in this project since it is not clear that it would assist in the solution. The ideas expressed have not been enlarged.

1.5 The Patterson Function

By definition the autocorrelation function is centrosymmetric, and the odd terms in the expansion for P(uvw) are zero. Therefore we may write

$$P(uvw) = \frac{1}{V} \Sigma\Sigma\Sigma_{hk\ell} |F(hk\ell)|^2 \cos 2\pi(hu+kv+\ell w)$$

This computation was done on the University's CDC 6400 machine using a Fourier program written by Dr. E. W. Radoslovich of the C.S.I.R.O. (Adelaide). This program required only minor modification to render it compatible with the 6400 and was subsequently used for the work described in this chapter. The use of projections was not considered at this stage since a three dimensional Fourier

with 1000 coefficients could be computed in approximately three minutes.

Lipson and Cochran (1966) give the least number of intervals along a cell edge to be $4h_{max}$ for any given direction. On this basis, the sampling of $^{a}/_{30}$, $^{b}/_{30}$, $^{c}/_{60}$ could have been a little finer in the a direction. Without hand sorting of the cards, the above sampling made best use of the facilities of the program.

1.5.1 Sharpening

The Patterson peaks were sharpened by applying an artificial temperature factor to the structure factors. The chosen value of B was 2·3. The diffraction pattern of a step function of height a and width T is

$$F(n) = aT\left(\frac{\sin(\pi nT)}{(\pi nT)}\right)$$

and therefore if the effect of applying the temperature factor is to increase the value of structure factors at the edge of the limiting sphere by a factor of 10, a similar increase in the amplitude of the ripple may be expected. In this case at $\sin\theta = 1$ we have

$$F_S = F \exp\left(2{\cdot}3 \left(\frac{1}{1{\cdot}54}\right)^2\right)$$

$$\approx 3F$$

i.e. $I_s \approx 9I$

and hence a 9 fold increase in the sharpened ripple over the unsharpened ripple will result. The value B = 2·3 has been found to give good compromise between maximum sharpening and minimum diffraction ripple.

1.5.2 Harker Sections

Symmetry related atoms in the $P2_1/c$ unit cell are found in the following general positions:-

(xyz)

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

$(\bar{x},\frac{1}{2}+y,\frac{1}{2}-z)$

$(\bar{x}\ \bar{y}\ \bar{z})$

The vector set of this array of four points will also be a set of four points with coordinates

	(000)	(weight 4),
	(2x,2y,2z)	(" 2),
	$(2x,\frac{1}{2},\frac{1}{2}+2z)$	(" 2),
and	$(0,\frac{1}{2}-2y,\frac{1}{2})$	(" 2).

When the set of interatomic vectors is generated the translational symmetry of the cell is lost and the Patterson symmetry is therefore $P2/m$. It is therefore

sufficient to calculate only one quarter of the Patterson cell.

1.5.3 Solutions of the Vector Set

The Harker plane, $v = \frac{1}{2}$, is densely populated with peaks, but the line section, $u = 0$, $w = \frac{1}{2}$, shows only two maxima. The peaks at $v = 0$, and $v = \frac{1}{3}$ correspond to scattering centres at $y = 1/4$ and $y = 1/12$ in the real cell. This apparent constraint on y coordinates could lead to the conclusion that there are two molecular planes perpendicular to b. Further evidence in support of this view is the density of peaks in $v = 0$ and the absence of other peaks until $v = 1/6$, a distance of approximately $\cdot 9\text{Å}$.

Such a conception, however, is not only contradictory to the optical evidence but is most unlikely in a structure such as this where the intermolecular bonds are almost certain to be hydrogen bonds. The absence of other peaks along the Harker line is apparently the result of overlap.

The fact that many peaks (seven) had arisen at $v = 0$ is not so easily explained. If the structure were planar and perpendicular to b, the absence of (oko) spectra would only serve to smear out the peak coordinates around $v = 0$.

The effect of these Fourier waves (when they are large and are included in the summation) is to add grossly to those peaks near v = 0 and to contribute little to those elsewhere. (This is the case for large F(010) and small F(020)). The density of peaks on v = 0 can best be attributed to chance vector relationships between atoms.

One way of making use of the two Harker line peaks is to treat the two molecules in the asymmetric unit as diffuse scatterers. The strongest peaks in the Harker plane were used in conjunction with two y values derived from the line section. The relative weights given to the scatterers in reciprocal space were 2:1 (parabanic acid has 58 electrons and urea, 32). The parabanic acid was placed to correspond to the heavier of the Patterson peaks and structure factors for this model were calculated. (This calculation was done on the 6400 by SFLSFU, a Flinders University version of the Oakridge least squares program. The program was made available by Dr. M. Taylor). After scaling $\Sigma F_o = \Sigma F_c$ the reliability index for 60 low angle reflections from zeroth and first b-axis layers was ·60. A Fourier map was computed using 30 coefficients whose phase angles were strongly indicated from the structure factor calculation, but there was no sign of any fine

structure and the density profile in the region of the diffuse scatterers was flat.

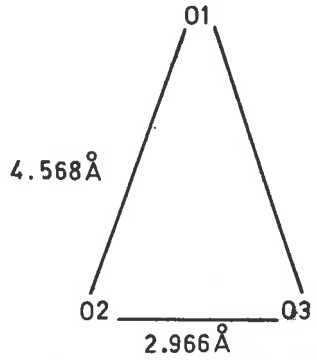
This was a surprising result since the Fourier had been loaded with those phases which would tend to transform the structure factors back into the model. Failure to reproduce the model from the Fourier was taken as an indication that this approach was unsatisfactory. (It is interesting to note here that the structure was finally solved from the parabanic acid phases alone). Although it might appear that this, in turn, suggests that there is no information of value in the Harker line peaks (because of overlap), one of the real cell coordinates implied by this line is $y = 1/4$, and this defines the glide plane. In parabanic acid (Davies and Blum (1955)) the space group symmetry is $P2_1/n$ and the molecules are centred on the diagonal glide plane, although they do not actually lie in the plane. At best the Harker line information infers the existence of a molecule centred on or near the glide plane. Furthermore the relative peak heights of these two Harker peaks imply that this molecule is more likely to be parabanic acid than urea.

1.5.4 Molecular Planes

The molecular structures of both parabanic acid and urea are known to be planar, and any distortions in this

planarity as a result of the formation of a hydrogen bonded complex will be negligible in the autocorrelation function. Molecular planes (hkℓ) in the real cell will manifest themselves as planes of the same orientation through the origin of the Patterson function. The location of such planes is possible either from a knowledge of characteristic images of parabanic acid and urea molecules or from some computation on the density of peaks in various planes through the Patterson origin. Since the former method supplies both the plane and orientation of the molecule (whilst the latter, only the plane) it was attempted first.

The largest scale known structure in the cell was the oxygen triangle of the parabanic acid molecule.



Large scale images were preferable to small scale images by virtue of their dominance over the origin peak of the Patterson function. This peak was in fact of the same size as the urea molecule.

The 6400 was programmed to compute peak distances from the origin and two possible images of the above triangle (O1 at the origin) were found. In the first the O2-O3 vector was only 2·2Å and the long sides of the network were 4·9Å. The image lay in the (211) plane. The second image had dimensions 4·9, 4·5, 3·4Å and again was in the (211) plane. The latter is more satisfactory for two reasons.

(i) There is evidence for the existence of an image of the triangle with O2 at the origin. Theoretically the vector set contains images of the fundamental set in all of the points of the fundamental set. Images of parabanic acid in carbon and nitrogen atoms are not seen since weaker interactions are involved. (The atomic numbers of carbon and nitrogen are only marginally less than that of oxygen yet the relative peak heights for interactions between these atoms are magnified as shown below:-

O-O 64

N-O 56

N-N 49

C-O 48

C-N 42

C-C 36).

Images of parabanic acid oxygen atoms are seen in both O1 and O2 in Fig. 1.3.

(ii) There is not sufficient energy in a hydrogen bond to distort each of the carbonyl groups (C2-O2 and C3-O3) by 25° as required by O2-O3 = 2·2Å.

The second image was therefore considered the better and was subsequently used as a starting point for models of the structure.

The Miller planes (211) and (422) are both strongly reflecting with unitary values ·3 and ·45 respectively, the latter being the second to largest U(hkℓ) recorded. This value of ·45 is significantly larger than may, at first, be apparent. The space group symmetry forces matter in (211) into $(2\bar{1}1)$ and $U(2\bar{1}1)$ is also ·45 ($F(hk\ell) = F(h\bar{k}\ell)$). The unitary values as used here were defined by

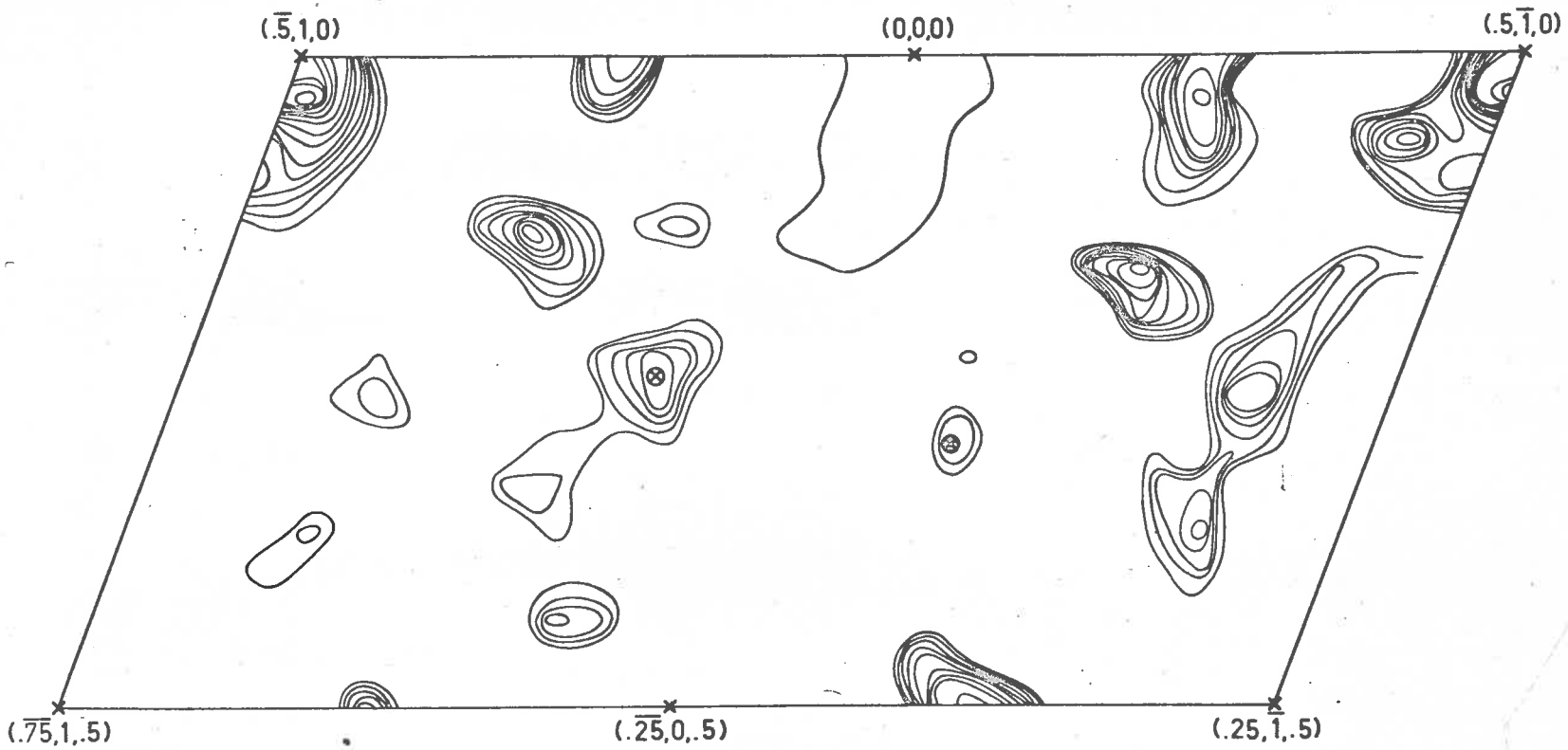
$$U_h = \frac{F_h}{\Sigma_j f_{hj}^2}$$

and no account was taken of symmetry related planes. Later in the analysis, when there was evidence for the (211) plane as the plane of the complex, the significance of these unitary values was fully realised. At most, half of the unit cell contents may be in the (211) plane

and therefore $U_{max}(211) = \cdot 5$. (This is not strictly so since some scattering material may lie on the line of intersection of the (211) and $(2\bar{1}1)$ planes, and therefore contributed strongly to both structure factors). However, it could not be concluded immediately that the urea molecule also occupied this plane since cleavage evidence had revealed the possibility of a molecular plane in the [010] zone.

The (211) plane of the Patterson was drawn out to scale from the three dimensional synthesis and was found to be densely populated with peaks (Fig. 1.3). In particular a strong peak at $(\frac{1}{2}, 1, 0)$ is in this plane. Detail of the imidazole ring is swamped by the origin peak and general overlap.

From the Harker section information it is theoretically possible to locate, the parabanic acid molecule in the cell once its orientation were known. At best the x and z coordinates could be determined from the $v = \frac{1}{2}$ section since the y information has been lost in overlap along the Harker line. However when the real cell has a centre of symmetry, as is the case for UPBA, the coordinates are oversolved by using all of the Harker information. In particular, the Harker peaks which result from



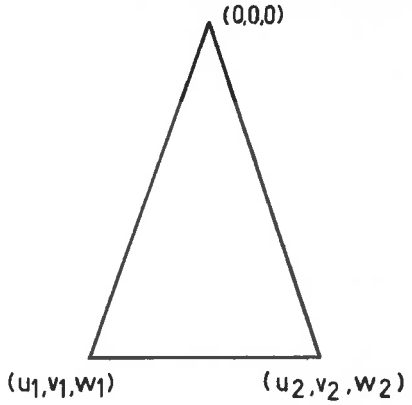
⊗ Parabanic acid image in origin

The (211) plane through the origin of the sharpened Patterson function (UPBA).

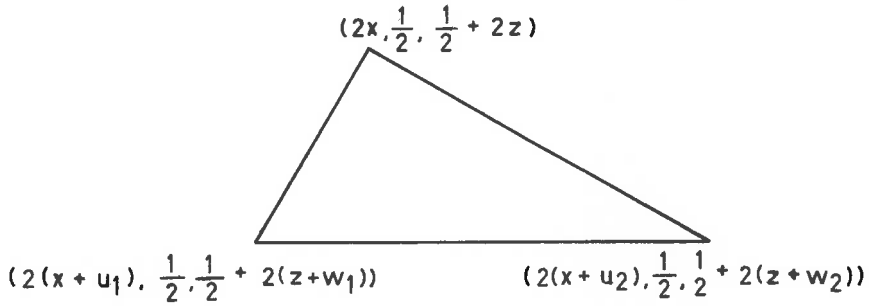
Fig. 1.3

interactions through the centre of symmetry may be used in this case. These peaks are not confined to a plane or a line but may be used as follows.

If in the (211) Patterson plane we assign the following coordinates to the parabanic acid image



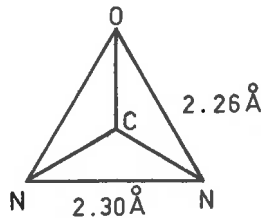
and if O1 is at (xyz) in the real cell, then on $v = \frac{1}{2}$, the interaction of this network with a screw related network appears as



Since $(u_1v_1w_1)$ and $(u_2v_2w_2)$ are known from the orientation

of the image in the origin, this figure is uniquely defined (at least with respect to orientation) on the Harker section. If such a figure were found, the x and z coordinates of O1, O2 and O3 are known and the y coordinates may be determined by seeking a consistent trio of (2x,2y,2z) peaks in the Patterson (i.e. consistent with v_1 and v_2 in the original image). A search of the computer output for these characteristic vectors on $v = \frac{1}{2}$ failed to realise a suitable (xyz). The use of superposition methods later proved more successful and did in fact lead to the structure.

Mention has already been made of two relevant facts concerning urea images in the Patterson; (i) the figure



is not large enough for an image to be seen in the origin. (ii) Oxygen-nitrogen vectors have less weight than oxygen-oxygen vectors in the Patterson.

Any image of the urea in the Patterson would necessarily be in one of the parabanic acid atoms. A search was made of the (211) plane of the Patterson through the

origin, on the assumption that urea might be in the same plane as parabanic acid, but no urea images were found. The listed output of the data reduction showed that several low angle planes were strongly reflecting. Besides (211) and (422), rows defined by (hoh), (hoh̄) and (okk) had large F values. The planes ($\bar{1}01$), (101) and (011) through the Patterson origin were all plotted, but no images of urea were found. The ($\bar{1}01$) plane was considered to be the most likely of these because it was parallel to the cleavage plane found earlier. Planes in the [010] zone provided a favourable packing arrangement for urea molecules up the b-axis. A hydrogen bonding scheme not unlike that found in the crystal structure of urea (Vaughan and Donohue (1952)) is possible (see section 1.7).

The (211) plane was again searched, this time for evidence of hydrogen bonding to the parabanic acid molecule. A number of peaks were found which were 3Å from O1, O2, O3, N1 and N2. At this point the intersection of the Harker plane with the (211) plane posed the problem of discerning between genuine Harker peaks and general peaks. Peaks 3Å from O2 and O3 were selected and the ($\bar{1}01$) and (101) planes through these points were plotted. No sign of a urea image was found.

At this stage of the analysis the shortness of the b-axis had presented the greatest difficulty in interpreting the Patterson function. Overlap along the Harker line and swamping of peaks near $v = \frac{1}{2}$ (especially on (211)) had led to loss of information which was needed to effect a solution of the vector set.

1.6 Direct Methods

1.6.1 Phase Determination

At this stage it was necessary to turn attention towards direct methods. Existing methods for extracting the phase information from the amplitude information have their roots in probability theory and, as such, do not guarantee the correct solution for a given phase angle. Statistically, one hopes that sufficient of the phase angles are correct to enable interpretation of the F_o synthesis. The probability of the angle being correct is usually greatest when the normalised structure amplitudes used in the phase determining procedure are large.

Normalised structure amplitudes

$$|E_h|^2 = \frac{|F_h|^2}{\epsilon \Sigma f_j^2}$$

(where $\epsilon = 1$, $hk\ell \neq 0$ and assumes other integral values

for the two and one dimensional subgroups of the $P2_1/c$ reciprocal lattice) had been computed on the 3200 and although they were unscaled and uncorrelated the proximity of the scaling constants to unity justified their use without correction. Hauptman and Karle (1953) give as a sign determining procedure for space group $P2_1/c$

$$s E_{2h,o,2\ell} \sim s\Sigma_k (-1)^{k+1} (E^2_{hk\ell}-1)$$

where s denotes 'sign of'.

On the zero layer, those reflections with largest E value which are suitable for this formula are (202), $(\bar{4}04)$ and $(\bar{6}06)$ but in no case was the phase strongly indicated. The fact that only four layers of b-axis data had been collected was probably accounting for this in part. Karle and Karle (1965) note that with organic crystals containing essentially equal atoms, few phases are likely to be determined. The failure of the formula for the largest E's to which it could be applied exemplifies this point.

The simplest of sign relationships for centrosymmetric crystals claims the high probability of F_{2h} being positive when U_h and U_{2h} are both large. On this basis the signs of $(\bar{2}\ 0\ 12)$, (404), (022), $(\bar{4}04)$ and (422) are

all positive. (In the final analysis, the last of these has opposite sign to the first four).

1.6.2 Line Fouriers

The Harker-Kasper sign relationship

$$s(h)s(h') = s(h+h')$$

was used to determine the signs of points along the row $(ho\bar{h})$. The presence of a significant peak in the transform of these reciprocal lattice points would indicate which, if any, of the $(\bar{1}01)$ planes was a molecular plane. The summation of Fourier coefficients of this type projects the electron density onto a line in the b-plane. This line may in fact be chosen arbitrarily, the only constraint being that it must pass through the $(ho\bar{h})$ planes (i.e. it cannot be in the $(\bar{1}01)$ plane). The best choice of this line is most apparent when the cell has cubic symmetry. In this case the line perpendicular to the $(ho\bar{h})$ planes would be chosen. In a monoclinic cell, however, the Fourier transform of the (hoo) type coefficients is usually thought to be a projection along the a-axis, although this line is not perpendicular to the (hoo) planes. This projection may equally as well be considered to be along the line $x = z$ provided it is recognised that no z information is contained in (hoo) diffraction data.

The Fourier transform relation is

$$\rho(xyz) = \sum_{h} F(hoo)\ \exp 2\pi i(hx+ky+\ell z)$$

and since k and ℓ are zero, the density is independent of y and z. The line y = constant, z = constant (i.e. the a-axis or a line parallel to it) is the best choice for a one dimensional projection in this case.

For the case in question

$$\rho(xyz) = \sum_{h} F(ho\bar{h})\ \exp 2\pi i(hx+ky+\ell z)$$

$$= \sum_{h} F(ho\bar{h})\ \exp 2\pi ih(x-z)$$

Clearly ρ is independent of y and is a function only of x and of z. This implies that the best line is in the b plane. However ρ depends only on the value of (x-z) and therefore any line $x = c_1 z + c_2$ ($c_1 \neq 1$) is satisfactory. If we choose $c_1 = c_2 = 0$ and a peak is found in the line Fourier at $z = \frac{1}{2}$, the implication is that the $(\bar{2}02)$ plane is a molecular plane.

Beevers-Lipson strips were used for this one dimensional calculation. Since all of the coefficients had been given the same sign, the synthesis had an origin peak but no others were generated. Whilst this might imply the existence of matter in (T01), changing the sign of (606)

generated a peak corresponding to scatterers in $(\bar{2}02)$. A transform of this type where only five coefficients are involved is very sensitive to phase and therefore could not be given much weight.

Similar attempts to determine phase angle along other reciprocal lattice rows which were considered important were not successful. The relationship

$$U_h^2 \leq \tfrac{1}{2}(1 + U_{2h})$$

was used, but failed to indicate strongly sufficient signs for the analysis to proceed directly. This was due to a lack of sufficient suitable pairs of reflections.

1.7 Model Building

Kitaigorodskii (1965) has emphasized the well known importance of molecular geometry in determining the crystal structure of organic crystals. By treating the interaction potential for two molecules as a rectangular function (classical 'billiard ball' approximation) it is possible to determine the closest packed molecular arrangement. Kitaigorodskii's argument is that this configuration is invariably the one which satisfies the condition of minimum free energy. Other properties of the molecule (such as the dipole moment of various bonds) play only a secondary role in determining the structure.

It was remarked in section 1.1 that the α-helix was determined in part from steric (i.e. packing) considerations. Recently Cekan and Pelo (1966) have made use of this technique in studying the effect of structural changes on the action of certain steroids. These and other examples are evidence that real structural information is contained in the size and shape of the molecules.

A perspex model of the unit cell and cardboard replicas of the planar molecules were constructed. The scale of the models was 2cm = 1Å. The molecules were so constructed that there was a 1·5Å radius around each of the outer atoms. Hydrogen bond facilities could therefore be quickly recognised by contact of nitrogen and oxygen atoms on neighbouring molecules.

It has previously been noted (section 1.5.4) that urea molecules will pack up the b-axis in a configuration similar to that found in the crystal structure of urea. In the urea structure, each oxygen atom is hydrogen bonded to four protons, two from a molecule in the plane of the oxygen atom and two from molecules at right angles to this plane. In UPBA it was originally postulated that the latter two hydrogen bonds would be to parabanic acid molecules (and not to the urea oxygen atom) whilst the former

were essentially the same. The urea plane was not known definitely at this stage and it was therefore necessary to consider both (101) and ($\bar{1}$01) packing possibilities.

Throughout the model building work it was recalled that the unique carbonyl group is not involved in hydrogen bonding in the crystal structure of parabanic acid. Rather, it is this group which is involved in a close contact with a carbon atom on a screw related molecule. Although the behaviour of this group in an environment of excess protons was not known, in the initial stages of model building it was presumed that it formed no hydrogen bond. The possibility of parabanic acid molecules sitting astride the c-glide plane and the link this has with the crystal structure of parabanic acid has already been discussed. Whilst molecules related by the diagonal glide in parabanic acid are hydrogen bonded to each other, in UPBA, c/2 = 7·5Å and duplication of the parabanic acid mechanism is forbidden (a shorter axis in the direction of the glide would be required).

The only unequivocal information that was available at this stage was the orientation of the parabanic acid molecule, as defined from the Patterson function. Neither its position, nor the orientation or position of the urea

molecule was known. Knowledge of active sites on each of the molecules for hydrogen bonding was of use but the usual problems associated with supporting a three dimensional model made this approach cumbersome. The subsequent mechanical simplification of the problem to two dimensions (chapter three) enabled more significant contributions to the structure to come from this technique.

It is well known that a deep understanding of the symmetry elements of a structure, together with the effects caused both in the point set and the vector set by these elements on displacement of the asymmetric unit in the point set, is essential for a deconvolution of the empirical data. The experience gained with these models led to such an understanding for this space group in particular and of the intellectual process in general.

CHAPTER TWO

THE CRYSTAL STRUCTURE OF THIOUREA PARABANATE

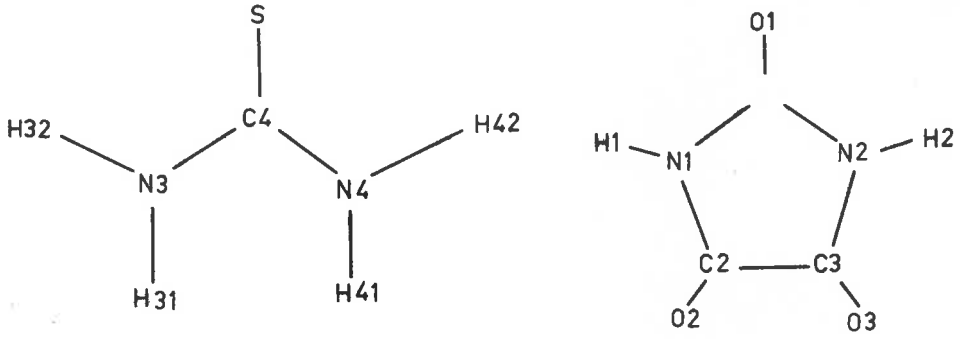
2.1 Introduction

The difficulties involved in deconvoluting the Patterson function are most severe when the structure is built up of light atoms alone. The convolution function is itself N images of the real structure (one image in each of the N atoms at the origin) and in the absence of a heavy atom none of these images is, in general, outstanding. The overall weight of a particular image depends on the imaging atom and if this is heavy all the other points in the image are weighted proportionately since they are, at worst, heavy atom-light atom peaks.

Accordingly, it was decided to grow crystals of thiourea parabanate, and to investigate its structure. A selenium substitution was also considered, but sulphur was selected because thiourea was readily available. Sulphur is not sufficiently heavy to enable phase determination in this structure (assuming a 1:1 thiourea: parabanic acid content). The parameter r, defined by Sim (1961), has the value ·55 and therefore only 65% of

signs would be determined if the structure were centrosymmetric. However, it was expected that the Patterson function would be more tractable than that for UPBA. Initially the information that was being sought from this structure concerned possible urea-parabanic acid hydrogen bonding mechanisms.

In the following discussion the atoms in the asymmetric unit will be referred to as



The possibility of this structure exhibiting the contacts mentioned in paragraph 1.1 should not be overlooked, even though the effect of the substitution is to weaken the affinity of the urea molecule for protons. (S---H-N hydrogen bonds are weaker than O---H-N hydrogen bonds, the electronegativity of S being less by comparison with that of O). If any weight is given Bolton's

second criterion this could be expected to reduce the possibility of contacts occurring in this structure.

2.2 Physical Properties

Thiourea was purified by successive filtration of the mother liquor. Half a gram of thiourea (excess) was subsequently added to one gram of parabanic acid in concentrated solution. Tabular prismatic crystals of the complex molecule settled out of the solution.

The faintly yellow coloured crystals have a well defined zone axis along which they are elongated, and they were apparently monoclinic. There is a well pronounced cleavage plane perpendicular to the unique axis and the possibility of hydrogen bonding up this axis seemed remote. Whilst no other cleavages as such were found, it is possible to cut the crystal, without severe fracturing, along two other planes. These planes have the unique axis as their zone axis. This was to prove useful later in obtaining crystals suitable for intensity work about some other axis.

The crystals melt at 213°C and at 220°C the clear yellow melt decomposes. The density was found by flotation in a mixture of benzene and ethylene dibromide to be 1·59 grm/cc and results of microanalysis implied the

presence of one molecule of thiourea to one of parabanic acid. A comparison of the observed (microanalysis) and calculated (1:1 complex) percentages of the elements is given in the following table.

Element	% Observed	% Calculated
H	3.12	3.11
C	24.52	25.26
N	29.00	29.47
O	26.00	25.26
S	16.44	16.84
	99.08	99.94

Approximate unit cell data were determined from rotation and Weissenberg photographs of the crystal in the b-axis setting. With a = 11·0Å, b = 6·34Å, c = 6·25Å and $\beta = 114^{\circ}$, there are two molecules of thiourea parabanate (TUPBA) in the unit cell. The absence of extinction along rows defined by h, ℓ = 2n on the (hoℓ) section eliminates the possibility of a glide reflection in either the a or c directions. The only extinction condition (found later when crystals were mounted about a second axis) was defined by (0,2n+1, 0) and therefore the only symmetry element is a two-fold screw axis parallel to b.

Diffraction amplitudes from a $P2_1$ unit cell are non-real and three dimensional analyses of noncentrosymmetric structures had not previously been attempted in this laboratory. However, excellent computing facilities had become available (section 2.5) and the problem of phase angle computation was therefore not serious.

2.2.1 Unit Cell Isomorphism

Initially, the main object of this structure determination was to get information which may be of value in solving the UPBA structure. The respective unit cells were therefore compared. The monoclinic angle in each case is approximately 110° and the length of the unique axis 6Å. The absence of the glide plane in TUPBA corresponds to the approximate halving of the length of c from UPBA to TUPBA. At best it could be said that there is some pseudo-isomorphism between the structures, whereby matter related by the glide plane in UPBA is related by the c translation group in TUPBA. This isomorphism was not expected to be directly useful in determining the UPBA structure. Already a very pronounced (oko) cleavage plane in TUPBA implied that the molecules were packed quite differently into the cell.

2.2.2 The b-plane

A perspex model of the unit cell was constructed (2cm = 1Å) and planar models of the complex in the b-plane were investigated. It was found that this plane was approximately the correct size to accommodate one molecule of the complex and this observation was considered highly significant in the light of the strong cleavage.

The absence of hydrogen bonds up the b-axis implied that the final position of any planar unit relative to the screw axis would be determined solely by the least energy condition between the two screw axis related layers. Since the least energy condition is not one which is readily computed, the best information that could be obtained at this stage was the orientation of the molecules relative to the a and c cell edges. This orientation is determined by hydrogen bonding with adjoining cells.

It was decided to leave this work until the Patterson function had been studied, since this was the only way in which the energetics of the problem could be effectively solved. However, the Patterson function yielded the structure, and model building techniques were not used. After the structure had been determined,

alternative packing arrangements for the complex in the b-plane were investigated. Only one other was found. The constraints imposed on the structure by the geometry of the molecules and unit cell, and the (oko) cleavage, are nearly sufficient to effect a two dimensional solution of the structure.

2.3 Intensity Data

2.3.1 b-axis Data

The crystal used for the collection of b-axis data was etched down to a cylinder of radius approximately 0·1 mms. For TUPBA the absorption coefficient μ = 34·8cm^{-1} and the optimum thickness $\left(\frac{2}{\mu}\right)$ is therefore ·6mms. Under these conditions absorption effects may be neglected. Four layers of unintegrated data were collected by the Weissenberg method on packs of four films. Exposures of the order of ten hours were found to be adequate.

2.3.2 [102] Axis Data

A parallepiped cut from the crystal by using the cleavage plane and the other two planes mentioned earlier, was mounted. It was at first thought that this crystal, which was elongated in some direction, was lined up about a. An approximate determination of the planes along

which it was possible to cut the crystal was made. The well developed face was close to the (601) plane whilst a second external face in the [010] zone was indexed as (101) (approximately 30° from (601)). One of the 'cleavages' was subsequently found to be $(\bar{1}01)$ whilst the other was parallel to the plate. The indexing of faces, by aligning them normal to the X-ray beam, and observing the position of the 'straight through' beam on the Weissenberg, becomes increasingly difficult as the plane in question reflects at higher angle. This work was not carried any further since the following study of the (hoℓ) reciprocal lattice section gave the rotation axis unequivocally.

The crystal was etched into a cylindrical shape of similar radius to the b-axis crystal, and four layers of unintegrated intensities were collected, again in packs of four films. The spacing between layers (okℓ), (1kℓ) etc. is ·152 reciprocal lattice units but the observed spacing was only ·121 r.l.u. The b* axis on the zero layer was identifiable by the 2_1 extinction condition. The spacing of the other axis was ·310 r.l.u. compared with ·267 r.l.u. up c*. A plot of the (hoℓ) section (see Fig. 2.1) showed the point $(20\bar{1})$ to be ·320 r.l.u. from the origin. Furthermore the spacing of ·121 units

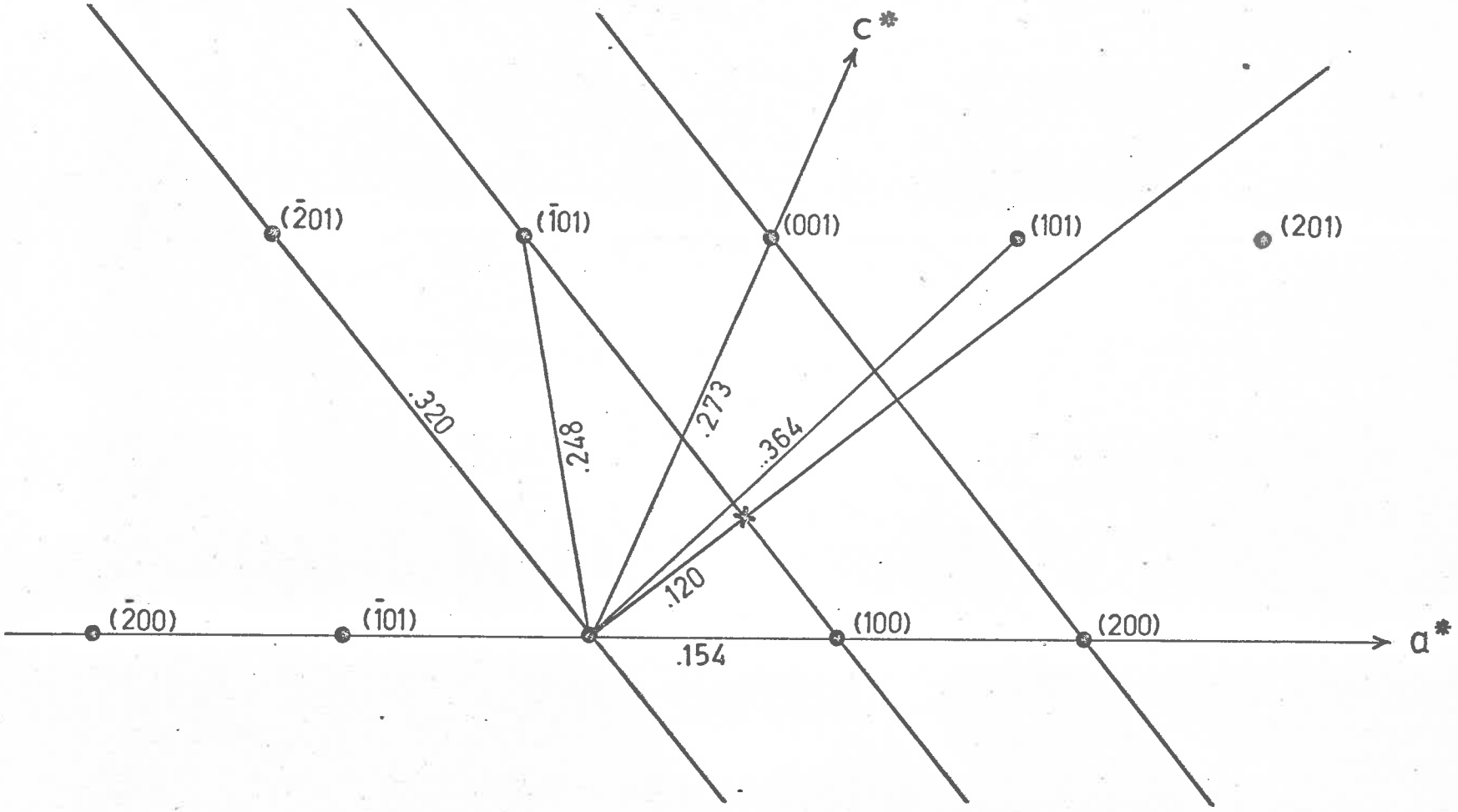


Fig. 2.1 (hol) section of reciprocal lattice (TUPBA).

up the rotation axis was also explicable. The zone axis of rotation [uvw] is therefore defined by

$$h_1u+k_1v+\ell_1w = h_2u+k_2v+\ell_2w = 0$$

where $(h_1k_1\ell_1) = (010)$

and $(h_2k_2\ell_2) = (20\bar{1})$

This yields [uvw] = [102] and the zone rules for the four layers of data about this axis are

$$h+2\ell = 0,1,2,3.$$

2.3.3 Data Reduction

There are approximately 900 reflections accessible with CuK_α radiation and of these 639 were recorded. Of these 113 were unobserved whilst the intensities of the remainder were estimated by eye from a calibration strip as described in chapter one.

The correction for expansion and contraction of upper level Weissenberg data was made using the method of Phillips (1954). Beyond a certain film coordinate, T_o, the arithmetic mean of reflections above and below the film equator was taken. This coordinate varied from layer to layer and was determined by the condition that the shape of contracted and elongated reflections was not

visibly different.

The b-axis data was treated by AUFAC (section 2.5) for film factor determination and Lorents-polarization corrections. The Lp corrections for the [102] axis data were made using a Cochran chart since AUFAC is not sufficiently general to handle other than principal axis data. Least squares correlation of the intersecting reciprocal lattice layers was executed on the 6400 by AULAC (section 2.5).

2.3.4 Scaling

The Wilson plot (Wilson (1942)) (Fig. 2.2) gave the scale factor and temperature factor (as defined in chapter one) to be

$$k = 0.32$$

$$B = 3.23$$

2.4 Unit Cell Data

The method described in chapter one for determining the cell constants of UPBA was used in this instance. Crystals mounted for both b and [102] axis rotation were dipped several times in cold concentrated NaCl solution. The resulting powder lines were used to calibrate the film and gave the following values for the cell edge constants:-

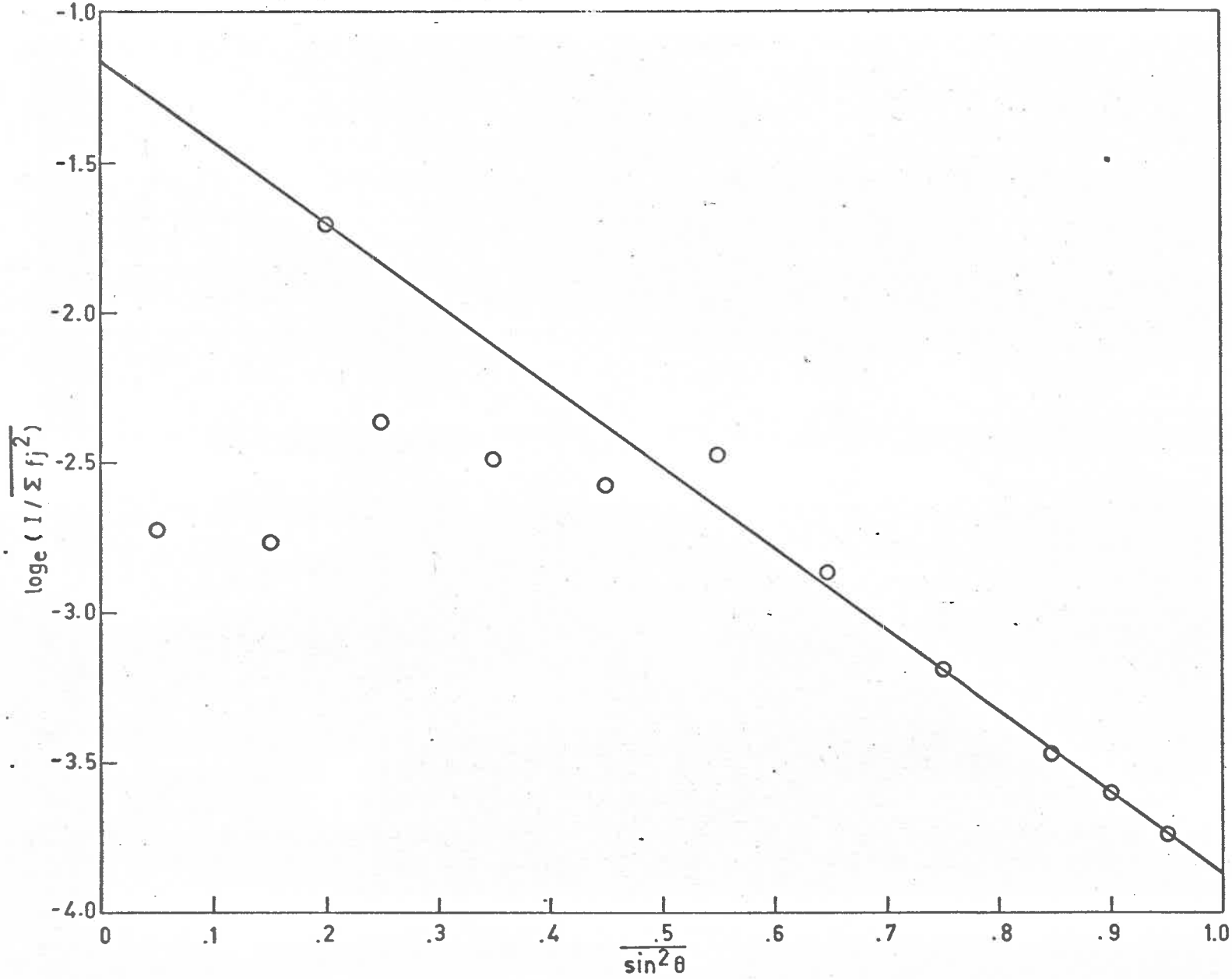


Fig. 2.2 Wilson plot TUPBA.

$$a^* = \cdot1556 \pm \cdot0001 \text{ r.l.u.}$$

$$b^* = \cdot2448 \pm \cdot0002 \text{ r.l.u.}$$

$$c^* = \cdot2740 \pm \cdot0002 \text{ r.l.u.}$$

The angle between the two well developed faces on three different crystals was measured and found to be $28^\circ43' \pm 01'$. The (hoℓ) reciprocal lattice section was drawn to scale with $\beta^* = 66^\circ$ and measurements revealed an uncertainty in the plane of the plate, viz. (501) or (601). Knowledge of the angle between either (101) and (601) or (101) and (501), together with the edge constants, is sufficient to solve for β^* and the two values obtained are

$$\beta^*_{(101)-(501)} = 68^\circ30' \pm 02'$$

and

$$\beta^*_{(101)-(601)} = 64^\circ26' \pm 02' .$$

Whilst the latter is closer to the 66° measured from the Weissenberg film a check was done by using the relationship

$$\delta = \frac{nm}{N_0V} = \frac{nmV^*}{N_0\lambda^3}$$

For $\beta^* = 68^\circ30'$, $\delta = 1\cdot68$gm/cc and for $\beta^* = 64^\circ28'$, $\delta = 1\cdot63$gm/cc. This further supports (601) as the plane of the plate in the light of the measured

density of 1·59 gm/cc. The real cell constants are therefore

$$a = 10{\cdot}984 \pm {\cdot}019\text{Å}$$

$$b = 6{\cdot}298 \pm {\cdot}003\text{Å}$$

$$c = 6{\cdot}238 \pm {\cdot}012\text{Å}$$

$$\beta = 115^{\circ}34' \pm 02'$$

The error in b is smallest since calculation of b from b* does not involve $\sin\beta^*$.

2.5 Computing Facilities

By the time the stage had been reached for handling the data for this structure, excellent computing facilities had become available to crystallographers at the University. The 6400 had been programmed to handle six of the major operations from intensity data to structure. These operations were performed by

(1) AUFAC - a least squares film factor program incorporating Lorentz-polarisation corrections,

(2) AULAC - a least squares interlayer scaling program,

(3) ABSFAC- a program for applying absorption corrections,

(4) PREPFLS - a routine to write magnetic tapes for (5) and (6),

(5) FUORFLS - a Flinders University version of the Oak Ridge least squares program,

and (6) FOURIER.

Some of these programs are modifications of existing routines. Stages (4) and (6) are Adelaide versions of programs written by F.R. Ahmed (Division of Pure Physics, National Research Council, Ottawa). The first two are extensions of programs written by G. Paul (Sydney). Drs. M. Snow (Physical and Inorganic Chemistry) and J. Jones (Geology) of this University and Dr. M. Taylor (School of Phys. Science) of Flinders University were jointly responsible for the setting up of this system.

Whilst the advent of these facilities eliminates otherwise boring and time consuming calculations, the time spent in numerous hand calculations (e.g. Lp corrections, one-dimensional Fouriers and several structure factors) was considered very valuable. The author had the benefit of executing programs in the developmental stages of this system which was subsequently used for the remainder of the work described in this thesis.

2.6 The Patterson Function and Trial Structures

2.6.1 Patterson Symmetry and Harker Sections

The $P2_1$ unit cell has atoms in the general positions (xyz) and $(\bar{x}, \frac{1}{2}+y, \bar{z})$. Convolution of this cell with itself generates a cell with space group symmetry P2/m and therefore only one quarter of the Patterson need be computed. The only Patterson peaks which arise through the interaction of symmetry related atoms are the peaks on the Harker section $v = \frac{1}{2}$. The sulphur-sulphur peak, theoretically the heaviest in the Patterson, lies on the Harker section at $(2x_s, \frac{1}{2}, 2z_s)$. The lack of y information from the Harker section in this case is related to the absence of symmetry elements perpendicular to the unique axis and illustrates that the origin may be arbitrarily specified up this axis.

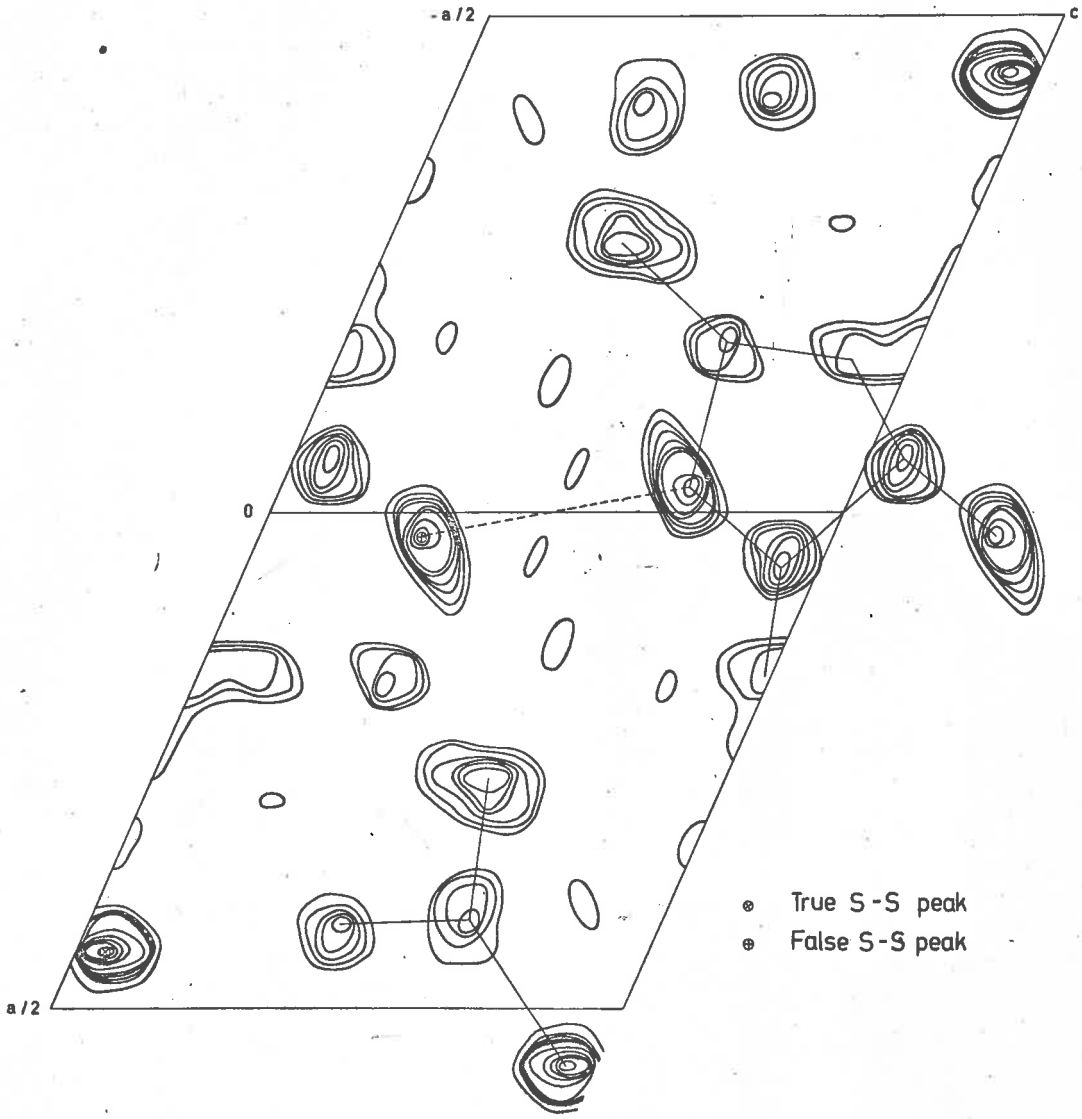
2.6.2 Patterson Structure

The unsharpened three dimensional Patterson function showed all the vector interactions to be in the b-plane, i.e. peaks were confined to $v = 0, \frac{1}{2}$. This was further evidence in support of the complex lying in (020) planes. Between v = 0·1 and 0·4 the value of the function was everywhere negative except in two regions where it appeared that large scale planarity may be swamping a general interaction with $v \neq 0$.

The Patterson was sharpened using an oxygen form factor, the coefficients becoming $|F^2/f|^2$. The sharpened synthesis was subsequently used in the determination of the structure.

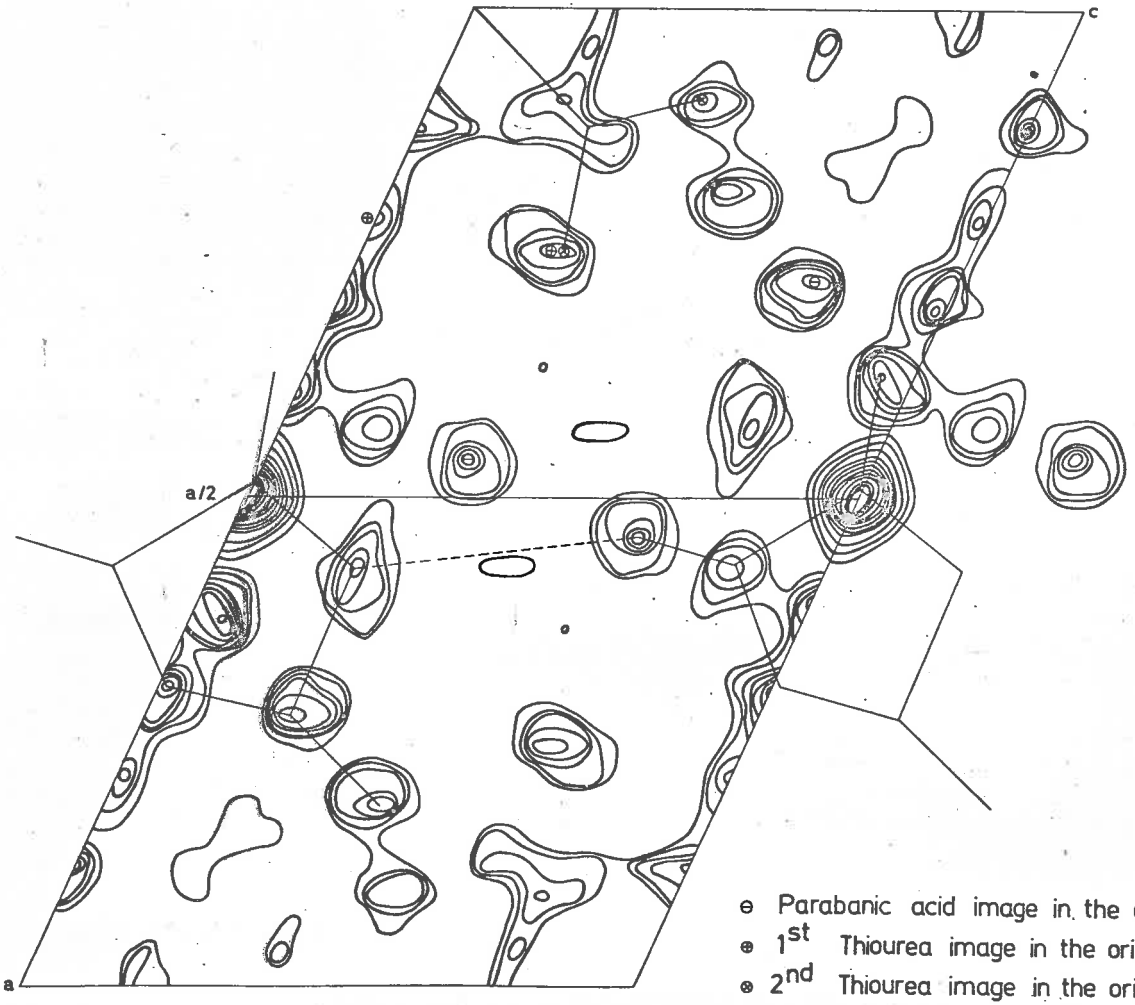
The presence of two large peaks of approximately equal weight on the Harker plane prevented unequivocal determination of the sulphur position. (See Fig. 2.3). Matthews (1963), in solving the structure of the sodium salt of 5-phenyl-thiazolidine-2:4-dione, had similar problems with sulphur as a heavy atom.

For the moment attention was turned towards the parabanic acid figure which had been located in the UPBA Patterson function. An examination of the v = 0 section revealed an image of this figure. (See Fig. 2.4). The dimensions of the image gave the O1-O2 and O1-O3 vectors as 4·4Å and the O2-O3 vector as 3·8Å. These figures compare favourably with 4·6Å and 3·0Å in parabanic acid. In addition this image provides for hydrogen bonding of parabanic acid molecules up the c-axis through O3---H1-N1 (Fig. 2.4). An attempt to locate the molecule in the cell from the v = $\frac{1}{2}$ information resulted in the location of two possible positions, neither being indicated more strongly than the other.



The Harker Section v = 1/2 of the sharpened Patterson function (TUPBA).

Fig. 2.3



The v=0 section of the sharpened Patterson function (TUPBA).

Fig. 2.4

When the Patterson was sharpened, 8 peaks with v coordinates ≈ 1/4 had arisen, the two strongest of these being in the regions previously mentioned. Even these peaks were weak compared with the general peaks on v = 0 and at best they could have arisen from light atom - light atom interactions. However, since there is only one heavy atom per asymmetric unit, the interpretation of heavy atom-light atom vectors is not ambiguous and it was therefore decided to attempt a solution based on these interactions.

The v = 0 section was found to show two possible images of the thiourea molecule in the sulphur atom. The scale of this molecule is sufficiently larger than that of urea to enable the image to dominate against the origin peak, whilst the weight of the sulphur atom further enhances the image in this case. There was now no doubt that the complex was planar and that the peaks off v = $0,\frac{1}{2}$ were purely a result of sharpening.

Of the two thiourea images (Fig. 2.4) the first was not as dimensionally accurate as the second (N3-N4 was too short) nor did it offer many possibilities for hydrogen bonding. The ambiguity in the sulphur (and hence the thiourea) position was resolved in the following way. The

strongest peak in the three dimensional sharpened Patterson function is at $(\frac{1}{2},0,0)$. Since this peak cannot be a heavy atom-heavy atom peak it must result from the overlap of either heavy atom-light atom and light atom-light atom vectors or of many light atom-light atom vectors. The former postulate is the more reasonable. If the sulphur is at (xyz) in the real cell then a light atom, L, will be found at $(x+\frac{1}{2},y,z)$ and on the Harker section $S-S^B$ and $L-L^B$ will overlap at $(2x,\frac{1}{2},2z)$. More importantly the $S-L^B$ interaction will be found at $(2x+\frac{1}{2}, \frac{1}{2},2z)$, i.e. since the S-L interaction is perpendicular to the symmetry element an undistorted image of this figure will appear on the Harker section. This criterion was sufficient to identify the $S-S^B$ peak. In fact by virtue of the (020) planarity of the thiourea molecule, an image (undistorted) of the whole molecule is evident in the true $S-S^B$ peak (Fig. 2.3).

The parabanic acid molecule was located by considering the active sites on the thiourea molecule for hydrogen bonding. Both N3 and N4 are proton donors for hydrogen bonds and acceptor atoms must lie in the plane of the thiourea molecule. A thorough investigation of all peaks 3Å from the donor sites revealed two possible parabanic acid oxygen networks (see Fig. 2.5). Although

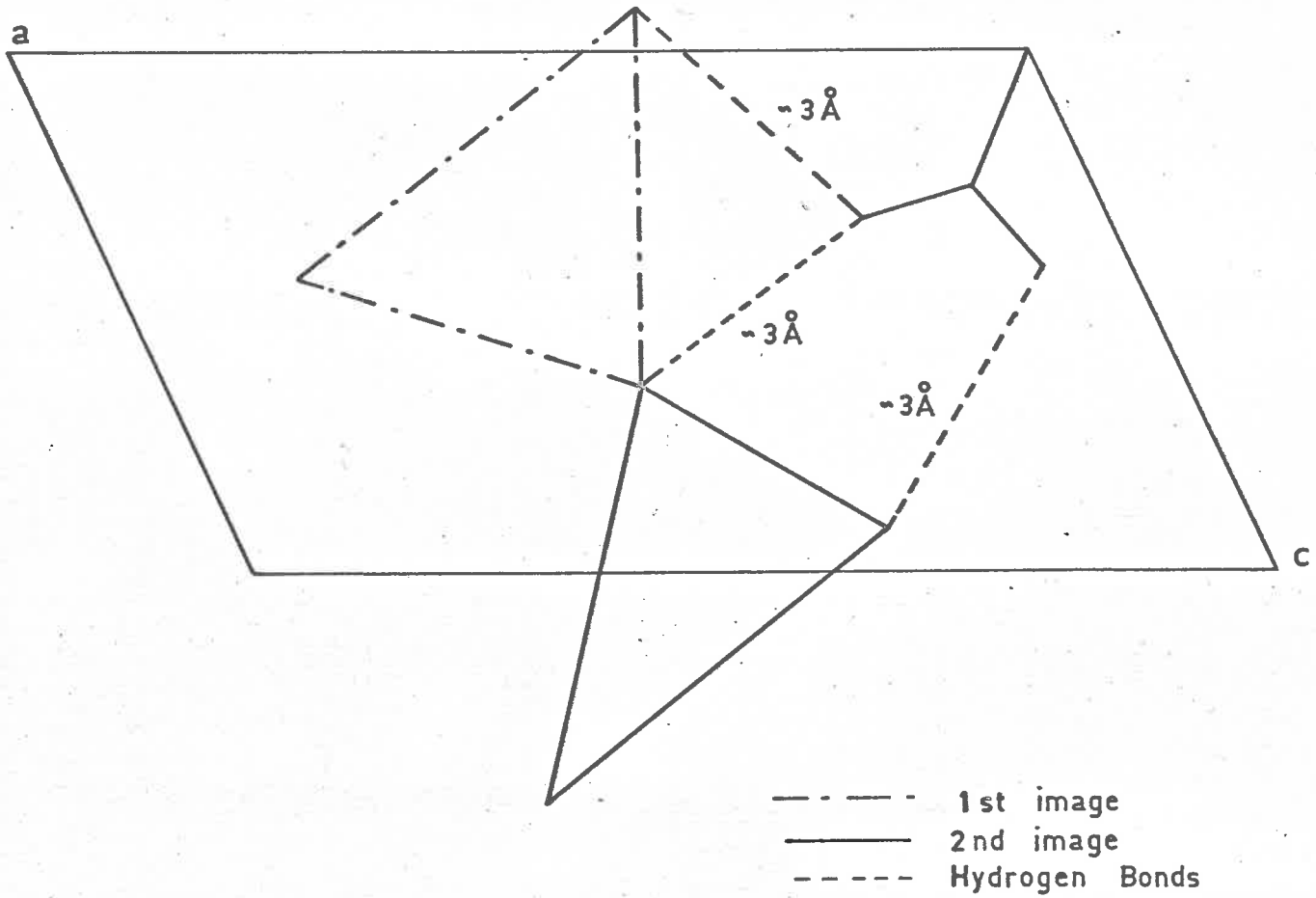


Fig. 2.5 Parabanic acid triangles in v = 0 section of Patterson function (TUPBA).

both of these provide for hydrogen bonding of parabanic acid molecules in the c direction, the first puts N2 and N3 in an unstable configuration. In addition the second is a better match to the parabanic acid dimensions. Other peaks, besides those shown, were found 3Å from N4 but they led to violation of the c translation group symmetry and were therefore rejected.

When the complete Patterson section v = 0 is drawn out, an entire image of the complex is visible in detail, with only slight distortion of the imidazole ring. An undistorted image is also clear in the Harker section, this being a consequence of the orthogonality of the complex to the screw axis. The peaks chosen for the original parabanic acid image are light atom-light atom peaks as expected. It was encouraging to observe that this image did yield the correct orientation for the parabanic acid molecule. It was therefore reasonable to postulate that the image found in the UPBA Patterson was also genuine.

2.6.3 Trial Structures

A trial structure based on the coordinates obtained from the Patterson, as described above, was set up. Structure factors were calculated and after scaling

$\Sigma F_o = \Sigma F_c$ the residual was ·57. This is the value that Wilson (1950) gives as the most probable value of R for a random set of noncentric points, and was most unusual in light of the detailed structure in the Patterson.

Due to the disposition of the molecules with respect to the screw axis, the b-axis projection does not suffer greatly from overlap and a Fourier projection was computed using the phases of the trial structure. No shifts were evident and it was apparent that the phase information was grossly loading the Fourier in favour of the trial structure. A few new peaks were generated but no structural sense could be made of them.

The structure factors F_o and F_c for the centrosymmetric (hoℓ) section were plotted on a lattice and examined. Gross disagreement was found in several regions of reciprocal space. Along the line $\ell = \bar{2}$, four points gave $\Sigma|F_o| = 21$, $\Sigma|F_c| = 155$ and along $\ell = \bar{4}$, $\Sigma|F_o| = 185$ and $\Sigma|F_c| = 120$. Shifts of the trial structure were made in an attempt to amend the largest of these discrepancies and although this method was successful in part, the shifts were not large enough to affect the overall R factor.

A three dimensional Fourier was computed using the

complex amplitudes of the model but this was of no assistance in interpreting the spurious peaks observed earlier in projection.

At this stage there could be no doubting the sulphur position. An image of the asymmetric unit was visible in the S-S^a peak. There was little value in doing a Fourier on the sulphur phases since only just over 50% of the signs on the (hoℓ) section would be determined (section 2.1). A Fourier using the thiourea phases was computed, but again no structural interpretation of the map was possible.

A re-examination of the F_o, F_c lists (output from FUORFLS) revealed that on the (hko) section systematic swapping of F_o and F_c for adjacent reflections would greatly improve the residual. There are 50 reflections of this type and by comparing F_o(hoo) with F_c(h10) and F_o(h20) with F_c(h30) (and vice versa) for 14 pairs of reflections, the residual for this section is reduced from ·92 to ·17. This was the most significant result to come from the exhaustive study of the structure factor listings.

It is well known that the centre of symmetry at the origin of the Patterson function may lead to the incorrect orientation of the solution of the vector set and that

this ambiguity may be resolved by Harker section information. In TUPBA, where there is only one heavy atom per asymmetric unit, the Harker section peaks at $v = \frac{1}{2}$ are, with one exception, light atom-light atom vectors. The exception is the S-S peak, but location of this is not sufficient to eliminate an uncertainty of π in the orientation of the asymmetric unit. There is, in this case, an abundance of peaks on $v = \frac{1}{2}$, but many of these arise from the fortuitous orientation of the complex relative to the b-axis and are not genuine Harker peaks. The high density of peaks in $v = \frac{1}{2}$ has caused gross overlap, and it was found that the alternative orientation of the complex gave no worse agreement with the Harker peaks in the structure.

The complex was rotated through 180° about an axis through S and parallel to b. The reliability index was ·31. This shift of the trial structure to an apparently satisfactory model is of the type that might be inferred from the peculiar property of the structure factors mentioned above.

2.7 Refinement

2.7.1 Methods of Crystal Structure Refinement

Once a suitable trial structure has been found, the remaining task in the analysis is to refine the structural parameters of the model to give better agreement with the experimental data, the intensities. The two most commonly used methods of refinement are

(i) Fourier Methods

(ii) Least Squares.

Information concerning the shifts of the trial coordinates may be obtained from a knowledge of the slope of the electron density in the region of the atomic centres. Series termination effects for which allowance must be made in this differential approach, may be neglected if difference Fourier maps are used for refinement. Since the coefficients of such a series are $(|F_o|-|F_c|)$ it may be assumed, to a high degree of accuracy, that beyond the $\sin\theta/\lambda$ limit of the data the values of F_o and F_c are equal and the coefficients therefore zero.

The method of least squares is the one which is best adapted to automatic data processing. The quantity minimised is

$$R = \sum_i w_i(|F_o|-|F_c|)_i^2$$

the sum being over all independent structure amplitudes. This method is essentially the same as the differential Fourier method when the amplitudes are appropriately weighted (Lipson and Cochran (1966)). The computing facilities available to the author for the execution of least squares refinement influenced the choice of this method. There seemed little value in using the differential method when programs would have to be written for its execution, and no results which were not obtainable by least squares could be produced. The program FUORFLS (section 2.5) was used for the work described hereafter.

2.7.2 Least Squares Refinement in the $P2_1$ space Group

The least squares refinement of atomic coordinates in certain noncentrosymmetric structures may lead to difficulties arising from the independence of $|F_o|$ on one or more of the coordinate parameters. In the space group $P2_1$ (b unique), the effect of a gross shift of all of the y coordinates is seen only in the phase angle and not the amplitude of the structure factors. In other words, the origin of the $P2_1$ cell may be specified arbitrarily along the b axis (Rollett (1965)). A shift of

the origin by b/4 has the effect shown in Fig. 2.6. $|F_o|$ remains unchanged. Any space group in which the displacement of an atom by $(\Delta x, \Delta y, \Delta z)$ does not result in shifts in any of the symmetry related atoms of $(-\Delta x, -\Delta y, -\Delta z)$ will exhibit this feature. The effect of attempting least squares refinement under such conditions may be formulated as follows.

The structure factor equations, in their most general form, may be written as

$$F_c(hk\ell) = \sum_j f_j \exp 2\pi i(hx_j + ky_j + \ell z_j)$$

the summation being over all atoms in the unit cell. If we consider, for the moment, only refinement of the positional parameters, R will be minimised when the partial derivatives

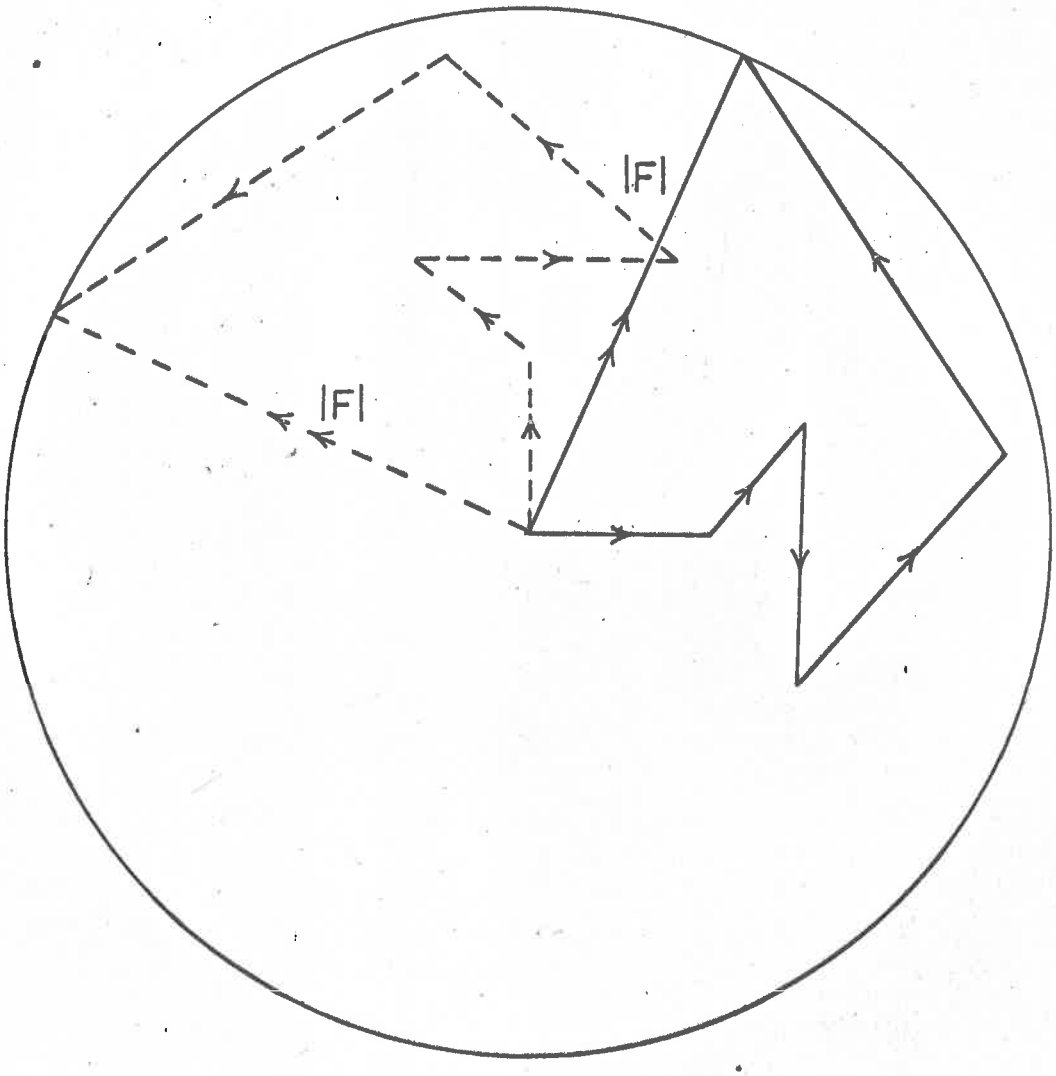
$$\frac{\partial R}{\partial x_j}, \quad \frac{\partial R}{\partial y_j}, \quad \frac{\partial R}{\partial z_j}$$

have all vanished.

If we write

$$R = \sum_i w_i(hk\ell)\Delta_i^2(hk\ell)$$

where



Phase—amplitude diagram showing effect on $\underline{F}(hkl)$ of moving origin through b/4. (five atoms)

Fig. 2.6

$$\Delta_i(hk\ell) = |F_o(hk\ell)| - |F_c(hk\ell)|$$

then the condition for a minimum is that

$$\sum_i w_i \Delta_i \frac{\partial \Delta_i}{\partial x_j} = 0, \text{ similarly for } y_j, z_j.$$

This may be further simplified since $\frac{\partial F_o}{\partial x_j} = 0$ etc. and the condition for minimum R is therefore

$$\sum_i w_i \Delta_i \frac{\partial |F_c|}{\partial x_j} = 0 \text{ etc.}$$

For the space group $P2_1$, the real and imaginary contributions of the jth atom to the structure factor $F(hk\ell)$ are

$$f_j A_j = 2f_j \cos 2\pi(hx_j + \ell z_j + \frac{k}{4}) \cos 2\pi(ky_j - \frac{k}{4})$$

and

$$f_j B_j = 2f_j \cos 2\pi(hx_j + \ell z_j + \frac{k}{4}) \sin 2\pi(ky_j - \frac{k}{4})$$

where

$$|F(hk\ell)| = \sqrt{(\Sigma f_j A_j)^2 + (\Sigma f_j B_j)^2}$$

Consider the partial derivative

$$\frac{\partial F}{\partial y_j} = f_j \frac{\partial A_j}{\partial y_j} \left(\Sigma f_j A_j\right) \frac{1}{F} + f_j \frac{\partial B_j}{\partial y_j} \left(\Sigma f_j B_j\right) \frac{1}{F}$$

The trigonometric functions of the phase angle of the

structure factor are defined by

$$\sin\alpha = (\Sigma f_j B_j)/|F|$$

and

$$\cos\alpha = (\Sigma f_j A_j)/|F|$$

and therefore

$$\frac{\partial F}{\partial y_j} = f_j\left[\frac{-\partial A_j}{\partial y_j}\cos\alpha + \frac{\partial B_j}{\partial y_j}\sin\alpha\right]$$

$$= f_j\left[-2k\cos 2\pi\left(hx_j+\ell z_j+\frac{k}{4}\right)\sin 2\pi\left(ky_j-\frac{k}{4}\right)\cos\alpha\right.$$

$$\left. + 2k\cos 2\pi\left(hx_j+\ell z_j+\frac{k}{4}\right)\cos 2\pi\left(ky_j-\frac{k}{4}\right)\sin\alpha\right]$$

$$= kf_j(A_j\sin\alpha - B_j\cos\alpha)$$

This relationship is true for all atoms in the cell and for all structural factors. Thus when $k = 0$ $\frac{\partial F}{\partial y_j} = 0$, a result which is well known for all space groups since it is not possible to refine y coordinates on (hoℓ) data alone.

For non-zero k the partial derivative vanishes when

$$\tan\alpha(hk\ell) = \frac{B_j}{A_j}$$

$$= \tan 2\pi(hy_j - \frac{k}{4})$$

It immediately follows that if y_j = constant for all atoms in the cell then all of the partial derivatives $\frac{\partial F}{\partial y_j}$ will vanish. Thus when all the scatterers are in the b plane the normal equations for the shifts, δy_j, have an infinite number of solutions.

When the scattering density is spread throughout the cell in the b direction, at most one of the $\frac{\partial F}{\partial y_j}$ is zero. The structure amplitude, however, remains independent of the choice of origin along the screw axis and it has been found necessary (Karle and Karle (1968)) to hold several y coordinates constant to effect least squares refinement under these conditions.

The placement of several atoms in the screw related position is of no assistance in the present case since

$$\tan 2\pi(k(y_j+\tfrac{1}{2}) - \frac{k}{4}) = \tan[2\pi(ky_j - \frac{k}{4}) + \pi k]$$
$$= \tan 2\pi(ky_j - \frac{k}{4})$$

for all integral k.

The problem was overcome by holding some of the y_j constant and refining the others, y_i. A spread in y coordinate of ·1 of the cell edge was arbitrarily applied to the atoms. Since the structure factors are dependent upon relative shifts of atoms in the b direction,

constraints are forced upon the solutions of the normal equations for δy_i. Gross shifts are therefore intolerable.

It was found that if the atoms were put in around $y = 0$ large shifts resulted.

$$\left|\frac{\partial F}{\partial y_j}\right|_{y=o} = -2kf_j\left[\cos 2\pi\left(hx_j+\ell z_j+\frac{k}{4}\right)\sin 2\pi\left(-\frac{k}{4}\right)\cos\alpha\right.$$
$$\left.-\cos 2\pi\left(hx_j+\ell z_j+\frac{k}{4}\right)\cos 2\pi\left(-\frac{k}{4}\right)\sin\alpha\right]$$
$$= -2kf_j\cos 2\pi\left(hx_j+\ell z_j+\frac{k}{4}\right)\sin\left(\alpha+2\pi\,\frac{k}{4}\right)$$

when $y_j = 0$ for all j

$$\tan\alpha(hk\ell) = \frac{[\Sigma f_j\cos 2\pi(hx_j+\frac{k}{4}+\ell z_j)]\sin(-\frac{2\pi k}{4})}{[\Sigma f_j\cos 2\pi(hx_j+\frac{k}{4}+\ell z_j)]\cos(-\frac{2\pi k}{4})}$$
$$= -\tan\left(\frac{\pi k}{2}\right)$$

$\therefore \alpha = 0, \pi$ (k even)
or $\frac{\pi}{2}, \frac{3\pi}{2}$ (k odd)

and $\sin\left(\alpha+\frac{2\pi k}{4}\right) = 0$ for all k. Therefore when $y_j \approx 0$, $\frac{\partial F}{\partial y_j}$ has a correspondingly small value.

2.7.3 Least Squares Refinement of TUPBA

On each cycle of least squares at least half of the

y coordinates were held whilst the others were refined. (It was previously found that the sulphur atom was not heavy enough to be used alone). On the next cycle the roles of the two sets were reversed and on subsequent cycles the parameters were mixed so that no parameter was refined independently of any other. Although this scheme was not followed to the letter, it provided the basis for the y coordinate refinement. Initially these coordinates were distributed randomly through y = ·2, ·21.

The first three refinement cycles reduced R from 31% to 18%. This refinement was carried out on the coordinate parameters alone. Two further cycles on the isotropic temperature factors further reduced R to 16%. Since the second of these cycles had had very little effect it was decided that further convergence of R would result only from the use of anisotropic atoms.

2.7.4 Anisotropic Refinement

The initial values of B_{ij} in the temperature factor matrix were

$$\begin{pmatrix} B_i \frac{a^{*2}}{4} & 0 & B_i \frac{a^*c^*}{4}\cos\beta^* \\ 0 & B_i \frac{b^{*2}}{4} & 0 \\ B_i \frac{a^*c^*}{4}\cos\beta^* & 0 & B_i \frac{c^{*2}}{4} \end{pmatrix}$$

where B_i is the isotropic temperature factor of the ith atom and the anisotropic temperature factor has the form

$$f_T = f_o \exp - (\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + \beta_{12}hk + \beta_{13}h\ell + \beta_{23}k\ell)$$

This conversion to anisotropic atoms introduced certain problems in the refinement.

At the end of each least squares cycle it is necessary to check that the new temperature factor matrix represents a physical reality. (This condition is satisfied when the diagonal elements of the matrix are positive, the 2x2 minors of the matrix are positive and the determinant of the matrix is positive). The atoms which were most severely anisotropic had a large error in one or more of the B_{ij} components at the start of this refinement, and therefore there was a tendency to either close in on an invalid minimum or else to overshoot the genuine solution. Either of these results may yield an unrealistic temperature factor. Under these conditions it was necessary to compute a difference synthesis to check the temperature factor refinement and this was done after least squares had further refined the structure to R = 13·5%.

The most severe anisotropy, and for which no account had yet been taken, was in the region of the sulphur atom. Negative difference density in the direction of the S-C4 bond implied that the model had too much thermal motion in this direction. The temperature factor of the sulphur atom had in fact been overestimated in the whole of the b-plane.

2.7.5 Hydrogen Atoms

In addition to this vibrational information the difference map also revealed the hydrogen atoms in the structure. A coordinate for each of these six atoms had previously been postulated on the basis that the proton should lie approximately 1Å from the nitrogen atom (to which it was bonded) on the line joining the nitrogen atom to the oxygen atom (to which it was hydrogen bonded). Four of the six hydrogen atoms were found at the predicted sites whilst H32 and H2 were removed from this position. The postulate that an N2-H2---S bond had formed was not justifiable at this stage since the N2-S approach was 3·3Å. Similarly the N3-O2 approach was 3·2Å and under these conditions collinearity of N3, H32 and O2 is not required.

Each of these departures from the predicted coordinates was less than ·5Å in the z direction and so the six

postulated coordinates were used as the starting values for the least squares. The fact that R was not significantly altered by the inclusion of these atoms was the result of a simultaneous attempt to modify the B_{ij} for the sulphur atom. This was not successful.

The reason for this would seem to be related to the size of the monoclinic angle ($\beta^* = 64^\circ 26'$). It is therefore difficult to separate the effect of the matrix components β_{11}, β_{33} and β_{13}, and in fact the least squares analysis had shown that in particular β_{11} and β_{13}, and β_{13} and β_{33} were highly correlated (>·4).

Least squares refinement of the y coordinate of hydrogen atoms was not possible. The planarity of the molecule was used to assign them the same y coordinate as the nitrogen atom to which they were covalently bonded.

2.7.6 Secondary Extinction

An investigation of the structure factor lists showed that $\Delta(= |F_o| - |F_c|)$ was large and negative for the three strongest reflections.

hkℓ	F_o	F_c	Δ
020	107	132	-25
040	53	58	-5
$20\bar{1}$	30	51	-21

A number of planes had F_o values near 25 but for these Δ was neither consistently positive nor negative. The data from three orders of diffraction is not sufficient to treat the problem of secondary extinction statistically and for this reason crystals were dipped in liquid air and a new set of intensities were read for these and twenty other reflections.

The intensity of $(20\bar{1})$ was found to be both extinction effected and in error as a result of a poor film reading. The new F_o values assigned to these reflections were 123,64 and 38 respectively. $\Delta(20\bar{1})$ remains the largest low angle difference in the data.

2.7.7 Final Refinement

Least squares refinement ultimately converged at R = ·117. The reliability index for the observed amplitudes alone is ·097 and agreement factors for other reciprocal lattice regions of interest are as shown:

R	Data
·117	hkℓ
·139	hoℓ
·117	hko
·100	okℓ

R	sinθ/λ range	Number of reflections
·114	0 - ·379	211
·098	·379 - ·478	150
·125	·478 - ·547	122
·134	·547 - ·602	98
·182	·602 - ·713	62

On the last cycle of refinement most parameters had shifts less than one half their standard deviations. The two exceptions to this were the 3 coordinates of H32 and H41 which oscillated through ·6Å and ·2Å respectively. The temperature factor components generally had large standard deviations (possibly attributable to high correlation coefficients between them) and whilst they had all converged, a final difference map showed further anisotropy, again chiefly around the sulphur atom. These anomalies are discussed in the next section.

The final parameters and bond lengths and angles are given in Tables 2.1 and 2.2. The values used for

H32 and H41 are the average least squares values. The standard deviations of bond lengths and angles are those of Ahmed and Cruickshank (1953) and are given in section 3.2.5. It was necessary to estimate the standard deviations of the H(y) parameters and this was based on the relative standard deviations of other (xyz) parameters. The standard deviations of H32 and H41 are the least squares values.

The molecular dimensions and planar structure of the complex are shown in Figures 2.7 and 2.8 and the F_o, F_c values are given in appendix C.

TABLE 2.1A

Final Coordinate Parameters

	x	y	z	σ(x)	σ(y)	σ(z)
O1	·4533	·2308	·0148	·0007	·0030	·0011
O2	·8978	·1947	·5213	·0006	·0034	·0011
O3	·7364	·1884	·8052	·0006	·0028	·0010
N1	·6820	·2045	·2090	·0007	·0033	·0011
N2	·5616	·2025	·4243	·0007	·0040	·0011
C1	·5576	·1948	·1983	·0008	·0044	·0014
C2	·7790	·2201	·4378	·0008	·0046	·0015
C3	·6927	·1916	·5840	·0009	·0048	·0015
S	·2705	·2090	·4640	·0002	·0016	·0003
N3	·0194	·2104	·1510	·0008	·0047	·0014
N4	·1765	·1829	-·0131	·0008	·0042	·0014
C4	·1461	·1906	·1832	·0009	·0045	·0017
H1	·6626	·2045	·0491	·0133	·05	·0288
H2	·4834	·2025	·5831	·0123	·05	·0209
H31	·9345	·2104	·0096	·0141	·05	·0248
H32	·0102	·2104	·3000	·0138	·05	·0259
H41	·0771	·1829	-·1925	·0148	·05	·0243
H42	·2716	·1829	-·0078	·0140	·05	·0232

TABLE 2.1B

Final Thermal Parameters x10^4

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O1	39	202	88	23	-26	-30
O2	24	191	161	-26	19	22
O3	38	158	64	-13	14	-83
N1	42	231	108	46	39	41
N2	34	222	85	-13	13	-54
C1	23	244	117	48	8	0
C2	28	186	103	53	11	-38
C3	44	171	85	51	-7	68
S	38	176	111	-26	7	-20
N3	31	530	149	-12	-2	-92
N4	54	207	117	-49	25	67
C4	30	198	161	55	31	44

H1	AS FOR N1
H2	AS FOR N2
H31	AS FOR N3
H32	AS FOR N3
H41	AS FOR N4
H42	AS FOR N4

TABLE 2.2A

Bond Lengths

Bond	d	σ(d)	Bond	d	σ(d)
O1-C1	1·242	·013	N4-O1	2·985	·016
C1-N1	1·340	·016	H42-O1	1·962	·218
C1-N2	1·392	·011	S-N2	3·312	·011
N1-H1	·926	·134	S-H2	2·127	·185
N2-H2	1·566	·171	N1-O3	2·830	·011
N1-C2	1·367	·012	H1-O3	2·012	·175
N2-C3	1·354	·015	N3-O2	3·129	·014
C2-O2	1·189	·016	H32-O2	2·216	·200
C3-O3	1·250	·010	N4-O2	3·184	·012
C2-C3	1·584	·018	H41-O2	1·995	·176
S-C4	1·698	·011	N3-O3	2·924	·013
C4-N3	1·323	·019	H31-O3	1·996	·199
C4-N4	1·402	·015	S-O1	3·147	·007
N3-H31	·968	·171			
N3-H32	·977	·169	S-C2[a]	3·231	·029
N4-H41	1·196	·164	S-C3[a]	3·313	·031
N4-H42	1·031	·216			

1st column is intramolecular data.
2nd column is intermolecular data.
All bond lengths in the plane of the complex except the last two which are between adjacent layers.

TABLE 2.2B

Bond Angles

Angle	θ°	σ(θ)	Angle	θ	σ(θ)
O1-C1-N1	123·6	·9	N4-H42-O1	170·9	39·3
O1-C1-N2	122·7	·9	N2-H2-S	126·8	5·0
C1-N1-C2	111·9	·8	N1-H1-O3	146·5	14·9
C1-N2-C3	107·6	·9	N3-H32-O2	155·0	18·8
N1-C2-C3	101·7	·9	N4-H41-O2	172·1	28·1
N2-C3-C2	106·3	·7	N3-H31-O3	159·7	21·1
N1-C2-O2	131·4	1·0	C4-S-O1	168·4	1·8
N2-C3-O3	126·4	·9	C4-S-C2^{s}	90·2	1·0
C1-N1-H1	101·0	13·1	C4-S-C3^{s}	85·1	1·0
C1-N2-H2	148·7	9·4			
S-C4-N3	118·4	·7			
S-C4-N4	120·9	·7			
C4-N3-H31	132·4	17·8			
C4-N3-H32	112·9	14·0			
C4-N4-H41	112·2	9·2			
C4-N4-H42	126·3	11·6			

1st column - intramolecular angles.
2nd column - intermolecular angles.
All angles in the plane of the complex except the last two.

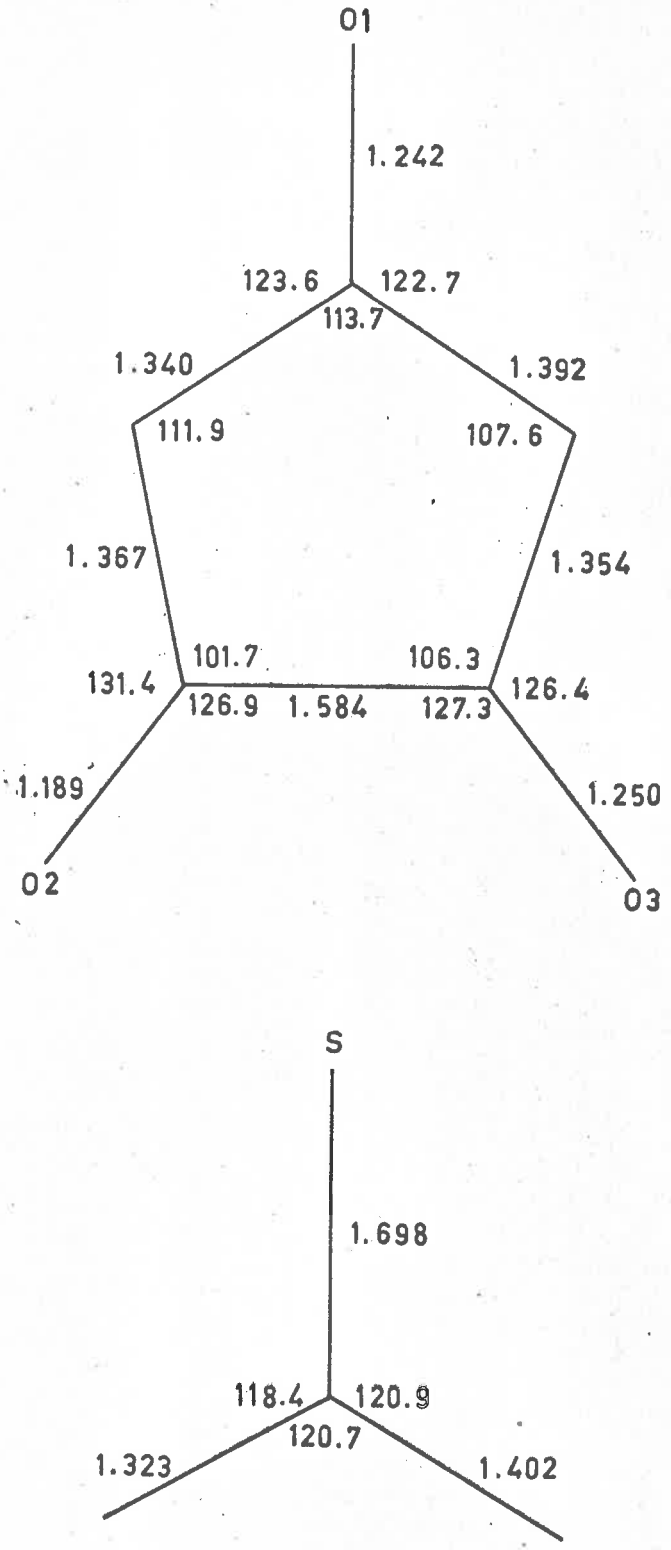
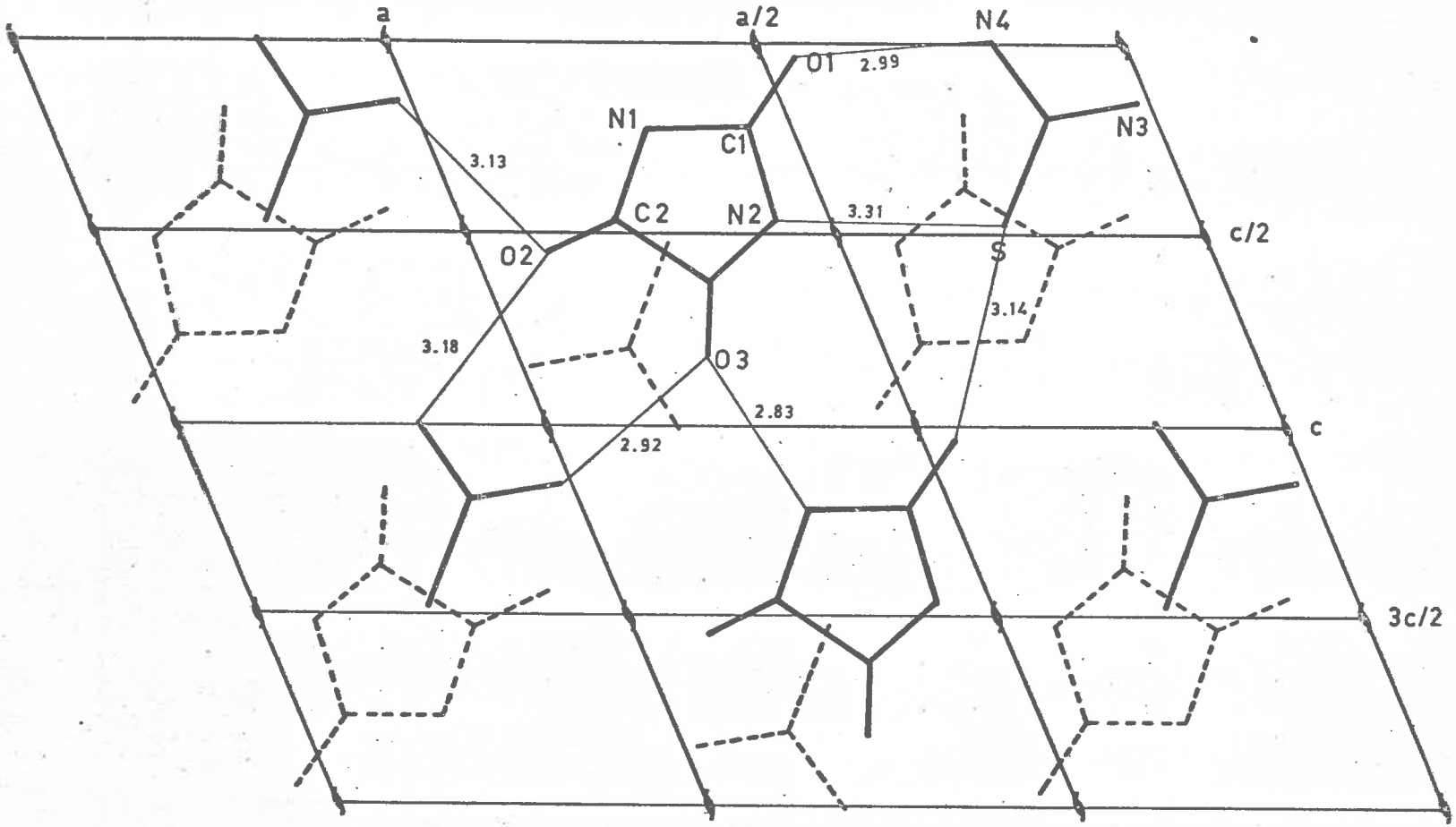


Fig. 2.7 Dimensions of thiourea and parabanic molecules in TUPBA.



The disposition of thiourea and parabanic acid molecules on symmetry related (020) planes.

Fig. 2.8

2.7.8 The Reliability of the Structure

A discussion of the structure is found in chapter four. Some final comments on the $(\rho_o-\rho_c)$ and ρ_o maps are in context at this point.

Mention has already been made of several features of this structure which might warrant further refinement. The difference map showed that there was further anisotropy, especially for the sulphur atom, whilst a number of other peaks (typically of height $\cdot 6e/A^3$) bore no apparent relation to the trial structure. In addition to this, correlation existed between parameters in the least squares and the refinement was hampered to some extent.

The original aim of this structure analysis was to derive information on possible urea-parabanic acid hydrogen bonding mechanisms. Despite the fact that UPBA and TUPBA were not isomorphous pairs, valuable information on the activity of the unique carbonyl group in parabanic acid had been obtained. The fact that the β_{ij} parameters were uncertain was considered to be of only secondary importance since the correlation between these and the coordinate parameters was not large enough to suggest that an error in one might lead to a false solution in the other. No further attempt was made to refine

the β_{ij} parameters. It should be noted however that the quoted values for sulphur are too large in the b-plane.

In order to investigate the other spurious peaks in the difference map an F_o synthesis was computed. Those regions in the difference map which were causing greatest concern were where $\rho_o-\rho_c \approx +\cdot 6$. It was found that at several of these coordinates ρ_o was negative and this requires ρ_c to be also negative. The calculated density may only be negative as a result of termination effects, whilst ρ_o may suffer from poor $|F_o|$ values and incorrect phase angles as well as termination errors. If F_o and F_c have different cut-off levels at the $\sin\theta$ limit then the above peaks may, in part, be explained. The table on page 80 illustrates how R increases with angle. For the highest $\sin\theta/\lambda$ zone $|F_o| = \cdot 87|F_c|$ and the termination ripple in ρ_c is therefore more severe than in ρ_o. Whilst this argument may not stand quantitative analysis it does show that the effect in question is working in the right direction to enhance any fortuitous build up of difference density. A summary of peak heights at the atomic centres in the two maps is given in table 2.3.

The anomalies in these peak heights may be explained in terms of the slight tilt the complex has to the (020)

TABLE 2.3

Summary of Final Fourier Maps

Atom	Pk. ht. in ρ_e (e/A^3)	Pk. ht. in $\rho_e - \rho_o$ (e/A^3)
O1	11·28	-·25
O2	12·70	-·20
O3	11·90	-·37
N1	10·70	-·08
N2	10·00	·20
C1	8·62	-·55
C2	10·50	-·33
C3	6·90	·05
S	31·81	·05
N3	8·85	-·33
N4	9·55	-·13
C4	9·06	-·28
H1	·82	-·16
H2	·12	·08
H31	1·50	-·30
H32	1·08	·43
H41	1·00	-·10
H42	1·75	·10

plane. The peak height at H2 in the ρ_o map requires explanation. The ρ_o density is ~ 2·5e/A^3 near H2 (in fact on the line joining N2 to S) and the extra stability that this configuration gives the N2-H2---S hydrogen bond makes it a preferred orientation. However, the difference peak at H2 supports the least squares solution for its coordinate and this value was subsequently used.

Two peaks in the difference and ρ_o maps are of great interest. They are the only significant peaks out of the molecular plane and they lie ~ ·8Å above and below the parabanic molecule on the line through the sulphur atom normal to the (020) plane. The peak heights are very similar (although not related by symmetry) and are ·5e/A^3 (ρ_o-ρ_c) and 3·3e/A^3 (ρ_o). The significance of these is discussed in chapter four.

It is seen in table 2.2 that the standard deviations of bond lengths and angles is somewhat larger than usual. This is particularly true when hydrogen atoms are involved. Despite this there is sufficient accuracy to place high levels of significance on a number of anomalies in the structure (see chapter four).

CHAPTER THREE

THE CRYSTAL STRUCTURE OF UREA PARABANATE

3.1 The Structure Determination

Information concerning the intermolecular bonding mechanism for thiourea and parabanic acid was now available. The planarity of the complex indicated the possibility of the urea-parabanic acid complex also being planar, and in the following approach to the structure, this was subsequently verified from the Patterson.

Earlier attempts to determine the UPBA structure were prejudiced against involving O1 in hydrogen bonds, but it was now apparent that in an environment of excess protons this particular carbonyl group could accept a hydrogen bond.

The length of the b-axis shows that there is no overlap of carbon and oxygen Van der Waal's radii in TUPBA but the situation in UPBA was thought to be quite different. If UPBA were a planar complex then it was most likely that the (211) plane would be the molecular plane. Each such plane is intersected by a set of symmetry related $(2\bar{1}1)$ planes and the likelihood for

contact formation is probably greatest in the vicinity of these lines.

An extensive search of the Patterson function finally resulted in the location of the parabanic acid molecule. Sufficient phases were determined from this molecule alone to enable an F_o synthesis to reveal the urea as a slab of high density in the map.

3.1.1 The (211) Plane

Although the orientation of the parabanic acid molecule was known, previous attempts to determine its absolute position had been unsuccessful. Whilst this may be a reflection on the quality and even validity of the original image, the parabanic acid image in the origin of the TUPBA Patterson function was equally distorted yet still defined the correct orientation of the molecule.

Each (211) plane in the cell is defined uniquely by a constant d where

$$2x + y + z = d$$

and d is a function of the distance of the plane from the origin. Determination of this constant for the molecular plane was attempted in the following way. If

d is nonzero, in the real cell there are two planes

$$2x + y + z = \pm d$$

related by a centre of symmetry at the origin. In vector space there are four such planes, two coincident at

$$2x + y + z = 0$$

and two others defined by

$$2x + y + z = \pm 2d.$$

Density of peaks in these planes results from vector interactions between the real space planes. The UPBA Patterson function satisfies these conditions only when $d = 0$, and the parabanic acid molecule is therefore forced into a plane containing a centre of a symmetry. This result checks with significantly large values of U(211) and U(422). For both of these planes to be strongly reflecting, the optimum condition is that there be only one (211) molecular plane per unit cell. If d is other than zero, symmetry conditions dictate a second plane. If there were 2 planes per cell, where $d_1 - d_2 = \frac{1}{2}$, for example, then U(211) would be small whilst U(422) would remain large.

For a general (211) molecular plane in a unit cell

with space group symmetry $P2_1/c$, the four asymmetric units may be defined in such a way that their planes are given by

$$2x + y + z = d$$

$$-2x - y - z = d_c \qquad \text{(centre related)}$$

$$3x - (\tfrac{1}{2}-y) + (z+\tfrac{1}{2}) = d_g \qquad \text{(glide related)}$$

$$2(1-x) - (y+\tfrac{1}{2}) + (\tfrac{1}{2}-z) = d_s \qquad \text{(screw related)}$$

where $d = -d_c$

$d_s = -d_g$

and $d = d_g$

Therefore the planes $(2\bar{1}1)$ which contain the screw and glide related molecules also pass through centres of symmetry. This result was not unexpected in the light of the TUPBA structure and of other hydrogen bonded structures in general.

The problem was greatly simplified by this condition. Model building was now possible in the (211) plane through the origin and the difficulty of supporting the models in three dimensions was thus overcome. This plane of the cell was drawn out to scale (2 cm = 1Å) and a study was made of the influence of the symmetry elements on points in the plane. Two features in particular were noted. It

was not possible for a molecule in (211) to straddle the screw axis, since this symmetry element was violated under these circumstances. Also, the glide translation $(0, \frac{1}{2}-2y, \frac{1}{2})$ is a vector in the plane when $y = 0$, and care was necessary to allow enough space for packing around the endpoints of these vectors. A number of hydrogen bonded 'models' were conceivable. Many of these, however, were unsatisfactory for the reasons outlined above. The interaction of matter in (211) and $(2\bar{1}1)$ planes had to be considered before a model could be reckoned satisfactory.

3.1.2 Harker Peaks

In order to put the model building on a more formal basis, the $v = \frac{1}{2}$ Harker peaks were re-examined for evidence of locatable scatterers in the real cell.

It is to be expected that peaks on this section may arise from vector interactions between either screw related atoms or atoms which are fortuitously separated by b/2. The type of interaction which gives rise to a given peak may be determined by using that information in the Patterson which results from the real cell centre of symmetry. The genuine Harker peak $(2x, \frac{1}{2}, \frac{1}{2}+2z)$ arises from a scatterer at (xyz) in the $P2_1/c$ unit cell. A

second peak at (2x, 2y, 2z) should therefore appear in the Patterson since the real cell has a centre of symmetry. When the two peaks occur together in the Patterson the v = $\frac{1}{2}$ peak is a genuine Harker peak. However the location of the scatterer at (xyz) as the source of these peaks is not unique. The mirror plane in the Patterson introduces an uncertainty in the sign of the y coordinate, and the two fold axes imply that the choice of (x,z) is no better than that of ($\frac{1}{2}$-x, $\frac{1}{2}$-z). In addition the translation group symmetry of the Patterson makes each real cell coordinate uncertain by one half of a cell edge.

Eleven of the fourteen v = $\frac{1}{2}$ peaks were found to be a result of interaction between screw related atoms, and the various possible real cell coordinates were computed using the rules outlined above. Before the application of the translational symmetry effect, eight real space peaks were found to satisfy 2x + y + z = 0. Shifts of either

i) b/2 - c/2

ii) a/2 - b/2 - c/2

iii) a/2 - b

or iv) a/2 - c

do not move the peaks out of the plane and all possibilities were plotted. Images of parabanic acid were then sought. Care was exercised to ensure that only one peak of a symmetry related set was considered in any given image. Whilst the best image found did provide for hydrogen bonding of the molecules through the centre of symmetry, its dimensions were inaccurate by up to ·7Å. This was considered intolerable. (In fact, this hydrogen bonding mechanism is not the correct one). At no stage during this examination of real cell coordinates did there appear evidence for $(\bar{1}01)$ or (101) molecular planes.

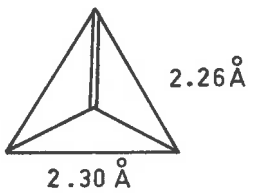
Mention has already been made of the two Harker line peaks. The peak at $(0,0,\frac{1}{2})$ shows streaking in the (211) plane through its centre. This particular line peak is the one which implies the centering of molecules on the glide plane and as such was further confirmation for a molecular structure in which molecules in (211) straddled this symmetry element.

3.1.3 General Peaks

At this stage of the analysis, there had been no indication as to the molecular plane of the urea molecule. There was no image in the origin since the origin peak

itself was of similar size to the urea molecule. One property of vector sets which is useful if only the orientation of a molecular group is required is that there are N images of the group in the origin, where N is the total number of scatterers in the cell. Under the present conditions, images of urea molecules in the parabanic acid atoms could be expected. These images have the advantage of being sufficiently removed from the origin to be unaffected by the origin peak (section 1.5.4).

Accordingly the 6400 was programmed to compute distances between the general peaks and a search was made for the urea figure



Parabanic acid figures were also sought. To allow for the possibility of images straddling the Patterson cell edge, all peaks defined by

$$-a/2 \leq x \leq a$$

$$-b/2 \leq y \leq b$$

$$-c/2 \leq z \leq c$$

were considered. The mirror plane enables this volume to cover the largest scale structure being sought. This exhaustive analysis resulted in the discovery of one urea image in a plane defined by $2x + y + z = \frac{1}{2}$. The dimensions of the image were accurate to $\cdot 1\text{Å}$, but because of the symmetry of the triangular array it was not possible to assert which of the three possible orientations was the correct one. (Information from the peak heights was inconclusive). Several approximate parabanic acid figures were found. However, errors in their dimensions and the incompatibility of their orientations with that of the original image led to their rejection.

Although a planar group in

$$2x + y + z = \tfrac{1}{2}$$

cannot be generated from a $P2_1/c$ symmetry related group in

$$2x + y + z = 0$$

this is of little consequence. The urea image is in vector space and the value of d in this case merely relates to the distance of the imaging atom (at the origin in vector space) from the molecular plane. The

Patterson had now yielded sufficient information to justify the assertion that the complex was planar and defined by $2x + y + z = 0$.

Since there were several hydrogen bonded urea-parabanic acid structures conceivable in the (211) plane it was now necessary to decide upon the correct one. Confirmation of the presence of two parabanic acid molecules (related by a centre of symmetry) in the same plane led to a further search of the (211) plane through the Patterson origin. Superposition methods were used in this instance to locate other images of the molecule related by a centre to the first. These methods had not been used before when scanning the vector set. In three dimensions they are unwieldy but for a two dimensional problem they allow a quick assessment of the worth of an image with respect to both its dimensions and its orientation. Images found by this method were in fact dimensionally inaccurate but had the appropriate orientation. Only two of the images provided hydrogen bonding possibilities through the centre of symmetry. The first model built provided for a urea-parabanic acid link similar to one of the links in TUPBA (see fig. 3.1). The urea molecules were simply fitted into the vacant space in the plane, consideration being given to symmetry

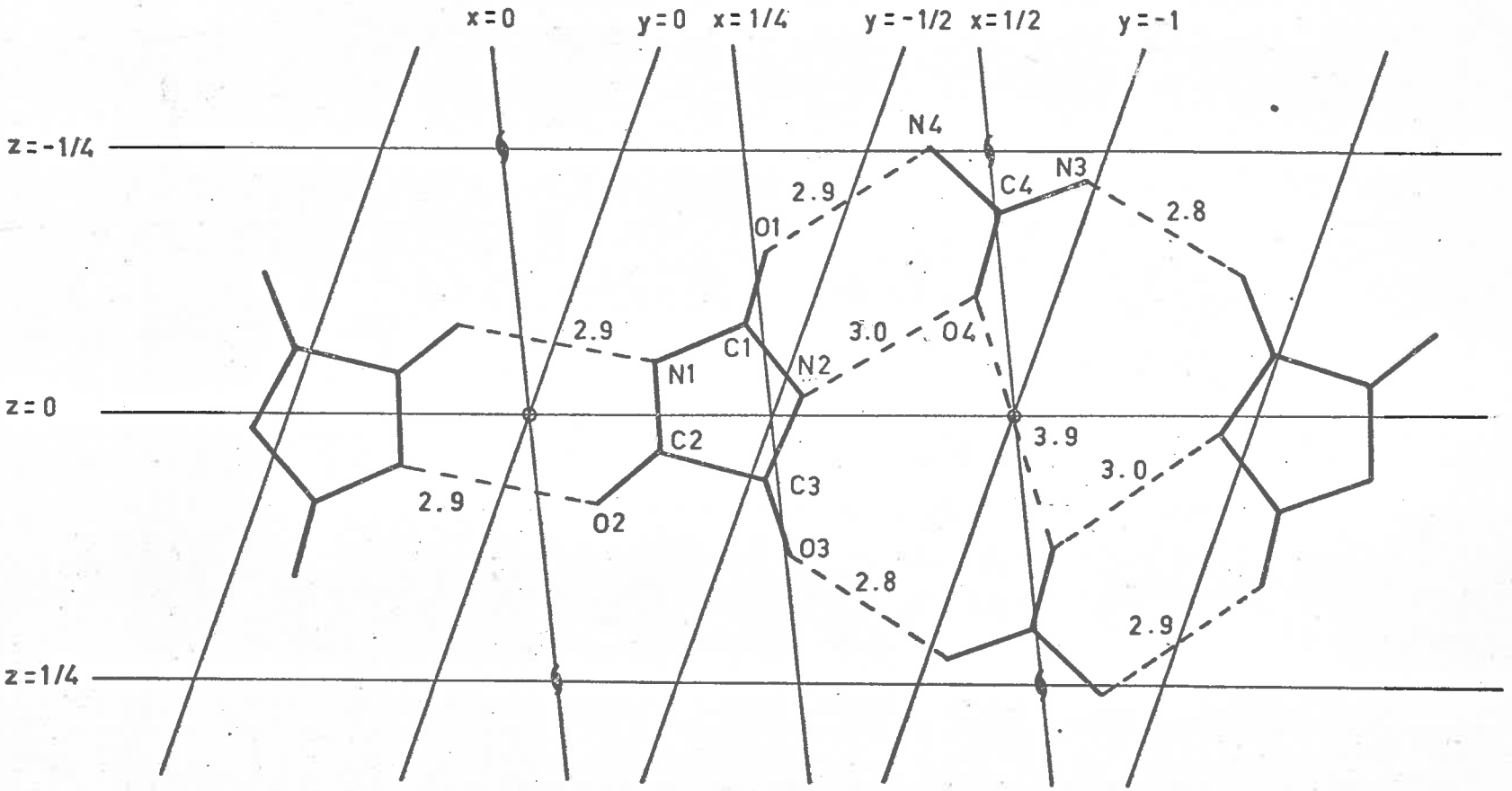


Fig. 3.1 Trial structure in the plane $2x + y + z = 0$. (UPBA)

element violation discussed earlier. The hydrogen bonds between parabanic acid molecules in this model are not unlike those found in the crystal structure of parabanic acid.

Structure factors were computed but the residual of ·8 was no better than could be expected from a random set of centrosymmetric points (Wilson 1950). The best of the projections was R(hko) = ·52 but since c = 15Å this was of little value.

The second of the above images which had a satisfactory hydrogen bond network failed to satisfy the symmetry operations.

3.1.4 Fo Syntheses

In section 1.5.4 a method is described for solving the Patterson function for coordinates (xys) in the real cell when Harker line information is lost in overlap. The method uses the information contained in the centre of symmetry in the real cell. Superposition methods were used with this technique in an attempt to find urea - urea^{s} images in the Harker plane. Seven such images were found and five of these were found to be related to real cell coordinates compatible with the original urea image. Of these, three were in the (211) plane through the

origin, and one allowed for urea-urea^{o} hydrogen bonding in the plane.

If we consider the urea molecule as a heavy atom ($Z = 28$, CON_2) then according to Sim (1961)

$$r = \frac{f_H^2}{\Sigma f_j^2} \approx 2$$

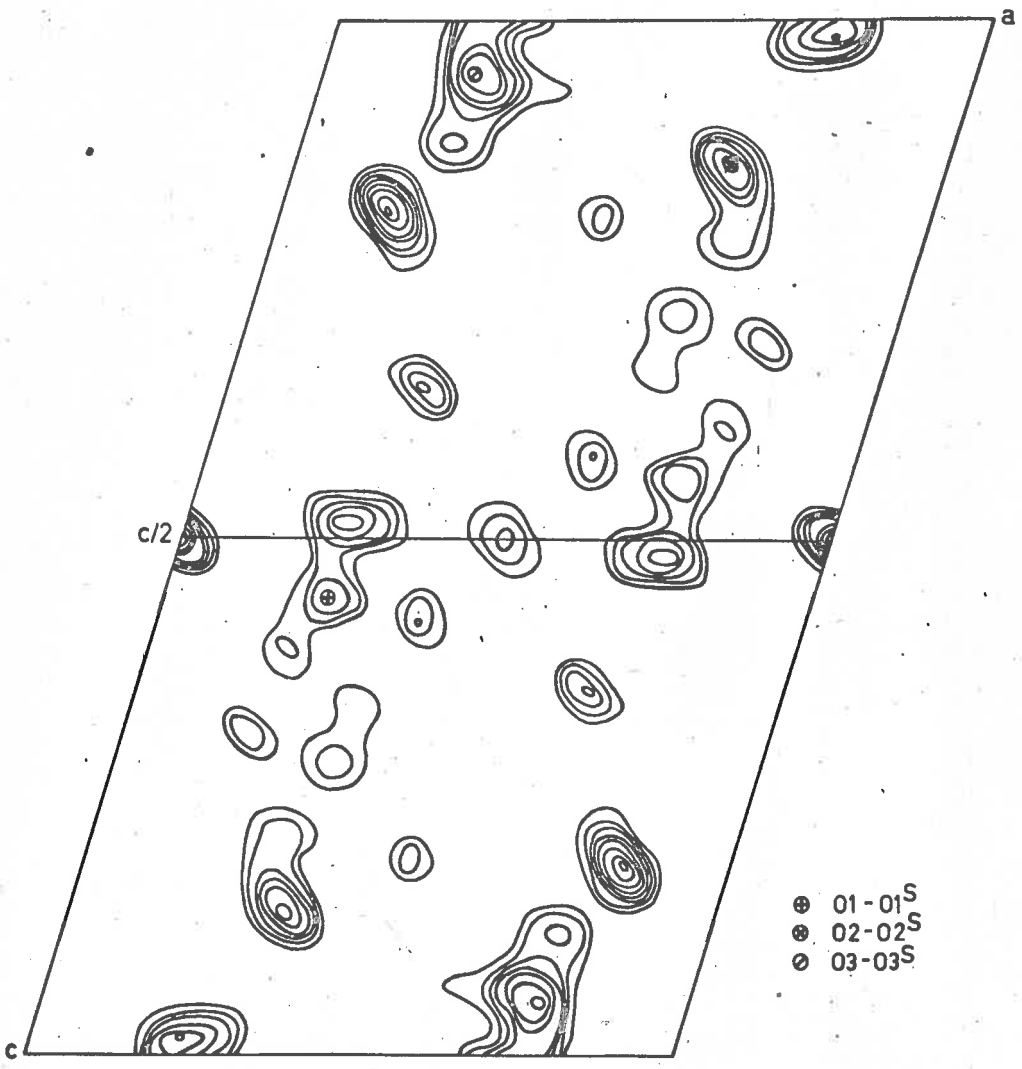
and 90% of the phases would be determined. Clearly the fact that urea is four discrete scatterers will reduce this figure. To give the Fourier every chance of yielding the structure, only those F_o values which had a large F_o value were used in the series. Either this method of discrimination was unsatisfactory or else the urea was wrongly placed for the Fourier map failed to generate the parabanic acid molecule. A number of small scale peaks were generated but they were apparently the result of termination effects and fortuitous reinforcements of Fourier waves for no structural meaning could be given them. F_o syntheses using phases from the other two urea positions were equally unsuccessful.

It may be recalled that a search for parabanic acid-parabanic acid^{s} images on $v = \frac{1}{2}$ was not successful. However the fact that seven such images were found for urea

by superposition methods led to the use of this technique in a second attempt to locate the parabanic acid molecule. On this occasion two images were found in $v = \frac{1}{2}$ and one of these (fig. 3.2) resulted from real space coordinates defined by $2x + y + z = 0$. Furthermore it provided for hydrogen bonding through the centre in a way not previously tried. Structure factors were computed and the phases were used in an F_o synthesis. The slab of high density which was generated in the Fourier was in marked contrast to the smaller, sharper peaks generated in the urea syntheses. This slab had the shape of the urea molecule with a central peak in the vicinity of the carbon atom. It lay in the same (211) plane as the parabanic acid molecule and was the correct distance from it to allow for hydrogen bonding to secure the complex. From the implied hydrogen bonding scheme the oxygen and nitrogen atoms of the urea molecule could be distinguished. Structure factors for this model (see fig. 3.3) had a reliability index of ·59, and a second Fourier map was computed. Shifts of up to ·1Å were implied and, when applied, these reduced R to ·47. One cycle of least squares gave further convergence to R = ·37.

3.2 Refinement

The least squares method of refinement has been



The Harker Section v = 1/2 of the sharpened Patterson function (UPBA).

Fig. 3.2

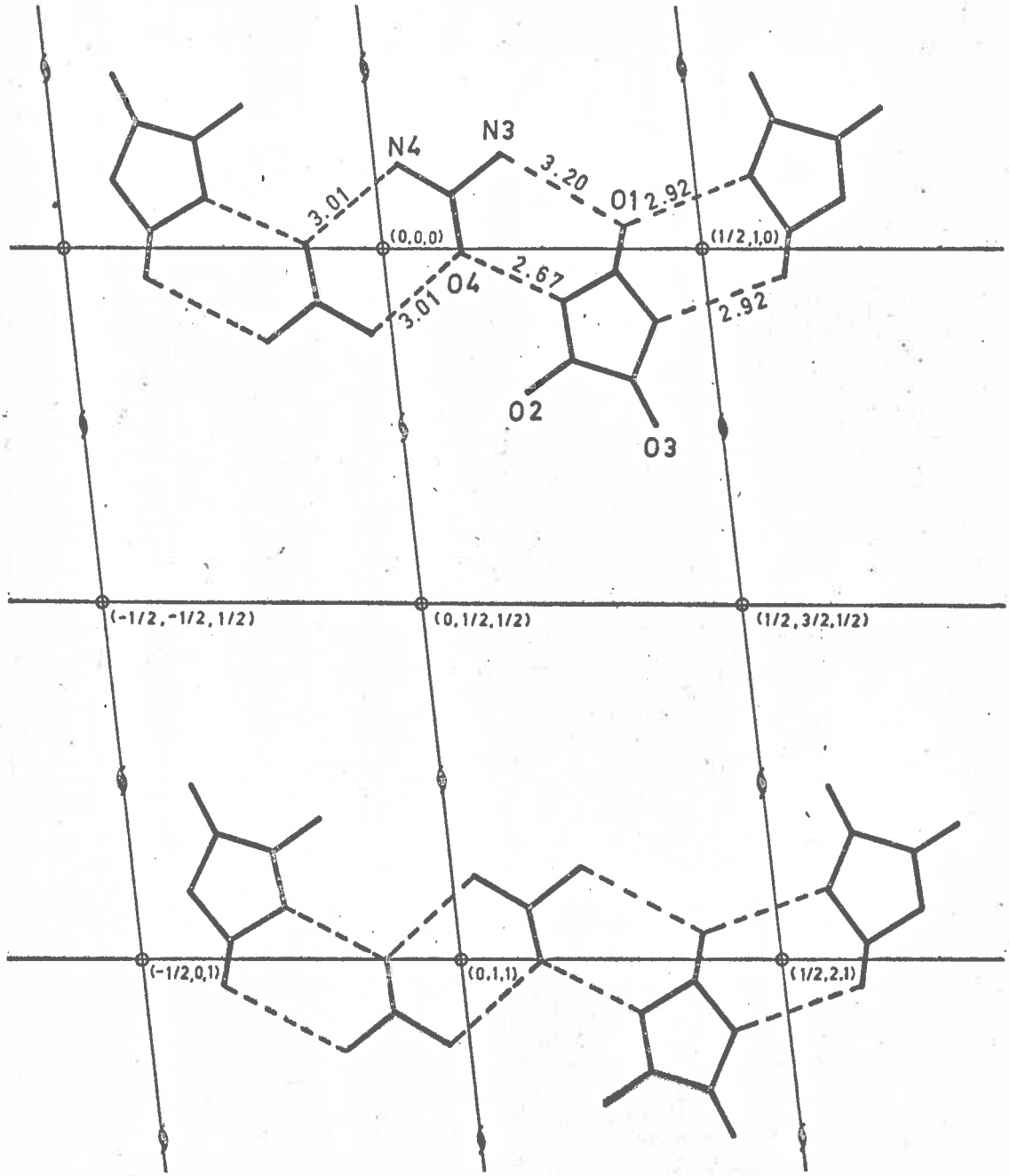


Fig. 3.3 Chains of the complex molecule in $2x - y + z = 0$.

outlined in chapter 2. The data reduction for this structure had been done by hand and to date only unit weight had been applied to all the intensities. Cruickshank's (1961) weighting scheme in which

$$w = (a + |F_o| + c|F_o|^2)^{-1}$$

was used. In this expression

$$a = 2F_{min}$$

$$\text{and} \quad c = 2/F_{max}$$

Lipson and Cochran (1966, P340) have given a test for deciding whether or not a suitable weighting shceme has been chosen. The least squares program FUORFLS lists the average value of $w(|F_o| - |F_c|)^2$ for various ranges of $|F_o|$ and these values were found to be approximately constant.

3.2.1 Interlayer Scale Factors

Three least squares cycles on the coordinate parameters alone reduced R to ·25 and since there was evidence of premature convergence the next cycle also adjusted the interlayer scale factors. The correlation that exists between interlayer scale factors and temperature factor parameters is well known (Lipson and Cochran

(1966)). However when measurements of these scale factors have been made (independent of F_c values) limits may be set on the values they might take and consequently it is possible to ascertain whether some temperature factor effects are leading to an incorrect least squares solution for these parameters. The strategy that was adopted in this case was to adjust the scale factors only after every two or three cycles on coordinate and temperature factor parameters, and, in fact, once anisotropic refinement was begun they were held constant.

3.2.2 Secondary Extinction

The refinement again showed signs of convergence, this time near R = ·20, and an examination of the listed output of structure factors revealed that there were seven diffraction amplitudes for which

$$|\Delta| > 15, \quad \text{where } \Delta = |F_o| - |F_c|$$

Furthermore, in each case Δ was negative. The fact that $|F_o|$ was large for each of these reflections implied that secondary extinction was a likely cause for the effect. The contribution of these seven reflections to the residual was 1·5%. Whilst this in itself is not very significant, the point of making allowance for extinction was not directly to reduce R but to remove the false minimum

which the extinction had generated on the least squares surface.

James (1958, P293) has given a correction factor for secondary extinction of the form

$$I_c = I_o/(1-2gI_o)$$

and in order to get an estimate of 2g, $1 - \frac{I_o}{I_c}$ was plotted against I_o (figure 3.4). The data used for this graph was in fact F_o and E_c, these being the film values for the intensities observed and calculated. It was considered that since the extinction effect depended on the strength of a Bragg reflected wave, allowance should be made for Lorents and polarisation effects which have already affected the intensity of diffracted X-rays. The James formula may be rewritten as

$$2g = \frac{1-I_o/I_c}{I_o}$$

and hence any scale factor which is applied to the intensities will influence the value of 2g. A correction factor in the form of Lp will therefore make 2g a function of $\sin\theta$. A correction for secondary extinction of $2g = 6{\cdot}3 \times 10^{-5}$ was applied to all intensities greater than 500. Evidence of extinction may be seen in the Wilson plot (paragraph 1.2.4). The observed dropping of the

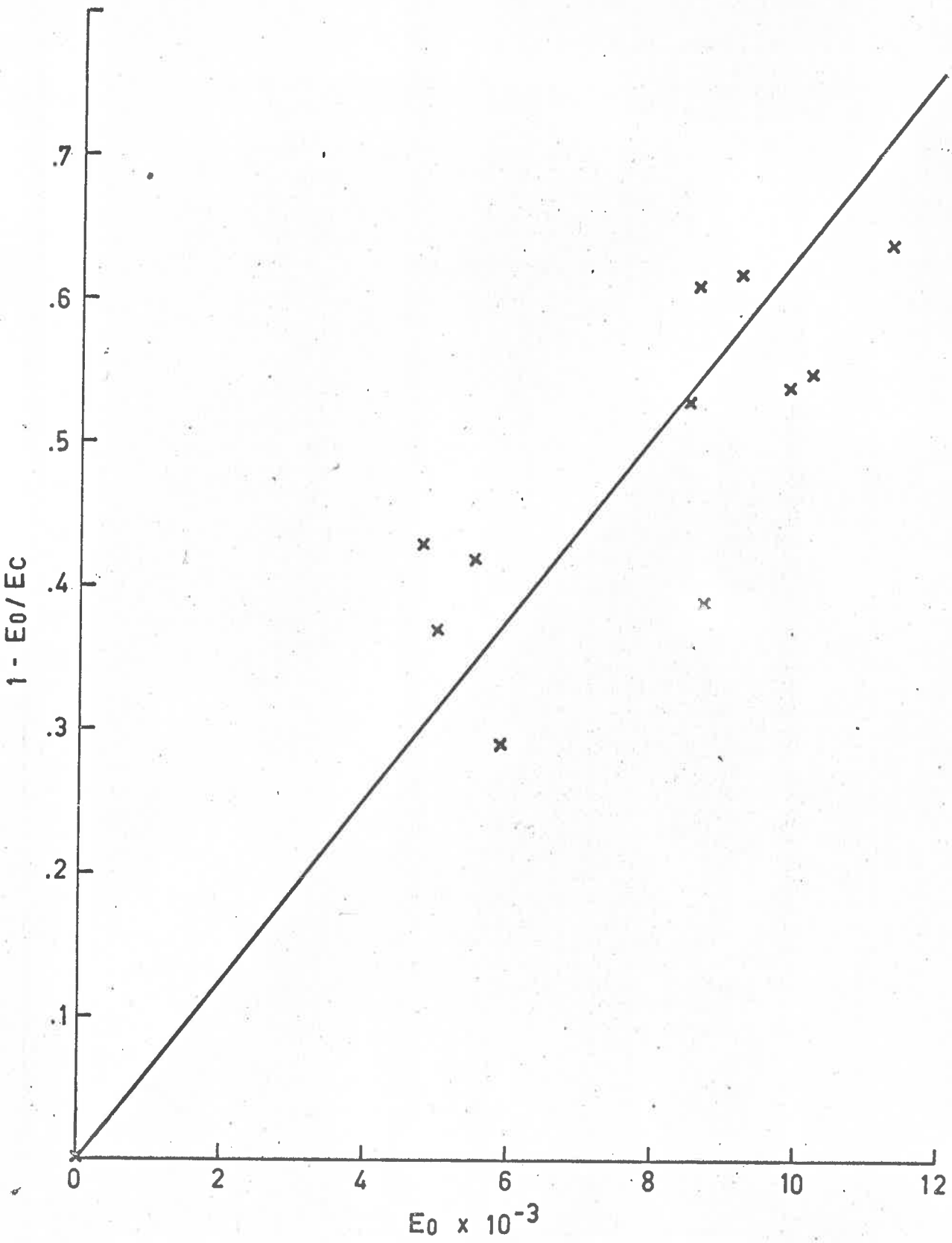


Fig. 3.4 Extinction correction graph (UPBA).

ordinate at low angle is characteristic of extinction effects and further justifies the correction made here.

3.2.3 Anisotropic Refinement

Least squares refinement of isotropic atoms proceeded until R was ·142. Conversion to anisotropic atoms was done as outlined in chapter 2. The standard deviations for the β_{22} component of β_{ij} were found to be considerably larger than those for the other elements of the temperature factor matrix. This was attributed to lack of data in the b* direction beyond k = 3. Large errors in the original values of β_{22} (as converted from the isotropic atoms) gave rise to large shifts in this parameter after one least squares cycle. Fudge factors of ·5 were applied to those shifts which had generated temperature factor matrices which were not positive definite (and hence did not represent a physical reality) and refinement then proceeded satisfactorily.

3.2.4 Hydrogen Atoms

At R = ·106 a difference map was computed to check the temperature factor refinement and to locate the hydrogen atoms.

Examination of the difference density in the region of the heavy (non hydrogen) atoms revealed maximum peak

heights of $\cdot 3e/A^3$. These were in the vicinity of the imidazole ring and were not readily attributed to the thermal motion of any one atom. In any event these peak heights are not serious at this stage of such an analysis.

Four of the six hydrogen atoms were located unequivocally. H1 was apparent only as a peak of height $\cdot 3e/A^3$ at a site which was further removed from N1 than expected. There was also some uncertainty in the position of H32. The coordinates, peak heights and positions of the hydrogen atoms relative to $2x + y + z = 0$ are shown in the following table.

Atom	x	y	z	Pk.ht. (e/A^3)	$2x+y+z = d$
H1	·255	-·888	·567	·3	·19
H2	·514	-1·559	·593	·5	·06
H31	·183	-·644	·308	·5	·03
H32	·230	-1·000	·376	·4	-·16
H41	·071	-·408	·330	·6	·06
H42	·000	-·377	·426	·5	·05

The hydrogen atoms were inserted at these coordinates and the residual improved by nearly 1% to ·098. The results of the final three least squares cycles are tabulated.

R	·098	·090	·089	·089
$\Sigma w(F_o-F_c)^2$	139·4	120·5	117·3	117·1

Further convergence may have been possible if the extinction parameter (2g) had been refined. There was however no facility for this in FUORFLS and since the two largest Δ's were positive any improvement in R would only be marginal. The final residual for observed reflections only is ·086. All parameter shifts on the last cycle of least squares were appreciably less than half the corresponding standard deviation. The final parameters are given in Table 3.1

3.2.5 Bond Lengths and Angles

The 6400 was programmed to compute bond lengths and angles for intra- and inter-molecular bonds. The standard deviations for bond lengths and angles were calculated from the expressions given by Ahmed and Cruickshank (1953) viz.

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

and

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

This data is given in table 3.2 and the dimensions of the molecules are also shown in figure 3.5. The final structure listings are given in appendix B.

TABLE 3.1A

Coordinate Parameters

Atom	x/a	y/b	z/c	σ(x/a)	σ(y/b)	σ(z/c)
O1	·3921	-·2240	-·5325	·0004	·0009	·0002
O2	·2114	-·1155	-·2782	·0004	·0009	·0003
O3	·4007	-·5603	-·2501	·0004	·0010	·0003
N1	·2786	-·1126	-·4181	·0004	·0011	·0003
N2	·4262	-·4463	-·3953	·0004	·0010	·0003
C1	·3675	-·2575	-·4575	·0005	·0012	·0003
C2	·2762	-·1981	-·3322	·0005	·0013	·0003
C3	·3752	-·4250	-·3165	·0005	·0013	·0003
H1	·2340	·0186	-·4439	·0087	·0164	·0050
H2	·4956	-·5649	-·4099	·0081	·0150	·0044
O4	·1091	·2508	-·5110	·0005	·0010	·0003
N3	·1953	·2238	-·6396	·0006	·0014	·0004
N4	·0461	·5421	-·6197	·0005	·0012	·0003
C4	·1179	·3372	-·5874	·0005	·0013	·0003
H31	·2016	·3165	-·6855	·0093	·0182	·0054
H32	·2357	·0699	-·6179	·0101	·0207	·0059
H41	·0598	·5912	-·6673	·0088	·0175	·0051
H42	-·0046	·6249	-·5773	·0088	·0174	·0046

TABLE 3.1B

Temperature Factor Parmeters β_{ij} x 10^4

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O1	129	271	28	-54	33	-4
O2	129	303	42	-24	47	22
O3	129	313	43	-48	40	-56
N1	95	133	31	-50	24	-2
N2	85	146	30	-31	24	-4
C1	74	145	30	-13	17	10
C2	73	217	32	14	23	17
C3	75	241	31	9	27	5
H1	AS FOR N1					
H2	AS FOR N2					
O4	162	289	47	127	58	51
N3	154	201	54	45	61	17
N4	140	255	34	54	37	19
C4	78	178	32	11	28	1
H31	AS FOR N3					
H32	AS FOR N3					
H41	AS FOR N4					
H42	AS FOR N4					

TABLE 3.2A

Bond Lengths

Bond	d(Å)	σ(d)	Bond	d(Å)	σ(d)
O1-C1	1·233	·006	N1-O4	2·665	·008
C1-N1	1·410	·008	H1-O4	1·808	·011
C1-N2	1·399	·008	N4-O4	3·007	·007
N1-H1	·870	·011	H42-O4	1·997	·010
N2-H2	·993	·010	O1-N2	2·924	·007
N1-C2	1·383	·007	O1-H2	1·947	·010
N2-C3	1·412	·006	O1-N3	3·204	·009
C2-O2	1·240	·007	O1-H32	2·284	·012
C3-O3	1·214	·007	$O3^{s}$-N3	3·027	·008
C2-C3	1·537	·010	$O3^{g}$-H31	2·735	·012
O4-C4	1·272	·006	$O2^{s}$-N4	3·236	·007
C4-N3	1·373	·009	$O2^{g}$-H41	2·494	·010
C4-N4	1·336	·009	$O2^{g}$-N3	3·067	·008
N3-H31	·881	·011	$O2^{g}$-H31	2·203	·011
N3-H32	·955	·013	$C3^{s}$-C3	3·756	·009
N4-H41	·813	·010	$O3^{s}$-O3	3·346	·009
N4-H42	1·015	·011	$C3^{s}$-O3	2·838	·008

1st column shows intramolecular bonds.

2nd column shows intermolecular contacts. The first eight are in the plane of the complex (see fig. 3.3) and the last nine are to screw (s) and glide (g) related atoms in a different (211) plane.

TABLE 3.2B

Bond Angles

Angle	θ°	σ(θ)	Angle	θ°	σ(θ)
O1-C1-N1	126·7	·5	N1-H1-O4	168·1	2·5
O1-C1-N2	125·5	·5	N4-H42-O4	173·2	3·6
C1-N1-C2	112·2	·5	N2-H2-O1	167·2	1·8
C1-N2-C3	109·6	·5	N3-H32-O1	161·4	1·8
N1-C2-C3	104·1	·5	N3-H31-O3^{S}	100·8	·9
N2-C3-C2	106·3	·4	N4-H41-O2^{S}	152·2	1·4
N1-C2-O2	129·5	·5	N3-H31-O2^{S}	166·5	2·6
N2-C3-O3	127·4	·5	C3-O3-C3^{S}	131·6	·5
C1-N1-H1	123·6	1·0	O3-C3-O3^{S}	104·0	1·0
C1-N2-H2	119·7	·6	N2-C3-O3^{S}	88·0	1·0
O4-C4-N3	122·2	·5			
O4-C4-N4	119·2	·5			
C4-N3-H31	110·4	·9			
C4-N3-H32	116·1	·9			
C4-N4-H41	114·4	·9			
C4-N4-H42	116·0	·7			

1st column - intramolecular angles.

2nd column - intermolecular angles. The first four are in the plane of the complex (see fig. 3.3) and the last four are to screw and glide related atoms in a different (211) plane.

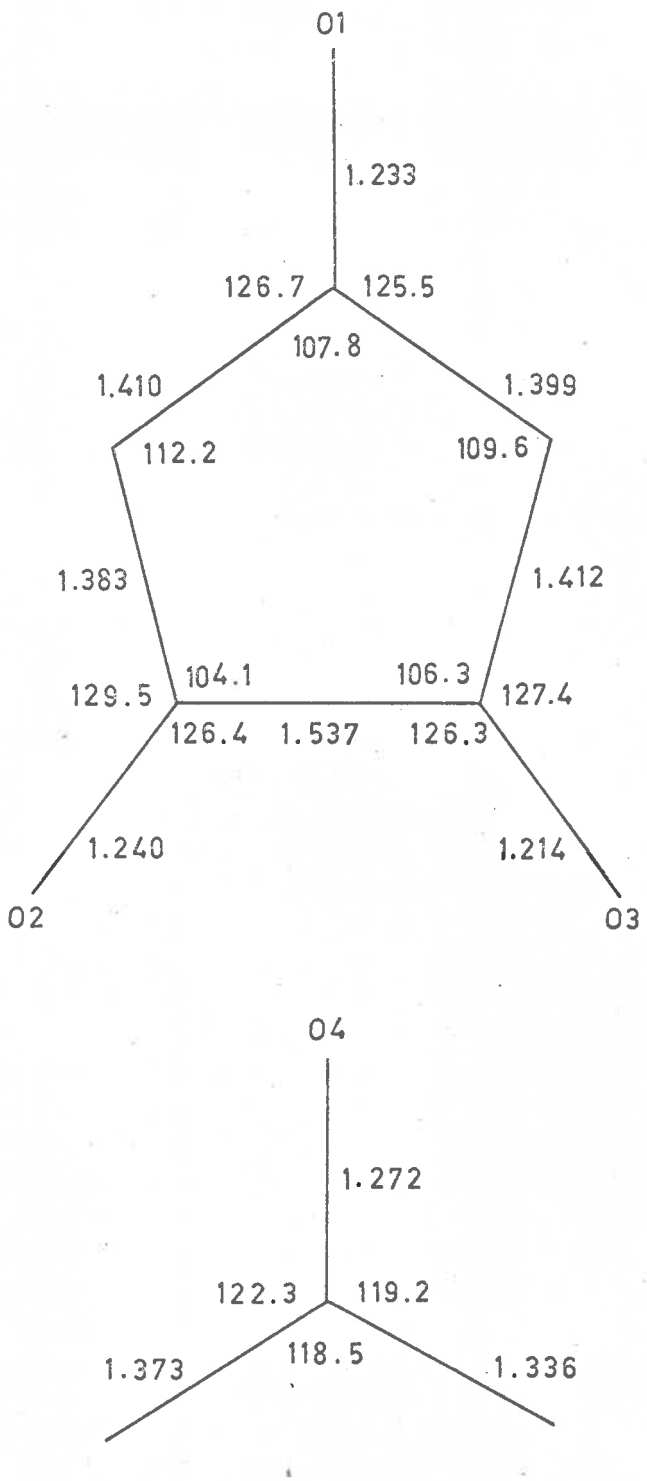


Fig. 3.5 Dimensions of urea and parabanic acid molecules in UPBA.

3.2.6 Final F_o Synthesis

A final electron density map, using the phases of the model, showed all but four of the hydrogen atoms to be resolved. The electron density was sampled at intervals of $\frac{a}{60}$, $\frac{b}{30}$ and $\frac{c}{90}$, and the (211) plane was drawn out to scale (figure 3.6). H41 and H42 are both resolved in this plane and the position of the remaining hydrogen atoms is indicated by the $1e/A^3$ contour in every case. Anomalies in the bond lengths and angles as determined from this section of the Fourier and from Tables 3.2A and 3.2B are a result of the slight tilt that the complex has to the plane.

This section of the map illustrates the intersection of symmetry related planes

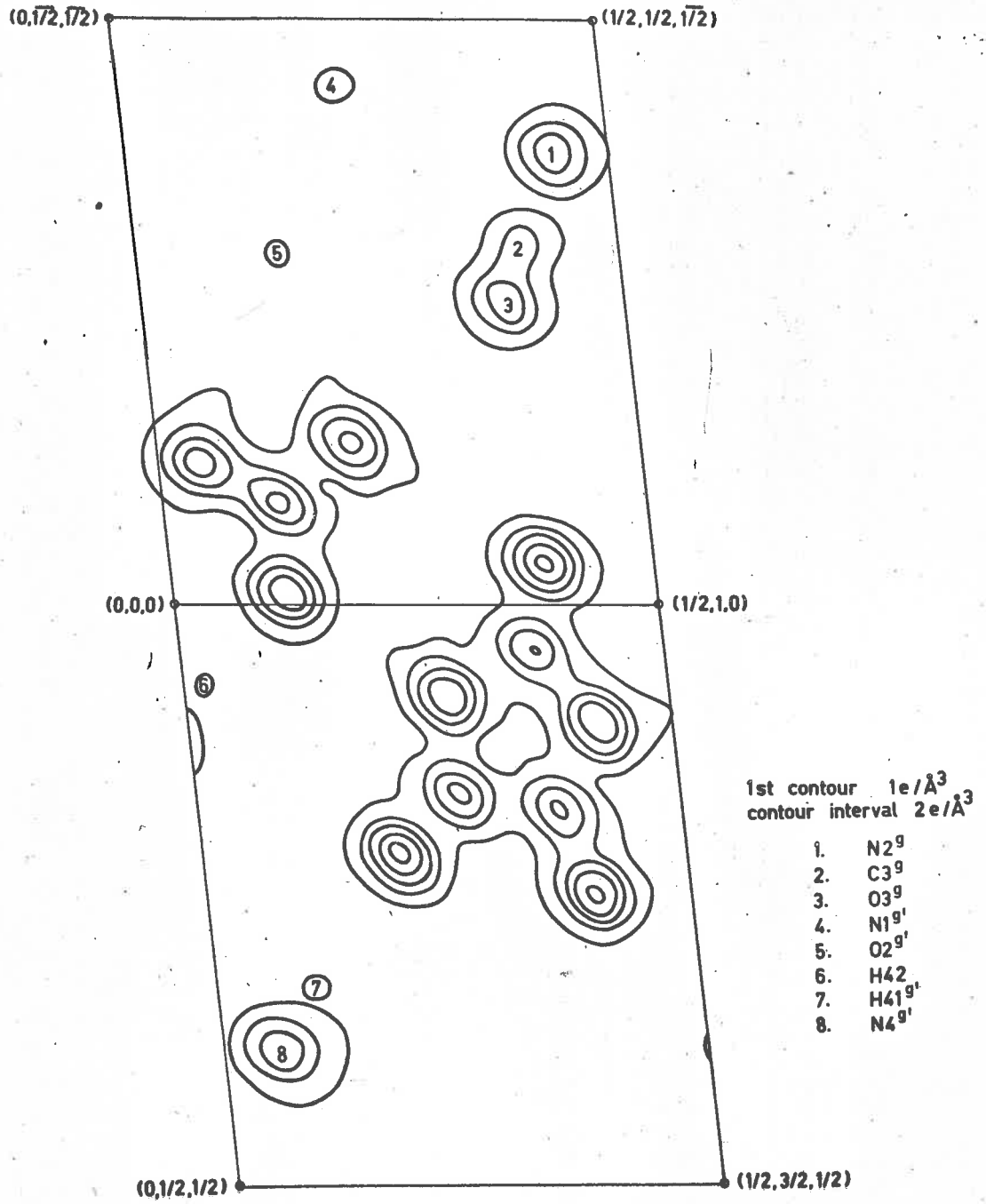
$$2x + y + z = d_1$$

and $$2x - y + z = d_2$$

along lines $y = n/2$ (d_1, d_2, n integral)

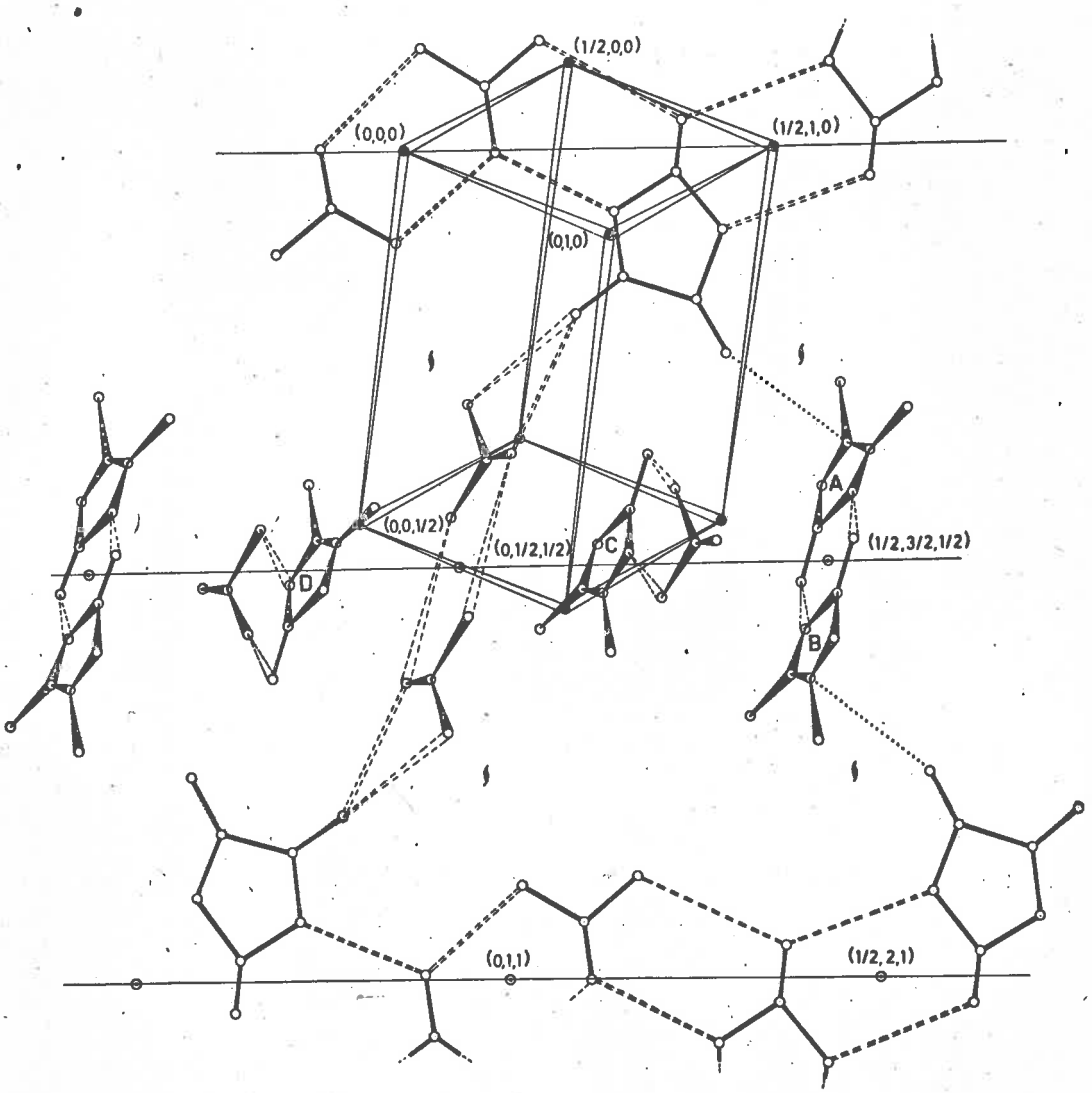
and the three dimensional packing of the molecules is shown in figure 3.7. This figure is drawn looking down the normal to the $(2\bar{1}1)$ plane. The hydrogen bonded pairs of molecules at $z = \frac{1}{2}$ are in the planes

$$2x + y + z = -1, 0, 1, 2, 3$$



Final Fourier map, (211) section.

Fig. 3.6

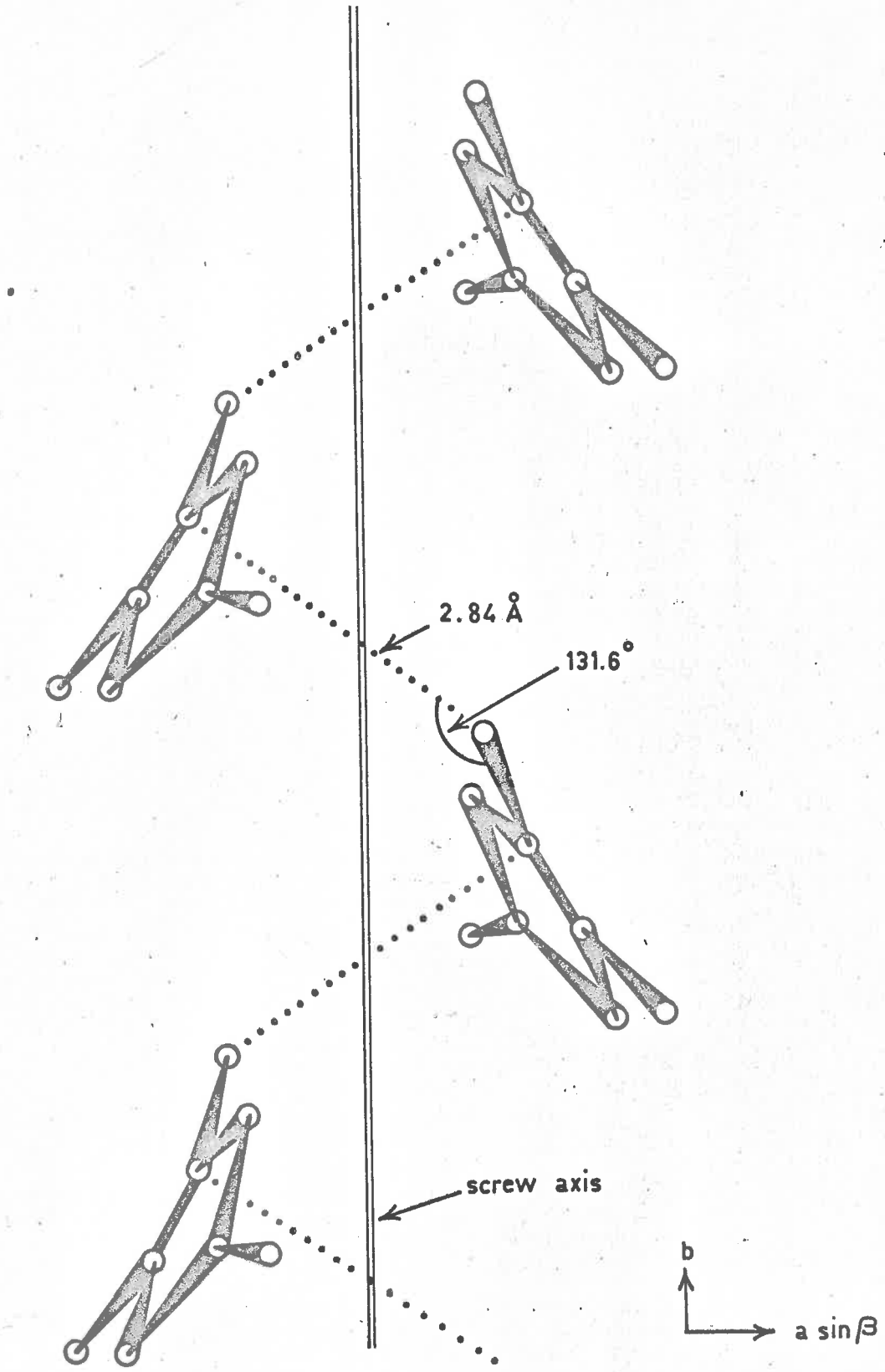


Three dimensional packing of UPBA as seen down the normal to the $(2\bar{1}1)$ plane.

Fig. 3.7

from left to right respectively. The parabanic acid molecules A and C are below the plane $2x - y + z = 0$ and B and D are above this plane. B and C are related by the b-translation and C and D by the centre of symmetry at $(0,\frac{1}{2},\frac{1}{2})$. The outline of one quarter of the unit cell is also shown. The packing of the parabanic acid molecules up the screw axis is shown in figure 3.8.

The structure is discussed in chapter four.



Arrangement of parabanic molecules up the symmetry axis at x = a/2.

Fig. 3.8

CHAPTER FOUR

A DISCUSSION OF THE STRUCTURES AND INTERMOLECULAR CONTACT MECHANISMS

4.1 Introduction

This chapter contains a discussion of the molecular and crystal structures of UPBA and TUPBA. Theoretical discussions have been included where relevant, although an attempt has been made to keep these as descriptive as possible.

It is customary to apply significance tests to crystal (and other) data in order to ascertain the reality of anomalies in the data. Standard deviations (σ) for all bond lengths and angles are known and we can therefore define a quantity δ by

$$\delta = \frac{\Delta}{\sigma}$$

where Δ is the departure of some observation from an expected or predicted value. The probability of δ exceeding 2·5, purely by chance, is 1%, and for $\delta > 3{\cdot}3$ the probability is only ·1%. The criteria adopted here are that observations with $\delta > 2{\cdot}5$ are quite significant whilst those with $\delta > 3{\cdot}3$ are highly significant. When two observations a_1 and a_2 with standard deviations σ_1

and σ_2 are being compared, δ is defined as

$$\delta = \frac{|a_1 - a_2|}{\sqrt{(\sigma_1^2 + \sigma_2^2)}}$$

4.2 The UPBA Structure

4.2.1 The Molecular Structure

4.2.1.1 Molecular Planes

The molecular structures of both urea and parabanic acid are planar (section 1.5.4) and this planarity is essentially retained in the complex since the intermolecular binding energies are insufficient to cause large distortions of the molecular units. (See later this section for significant aplanarity). Least squares fitting of the coordinate parameters for seven different groups of atoms defined the following planes (Schomaker et al. (1959)):-

I Imidazole ring plane.

$6 \cdot 374x + 3 \cdot 032y + 3 \cdot 260z = \cdot 073.$

II Parabanic acid plane (no hydrogen atoms)

$6 \cdot 443x + 2 \cdot 991y + 3 \cdot 180z = \cdot 137.$

III Parabanic acid plane.

$6 \cdot 368x + 3 \cdot 011y + 3 \cdot 339z = \cdot 053.$

IV Urea plane (no hydrogen atoms).

$6{\cdot}437x + 2{\cdot}784y + 3{\cdot}744z = -{\cdot}511.$

V Urea plane.

$6{\cdot}432x + 2{\cdot}632y + 4{\cdot}113z = -{\cdot}777.$

VI UPBA plane (no hydrogen atoms).

$6{\cdot}261x + 3{\cdot}198y + 3{\cdot}081z = {\cdot}035.$

VII UPBA plane.

$6{\cdot}391x + 3{\cdot}121y + 2{\cdot}944z = {\cdot}152.$

All atoms were given equal weight in this analysis. In each equation the R.H.S. defines the origin to plane distance in Å. Table 4.1 gives the distance (d) of relevant atoms from these planes and the corresponding value of δ indicates the significance of these displacements. The standard deviation of the atomic coordinate in this case is taken as the average of $\sigma(x)$, $\sigma(y)$ and $\sigma(z)$.

All three oxygen atoms are significantly displaced from the imidazole ring plane and O3 (the farthest atom from I) is on the opposite side of the plane to O1 and O2. Significant displacements of O1, O3 and N2 from II also occur. The large value of χ^2 ($= \sum_i (\delta_i)^2$) for this plane (8 degrees of freedom) will rarely occur by chance

TABLE 4.1

UPBA Planes Data

Atom	I		II		III		IV		V		VI		VII	
	d	δ	d	δ	d	δ	d	δ	d	δ	d	δ	d	δ
O1	·011	2·8	·025	6·3	-·008	2·0					·063	15·8	·087	21·8
O2	·017	4·3	-·006	1·5	·017	4·3					·063	15·8	·020	5·0
O3	-·033	8·3	-·027	6·8	-·023	5·8					-·088	22·0	-·076	19·0
N1	-·002	·4	-·009	1·8	-·014	2·8					·062	12·4	·047	9·4
N2	·002	·5	·016	4·0	-·002	·5					-·011	2·8	·016	4·0
C1	-·003	·6	·005	1·0	-·015	3·0					·033	6·6	·047	9·4
C2	·004	·8	-·007	1·2	·001	·2					·037	7·6	·017	3·4
C3	-·002	·4	·002	·4	·000	0·0					-·020	4·0	-·012	2·4
H1					·011	1·4							·095	11·9
H2					·034	4·9							·046	6·6
O4							-·002	·5	·027	6·8	-·124	31·0	-·176	44·0
N3							-·004	·7	-·026	4·3	-·067	11·2	-·088	14·7
N4							-·003	·6	-·053	10·6	·078	15·6	·011	2·2
C4							·009	1·8	-·004	·8	-·028	5·6	-·075	15·0
H31									·069	7·7			·106	11·8
H32									-·093	10·3			·246	27·3
H41									-·032	4·0			·111	13·9
H42									·018	2·3			·070	8·8

d in Å

δ in number of standard deviations.

and it must be concluded that these atoms are significantly non planar.

The fit to the urea plane (IV) is very good, but the inclusion of hydrogen atoms, in this and other planes, indicates that they are significantly displaced from the plane.

The complex itself is significantly nonplanar although the proximity of the two molecules to the (211) plane had been sufficient for Patterson methods to yield the solution.

The displacement of the urea and parabanic acid planes from the origin emphasises that whilst the planes of molecules related by a centre of symmetry are parallel, they are displaced slightly from each other (~1·0Å for urea and 0·3Å for parabanic acid). The angle between planes II and IV is 2·7°.

4.2.1.2 Bond Lengths and Angles

The dimensions of the molecules have been given in figure 3.5 and the following table indicates the differences in bond lengths of the molecules in the complex and in their respective crystal structures.

Bond	δ	Bond	δ
C1-O1	2·9	C4-O4	·8
C2-O2	4·0	C4-N3	3·0
C3-O3	·3	C4-N4	·1
C1-N1	3·4		
C1-N2	2·4		
N1-C2	3·0		
N2-C3	7·8		
C2-C3	-·4		

In only one case has there been a decrease in bond length and this by an insignificant amount. The severe lengthening of N2-C3 is discussed in section 4.4.2 and a mechanism for this anomaly is given in section 4.4.3.2. Figure 3.5 illustrates the loss in mirror symmetry of the two molecules in the complex.

Pauling (1960) gives the C = O bond length as 1·21Å and it is seen that only C3 = O3 has retained pure double bond character. The percentage double bond character (x) of the ring bonds was determined by Pauling's equation

$$R = R_1 - (R_1 - R_2)\frac{3x}{2x+1}$$

where R = observed bond length,

R_1 = single bond length

and R_2 = double bond length.

C2-C3 retains the pure single bond character found in the parabanic acid structure but the values for the other groups are

Bond	x(parabanic acid)	x(UPBA)
C1-N1	20%	12%
C1-N2	20%	12%
N1-C2	25%	18%
N2-C3	25%	12%

The percentage double bond character of the carbonyl groups may be estimated on the basis that the total double bond character around any carbon atom be unity. The implied bond lengths of the carbonyl groups are in good agreement with those observed.

Bond	Implied x	Implied length
C1-O1	76%	1.23
C2-O2	82%	1.23
C3-O3	88%	1·22

In the parabanic acid structure this method grossly over-estimated the length of C1-O1 (1·24 c.f. 1·21) but in the present case no additional ionic character need be assigned any of these groups to explain their length.

The significant asymmetry of the parabanic acid molecule in UPBA warrants further comment. The percentage

double bond character of various bonds may be represented by drawing out possible resonance structures of the molecule (e.g. Davies and Blum (1955)). One could then assert, for example, that those structures with a double bond between C3 and O3 contribute 88% to the final structure. It is a consequence of the asymmetrical environment of the molecule and the subsequent degeneration of point group symmetry from mm2 to 2m that a similar result does not hold for C2-O2.

The urea molecule in the complex was treated in the same way with the following results.

Bond	x
C4-N3	22%
C4-N4	31%
C4-O4	47%

The implied length of C4-O4 is 1·27Å and this agrees with the observed length of 1·272Å. The difference in length of the C-N groups is 2·9σ, i.e. quite significant.

4.2.2 The Crystal Structure

The packing of the molecules in the (211) and $(2\bar{1}1)$ planes is illustrated in figure 3.7. The angle between these two planes is 68·3° and, as such, is very close

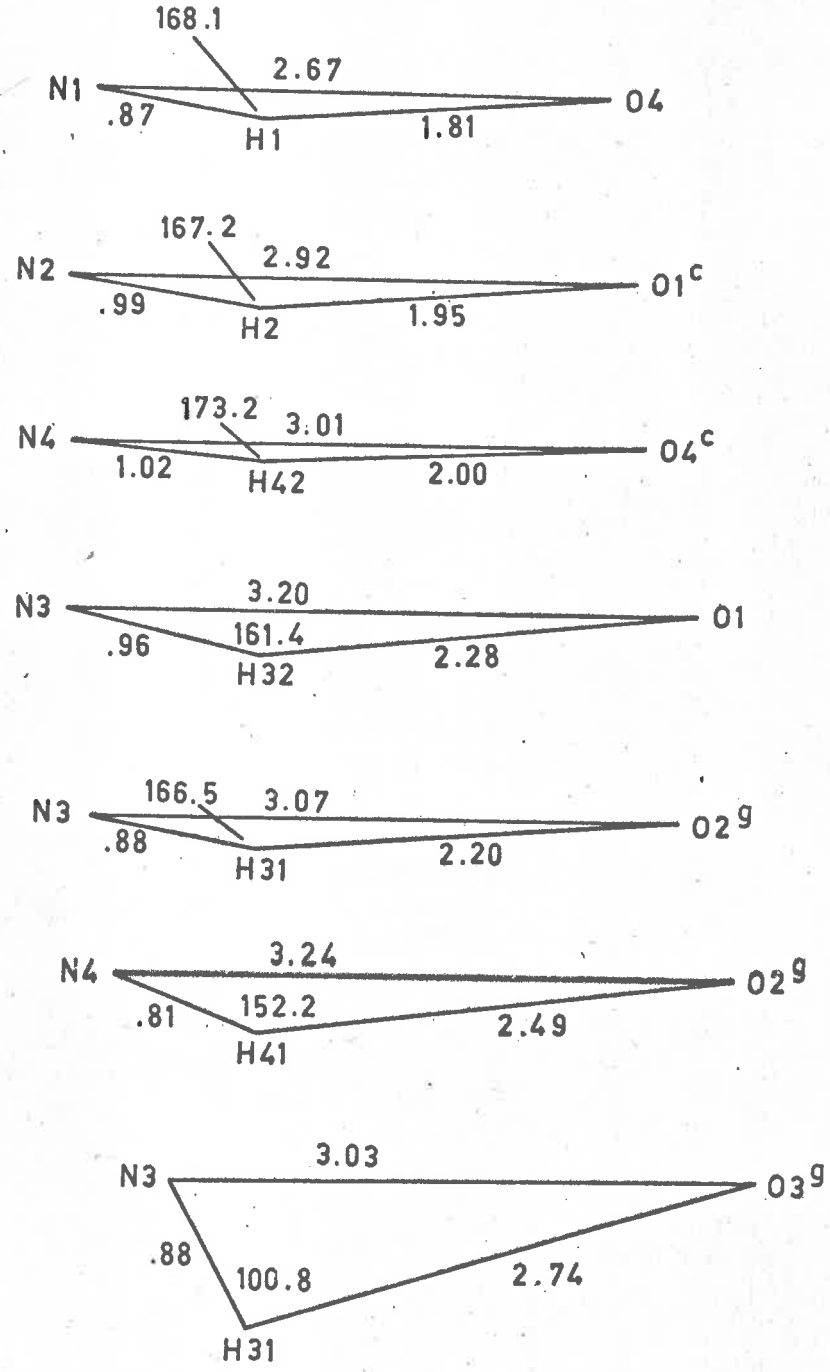
to the monoclinic angle of the cell (70·9°).

4.2.2.1 Hydrogen Bonds

The links in the chains of molecules in the (211) and ($2\bar{1}1$) planes are four hydrogen bonds and the interlooking of these planes is secured by two more hydrogen bonds and a carbon-oxygen contact of the type described in section 1.1 (see figure 3.7).

The geometry of possible hydrogen bonds is shown in figure 4.1, the first four bonds being in the plane of the complex and the last three between symmetry related planes. Included in this figure are the N3-H31...$O3^{E}$ approach and two weak hydrogen bonds involving H32 and H41. The first of these is included to illustrate that whilst the N3...$O3^{E}$ approach is conducive to hydrogen bonding, H31 secures this bond to $O2^{E}$. Since O3 is not involved in hydrogen bonding the six protons are equally shared by the remaining three carbonyl oxygen atoms.

The hydrogen atoms H1 and H2 are active in the only bonds shorter than 3Å. However, it is not shortness of N...O that is most important in hydrogen bonding, but rather overlap of H and O Van der Waal's radii. The contact distance for these atoms is 2·6Å and the bond



superscript c refers to centre of symmetry
superscript g refers to glide plane symmetry

Hydrogen bonding in UPBA.

Fig. 4.1

involving H41 is therefore very weak. If uncertainties in the Van der Waal's radii are neglected the overlap for this hydrogen bond is 10σ (i.e. highly significant). It is worth noting that this hydrogen bond is the least linear of all those in the structure and is therefore predictably weakest.

Fuller (1959) has reviewed the hydrogen bond data and included in thisreview are eleven compounds which exhibit N-H...O = C hydrogen bonds, where N and C are ring atoms. The fourteen hydrogen bonds in these compounds range in length from 2·62Å to 2·93Å, and the present observed distance of 2·92Å between N2 and $O1^{c}$ is just within this range. However, this distance is longer than the hydrogen bond lengths found in parabanic acid (2·873Å and 2·837Å) and this may be a result of the fact that the acceptor atom, O1, is active in two hydrogen bonds in UPBA.

The bond N4-H42...$O4^{c}$ (3·01Å) is of comparable length with the hydrogen bonds in urea, (Vaughan and Donohue (1952)) viz. 2·99Å and 3·04Å.

Aside from the unusually long hydrogen bonds involving H32 and H41, the one anomaly in this data is the failure of O3 to participate in hydrogen bonding.

Wallmark (1962) has claimed that the influence of atoms A and B in the hydrogen bond A-H...B is as follows. For a given A, the hydrogen bond distance roughly follows the change in the Van der Waal's radius of B atoms, and for a given B, the hydrogen bond length decreases with an increase in electronegativity of A. In fact the data shows an almost proportional relationship between the difference in electronegativity of A and H and the decrease in the length of H...B from the contact distance.

The UPBA data implicates the character of B in the length of the hydrogen bond in the following way. The carbonyl group C3=O3 has more double bond character than any of the other carbonyl groups. Therefore the contribution of resonance structures of the type

$$O^- - C^{\diagup\!\!\!\diagup}_{\diagdown}$$

to the final structure will be least for C3 = O3, and, since the O^- ion has a greater affinity for protons than the neutral oxygen atom, this group will compete less strongly for hydrogen bonds. By this argument the electron density in the region of B is critical in the participation of B in a hydrogen bond.

Consider the hypothesis that the C = O ... H-N

hydrogen bond length increases as

(i) the double bond character of C = O increases, and

(ii) the double bond character of groups attached to N increases.

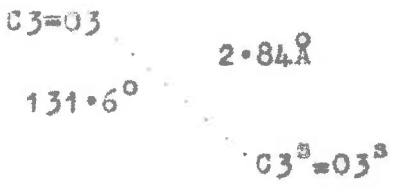
The first point has already been discussed. With regard to the second, the more tightly the proton is bound to the nitrogen atom, the less screening effect can the single hydrogen atom electron have. In other words the N-H dipole is strongest when the hydrogen atom electron is bound between N and H. Separation of these two effects on the hydrogen bond length (e.g. in anhydrous barbituric acid) is not possible without a more formal treatment of the problem.

4.2.2.2 The Carbon-Oxygen Contact

A report on the observed contacts in both UPBA and TUPBA has been published in the abstracts of The Eighth International Congress of Crystallography (Colman and Medlin (1969)).

The failure of the UPBA crystal structure to utilise facilities for hydrogen bonding correlates with the formation of carbon-oxygen contacts in the compounds discussed in section 1.1. In UPBA it is O3 that is involved in the

contact



by which chains of parabanic acid molecules are secured up every screw axis at x = (2n+1)a/2 (see figure 3.8).

The symmetry relationship between C and C′ in the contact C = O ...C′ has been observed before in anhydrous barbituric acid although it was not the case in parabanic acid. The contact length is within the range of previous data but the angle at the oxygen atom is smaller than has previously been observed. The angle which the contact makes with parabanic acid plane of C′ is specified by

$$|\underline{O3}^{i} - C3^{i} - O3 = 104^{\circ}$$

and $$|\underline{N2}^{i} - C3^{i} - O3 = 88^{\circ}$$

and this is consistent with the geometry of the contact in the other five compounds.

The displacement of O3 from the ring plane is such as to increase the contact length. A study of the Davies and Blum data for parabanic acid reveals a similar displacement of O1 in this structure.

The contact data is reviewed in section 4.4.2.

4.2.3 The Relationship of the Physical Properties to the Crystal Structure

Those physical properties which were investigated as a prelude to the structure determination were

(i) melting and decomposition points (thermal properties),

(ii) cleavage planes (mechanical properties),

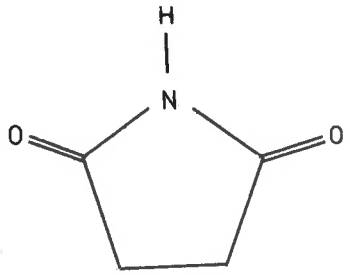
(iii) optical properties, and

(iv) density.

(i) The melting points of urea and parabanic acid are 133°C and 244°C respectively and the observed value for UPBA (183°C) is very close to the average. The relatively high melting points of all those organic solids which exhibit the contact may be due, in part, to the extra stability acquired by the structure through the contact. Melting points of other solids of interest are

Chloranil	290°C
Anhydrous barbituric acid	248°C
Alloxan	256°C
Succinimide	126°C

Succinimide,



is included here because it is one of a number of compounds which have insufficient protons for complete hydrogen bonding of all carbonyl groups and yet does not exhibit the contact (Mason (1956)). The low melting point of this compound correlates with the absence of contacts.

The decomposition point of a solid is a function of the molecular structure and bares little relation to the intermolecular binding.

(ii) The only mention in the literature of an attempt to find cleavage planes in the five compounds in question is in anhydrous barbituric acid (Bolton (1963)) where none were found. However, parabanic acid (Medlin (1955)) has an (oko) cleavage which requires no fracturing of hydrogen bonds, but rather severing of the O1...C2 contact. The UPBA cleavage information cannot be strongly weighted since no accurate determination of the planes was possible. Two hydrogen bonds must be cut to make the (211) cleavage

and four to make the $(\bar{1}01)$ cleavage. The poor definition of the latter is therefore explained.

(iii) Studies of optical anisotropy were inconclusive. The angle between the optic axes is near 90°.

(iv) The measured density is near the mean of urea (1·32 gm/cc) and parabanic acid (1·72 grm/cc). This is a predictable consequence of a hydrogen bonded complex.

This review has yielded one anomalous effect of the contact on the crystal structure, viz.

(a) structures are stabilized by the contacts more than by hydrogen bonds (M.P. data), but

(b) there is less energy in a contact than in a hydrogen bond (cleavage data).

The second inference may not be strictly correct. In the case of parabanic acid the only possible assertion is that it is simpler to cut one contact than two hydrogen bonds. Nevertheless, the cleavage in this case is very well defined and typical of cleavages which sever no hydrogen bonds.

4.3 The TUPBA Structure

4.3.1 The Molecular Structure

4.3.1.1 Planarity of the Complex

The least squares analysis of Schomaker (1959) was performed on four groups of atoms in order to find the best planes through these points. Hydrogen atoms were excluded from the analysis. The planes are

I Imidazole ring plane.

$-\cdot539x + 6\cdot290y + \cdot122z = \cdot986.$

II Parabanic acid plane.

$-\cdot015x + 6\cdot292y + \cdot252z = 1\cdot370.$

III Thiourea plane.

$\cdot721x + 6\cdot272y - \cdot535z = 1\cdot248.$

IV TUPBA plane.

$1\cdot626x + 5\cdot540y - \cdot294z = 1\cdot829.$

The origin to plane distance in Å is given by the R.H.S. of each equation. Table 4.2 contains the displacement data of the atoms from their planes; the standard deviations used in this instance were the σ values for the y coordinates since these are most relevant to displacements from the b-plane.

The oxygen atoms attached to the imidazole ring are are all significantly displaced from the ring plane. The

TABLE 4.2

Displacement of TUPBA Atoms from Planes

Atom	I		II		III		IV	
	d	δ	d	δ	d	δ	d	δ
O1	·242	12·7	·079	4·2			·182	9·6
O2	-·163	-7·8	-·028	-1·3			·556	26·5
O3	-·081	-4·5	·007	·4			·175	9·7
N1	-·023	-1·1	-·041	-2·0			·351	16·7
N2	·055	2·6	·002	·1			·081	3·9
C1	-·019	-·7	-·103	-3·7			·098	3·5
C2	·51	1·7	·113	3·9			·528	18·2
C3	-·064	-2·1	-·028	-·9			·186	6·2
S					·009	·9	-·368	-36·8
N3					·004	·1	-·676	-22·5
C4					-·046	-1·6	-·590	-21·1
N4					·033	1·3	-·525	-20·2

d in Å.

δ in number of standard deviations.

complex is non-planar at atomic dimensions and, in fact, the best fit plane passes between the two molecules.

4.3.1.2 Bond Lengths and Angles

A comparison of the bond lengths in TUPBA with those in parabanic acid and thiourea (Wyckoff (1966)) is drawn in the following table.

Bond	δ	Bond	δ
C1-O1	2·2	S-C4	-·9
C2-O2	-1·4	C4-N3	-·3
C3-O3	3·5	C4-N4	3·9
C1-N1	-2·5		
C2-N2	1·0		
N1-C2	·6		
N2-C3	-·4		
C2-C3	2·3		

The only two highly significant changes are in C3-O3 (an increase from 1·212Å to 1·250Å) and C4-N4 (an increase from 1·329 to 1·402Å).

The double bond character of the ring bonds is

C1-N1	33%
C1-N2	16%
C2-N1	25%
C3-N2	25%

and if we assume a pure single bond for C2-C3 the implied double bond character of the carbonyl groups is

	x	length
C1-O1	50%	1·26Å
C2-O2	75%	1·23Å
C3-O3	75%	1·23Å

The differences (δ) between these implied lengths and the observed lengths are 1·4, 2·0 and 2·5 respectively. The last two may be significant in light of the observed S...C2 and S...C3 contacts discussed in section 4.3.2.2.

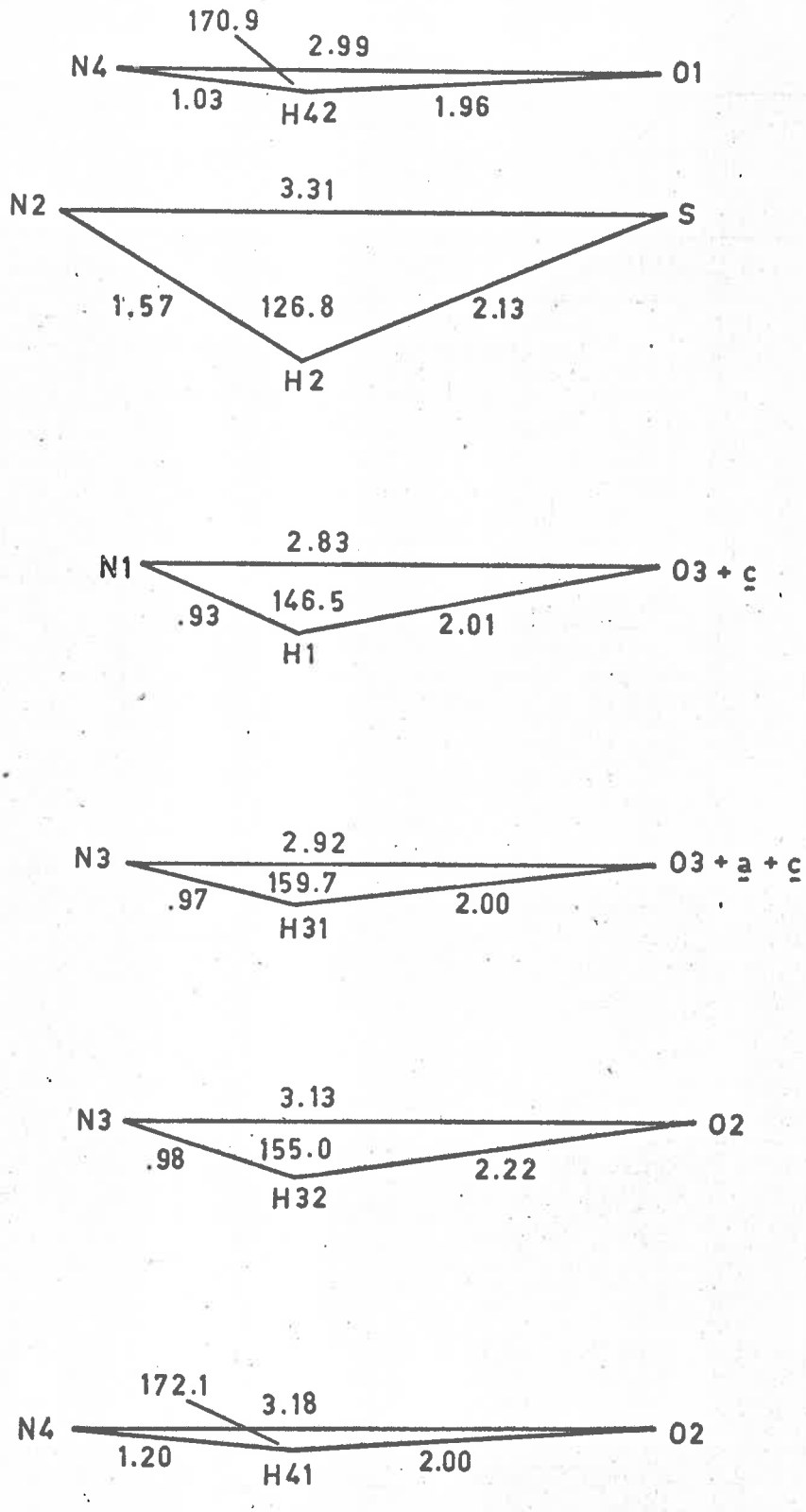
The relevance of the low estimation of the C4-S bond length (1·67Å by Pauling's equation) to the contacts is also discussed in section 4.3.2.2.

4.3.2 The Crystal Structure

4.3.2.1 Hydrogen Bonds

The complex unit is stabilised by a system of hydrogen bonds into sheets in the (020) plane. These hydrogen bonds are shown in figure 4.2. The relevant Van der Waal's contact radii for this data are

N...S	3·35Å
H...S	3·05Å
N...O	2·90Å
H...O	2·60Å (Hamilton (1968)).



Hydrogen bonding of TUPBA.

Fig. 4.2

The six protons are all involved in hydrogen bonds, two with each of O2 and O3 and one with each of O1 and S.

The oscillation of the z coordinates of H32 and H41 in the least squares analysis has been mentioned in section 2.7.7, and it is interesting to note that both of these atoms are weakly bonded to O2. The phenomenon of ferroelectricity (Megaw (1957)) has been associated with the tunnelling of protons across the hydrogen bond potential barrier. (The qualitative nature of this potential function is given by Hamilton (1968)). The effect of this tunnelling is to produce the transition

$$\begin{array}{cccc} \delta- & \delta+ & & \delta+ \quad \delta- \\ A - H \ldots B & \rightarrow & A \ldots H & - B \end{array}$$

and, in fact, the application of an electric field to a ferroelectric crystal will reverse the direction of the natural polarisation of the crystal, without any breakdown of the crystal structure. The possibility of transitions

$$N4\text{-}H41 \ldots O2\text{-}H32 \ldots N3 \rightarrow N4 \ldots H41\text{-}O2 \ldots H32\text{-}N3$$

was considered. However, the magnitude and direction of the least squares oscillations of the coordinates of H32 and H41 were such that further evidence was needed before

the effect could be considered real. The final difference map shows two peaks (height $\cdot 6e/A^3$) $1\cdot5\text{Å}$ and $1\cdot7\text{Å}$ from O2. These peaks were displaced from the lines H32-O2 and H41-O2 by up to 1Å and therefore they did not accurately represent the effect under consideration.

The hydrogen bonds on O3 are stronger than those on O2 and the N1-O3 hydrogen bond length lies within the range of data reviewed by Fuller (see section 4.2.2.1). The hydrogen bond on O2 is similar in length to those found in urea.

The use of sulphur in a hydrogen bond N-H...S has been reviewed by Wallmark (1962). Eighteen examples of N-H...S contacts which could be the result of hydrogen bonds were found. The lengths of these contacts (N...S) varies from $3\cdot23\text{Å}$ to 3.51Å, and the observed N...S distance in TUPBA ($3\cdot312\text{Å}$) is within this range. The angle of the hydrogen bond in the present case is 127° and this departure from collinearity of N,H and S atoms is considered serious. Hamilton (1968) has reviewed all A-H...B angles in hydrogen bonded systems studied by neutron diffraction and angles as low as 110° are reported. No H...B lengths are given.

From the growing list of compounds which exhibit significant overlap of H and S atoms, we can infer the

importance of these hydrogen bonds in biological systems. In the absence of more suitable acceptor atoms (e.g. oxygen) the sulphur atom may influence the crystal structure through this mechanism. However, since sulphur must compete with stronger acceptors, the H...S bond, in most cases, will be of only secondary importance.

4.3.2.2 Contacts Involving Carbon Atoms

The separation of screw related planes in the TUPBA unit cell is 3·15Å and the possibility of any O...C contact in this structure is therefore eliminated. However, the sulphur atom is involved in contacts which are shorter than the predicted S-O (3·25Å) and S-C (3·55Å) Van der Waals approaches.

The observed S-O distance (in the (020) plane) is 3·15Å and this represents an overlap of 1·4σ. Besides this weak contact, there is very significant overlap of S with C2 and C3 on screw related layers such that

$$S...C2^{a} = 3{\cdot}23\text{Å}$$

and $$S...C3^{a} = 3{\cdot}31\text{Å}\ .$$

Although the difference in these S--C lengths is only 2σ, the difference in length of C2-O2 and C3-O3 implies some genuine asymmetry in the contacts. The large

standard deviations of the contact lengths (~ ·03Å) is determined by the large standard deviation of all y coordinates in the structure. These errors are enhanced when bond lengths in the direction of the unique axis are considered.

The geometry of the contacts can be inferred from figure 2.8, in which the sulphur atom is seen to be almost directly above the centre of the C2-C3 bond. This may explain the observed slight elongation of this bond (1·58Å compared with 1·54Å for C-C single bonds). The contact angles are

$$C4\text{-}S\text{-}C2^{s} = 90{\cdot}2^{\circ}$$

and $$C4\text{-}S\text{-}C3^{s} = 85{\cdot}1^{\circ}$$

and the implication is that the p orbitals of sulphur may be involved in the contact with parabanic acid molecules above and below the thiourea plane.

If the p_z orbital of sulphur is to act as a bonding orbital, the S-C4 double bond would be weaker than expected since one of the two $3p_z$ electrons must vacate its orbital for $3p_x$ or $3p_y$. Such a transfer leaves a lone electron in $3p_z$ and facility for only a single bond between S and C4. The contribution from this resonance

state to the structure need only be slight since the S...C interaction is very weak, and in fact slight lengthening of S = C4 has been observed (section 4.3.1.2).

An alternative mechanism concerns the possible valence shell expansion of sulphur (Salmond (1968)). Sulphur is a second row element ($1s^2 2s^2 2p^6 3s^2 3p^4$) and therefore its valence shell has d atomic orbitals. Electrons in the valence shell are readily excited into the $3s^1 3p^3 3d^2$ state and hybridisation of these six atomic orbitals into equivalent orbitals gives an octohedral arrangement (i.e. six orbitals directed from the centre to the face-centres of a cube). It is unlikely that six equivalent orbitals are generated in this case although the geometry of the octohedral orbitals is consistent with the geometry of the contact and the covalent bond at S. Two of the four orbitals in the x-y plane may be used in S = C4 and the two orbitals in the ± z directions may be active in the contact.

The fundamental difference between ionic and covalent bonds is well known and recently Bader (1967) has shown experimentally that the former are secured by a bonding density at the atomic centres and the latter by a bonding density between the atomic centres. The density referred

to here is a difference density which determines the way in which the electrons of the bound atoms are redistributed when the bond forms. It may be recalled that the final difference electron density map for TUPBA shows a significant density along the line joining S and C2^{a}. These peaks are over 2$\mathring{A}$ from the sulphur atom and therefore are not likely to be the result of thermal motion of this atom. From the geometry of these peaks in the map (one above and below the plane of C2) it can be asserted that they represent a real bonding density.

It is not valid to argue the influence of the crystal field forces in explaining these contacts. There are configurations of the complex relative to the screw axis which require no overlap of Van der Waals' radii, and therefore a genuine minimum must exist in the interaction potential function for S and C2 in this structure.

4.3.3 Physical Properties and the Crystal Structure

The melting point of TUPBA (213°C) is near the average of the melting points of thiourea and parabanic acid and it is also compatible with the high melting points of other solids which are bound by intermolecular forces other than hydrogen bonds (see section 4.2.3).

The well pronounced (0k0) cleavage cuts through no hydrogen bonds but the S...S contact is severed. This is comparable with the cleavage plane in parabanic acid (see section 4.2.3). The two other 'cleavages' are less well defined and in fact the ($\bar{1}01$) cleavage breaks four hydrogen bonds whilst the (601) cleavage bears no apparent relation to the crystal structure.

4.4 Intermolecular Forces

4.4.1 Theoretical Introduction

The crystal structure of organic solids is determined by two factors:

(i) the size and shape of the molecular units, and

(ii) the capacity that these units offer for intermolecular bonding.

The relationship of the latter to certain physical properties of the two structures has already been discussed. Significant differences in the dimensions imply an interaction between crystal and molecular structure. Whether it is the perturbation in one that affects the other, or vice versa, is not important. The only significance in this interaction is that a certain mutual configuration is more stable than any other.

A rigorous treatment of intermolecular forces is beyond the scope of this work. Hirschfelder (1967) has discussed the increasing complexity of determining the intermolecular potential energy function with increasing complexity of the interacting molecules.

There is, however, one simple concept which is useful in this regard and that is the Van der Waals' radius of an atom. The Van der Waals' equation of state contains terms describing both attractive and repulsive forces. The attraction operates at large distances and arises through the interaction of permanent or induced dipoles on the molecules. The repulsion, active at distances of the order of the molecular dimensions, may be explained in terms of the Pauli exclusion principle, whereby no two electrons may occupy the same quantum state. The Van der Waals' radius of an atom may be defined as the equilibrium distance for these two opposing forces (Slater (1951)).

Covalent bonding arises from the overlap of atomic orbitals and if the electrons in these orbitals are defined by wave functions ψ_1 and ψ_2, then we can define a quantity called the Overlap Integral, S, where

$$S = \int_{\tau} \psi_1 \psi_2^* d\tau \ .$$

The numerical value of S is between zero (no overlap) and one (complete overlap of normalised wave functions). Since S is a useful parameter in determining the strength of covalent interactions, it would be interesting to know its value for two atoms separated by the sum of their Van der Waals' radii. However, Hartree's atomic charge density has fallen an order of magnitude from the r = 0 value at the Van der Waals' radius and the uncertainty of $|\psi|^2$ in this region prevents an accurate determination of S (Bondi (1964)).

It has been shown (Bondi (1964)) that a relationship exists between the Van der Waals' radius of an atom and the de Broglie wavelength of its outermost valence electron. This relationship has the form

$$r_v = k\lambda_B$$

where

$k = \cdot 61$ (rare gas elements)

$k = \cdot 53$ (halogen atoms)

$k = \cdot 48$ (other non-metallic atoms).

The expression for the de Broglie wavelength is

$$\lambda_B = \frac{h}{(2mI_e)^{\frac{1}{2}}}$$

where I_o is the first ionisation potential. A change in the energy structure of the atom can only decrease I_o, and r_v for an atom in an excited state is therefore greater.

The concept of hybridisation has been introduced in section 4.3.2.2 in discussing the sulphur contacts in TUPBA. A more formal discussion of this phenomenon now follows to provide a basis for some of the ideas expressed in section 4.4.3.2.

The valence shell structure of the carbon atom ($2s^2 2p^2$) implies a valency of two in which the bonding orbitals are at right angles to each other. The observed quadrivalence of carbon is consistent with the valence state $2s^1 2p^3$ but the geometry of the orbitals (tetrahedral) requires mixing of the s and p wave functions to give four equivalent sp^3 hybrid orbitals. Analytically, these new wave functions are generated as linear combinations of the existing s and p wave functions, and in particular they can be shown to satisfy the least energy criterion (Coulson (1956)). The strength and directional properties of these hybrids is such that S is maximised and the molecule stabilised.

The atomic orbitals of carbon are also found in sp^2

and sp hybrid states, according as to the environment of the atom in a particular molecule. The following table gives the relative strength and geometry of various s and p hybrid states (Schutte (1968), Coulson (1956))

No. of bonds	Hybrid	Strength	Geometry
1	s	1·000	omnidirectional
2	sp	1·932	linear
2	p^2	1·732	angular (90^0)
3	sp^2	1·991	trigonal plane
3	p^3	1·732	trigonal pyramid
4	sp^3	2·000	tetrahedral

When discussing bond energies and lengths, the overlap integral S is a more useful parameter than the strength of the orbital since the latter refers only to the maximum value of the probability density. For C-C bonds the overlap integral relationship (Maccoll (1950)) is

$$S(sp\text{-}sp) > S(sp^2\text{-}sp^2) > S(sp^3\text{-}sp^3) > S(s\text{-}s) \text{ or } S(p\text{-}p).$$

The hybrids listed above are not the only possible combinations available to the atom. They are the only ones which give a set of equivalent orbitals in each case.

but in general an arbitrary mixing of s and p wave functions may be expressed by

$$s + \lambda p_{x_i}$$

where λ is the mixing coefficient (Coulson (1956)) which may assume values from 0 (pure s) to ∞ (pure p).

The constant λ may be related to certain properties of the orbital. For example, the atomic dipole moment (Coulson (1956)) is largest when $\lambda = 1$ (sp hybridisation). The electronegativity of an atomic valency is also dependent on the hybridisation of that valency (Bent (1961)), increasing as the s character of the valency increases. It follows from this result that atomic s character concentrates in orbitals directed towards electropositive substituents and atomic p character concentrates in orbitals directed towards electronegative substituents. Bent has also shown that the stretching force constant of a bond increases with increasing s character.

The inclusion of s character into an otherwise pure p wave function will concentrate the probability density for this orbital nearer the nucleus. Such a reduction in the atomic radius will allow other atoms to approach closer than usual before the repulsive and attractive forces balance. If the orbital in question were a lone

pair orbital, such an increase in s character would reduce the contact radius of the atom in this particular direction.

It is apparent that perturbations in the lengths of covalent bonds and contact radii may be described in terms of hybridisation of atomic orbitals.

4.4.2 Review of Contact Data

Six examples of carbonyl oxygen-carbon (C = O...C') close approaches have now been observed. The contact data is as follows:-

Compound	Contact length (Å)	Contact angle θ (degrees)	cosθ	Number of H-bonds
Parabanic acid	2·77	157·4	·92	2
Chloranil	2·85	161·0	·95	-
Barbituric acid	2·90	162·5	·95	2
Alloxan	2·79	154·7	·90	-
Triketoindane	2·83	150·7	·87	-
UPBA	2·84	131·6	·66	6

Another feature of the data is the approximate collinearity of the contact with the direction of the C' p_z orbital in every case. Bolton (1964(b)) has previously claimed the significance of C = O being collinear with this orbital,

but the UPBA data establishes the contact direction as more consistent relative to the orbitals of C'.

The interaction between crystal and molecular structures in a compound has been discussed in the previous section. A careful comparison of bond lengths in the structures in question seemed justified since there was evidence that the lengths of some of the carbonyl groups were related to the contact formation. In the following table the nomenclature of the original publications is used.

Compound	C = O	ℓ(Å)	C' = O'	ℓ(Å)	Length of other C=O groups
Parabanic acid	C1 = O1	1·212	C2 = O2	1·212	1·212
Chloranil	C_{III} = O	1·195	C'_{III} = O'	1·195	-
Barbituric Acid	C6 = O6	1·189	C6' = O6'	1·189	1·202, 1·229
Alloxan	C6 = O6	1·213	C5 = O5	1·186	-
Triketoindane	C2 = O2	1·227	C1 = O1	1·189	-
UPBA	C3 = O3	1·214	C3' = O3'	1·214	1·233, 1·240

In each case C' = O' is either the shortest carbonyl group or, when C = O and C' = O' are equivalent, as short as the shortest carbonyl group.

Earlier discussion (section 4.2.2.1) on the preference for O1 and O2 to act as hydrogen bond acceptors in UPBA implied that shortness of the carbonyl group is critical in determining that no hydrogen bonds on O3. Whilst hydrogen bonds never form on the contact oxygen atom, C = O is not always the shortest carbonyl group. However, when carbonyl groups shorter than C = O occur (i.e. in alloxan and triketoindane) no hydrogen bonds form at all, despite the presence of two N-H groups in alloxan. Carbonyl shortening may be empirically related to two phenomena:-

(i) absence of hydrogen bonds on O, and

(ii) a carbon-oxygen contact involving C.

The data only weakly relates this shortening to oxygen activity in the contact.

The length of certain carbonyl groups in all structures except parabanic acid and UPBA is less than the normal double bond separation of carbon and oxygen atoms (1.21Å , Pauling (1960)). The application of Pauling's equation to a C' = O' length of 1·19Å indicates an electronegativity difference for these atoms of 1·25 (an increase of 0·25), and an increase in the ionic character

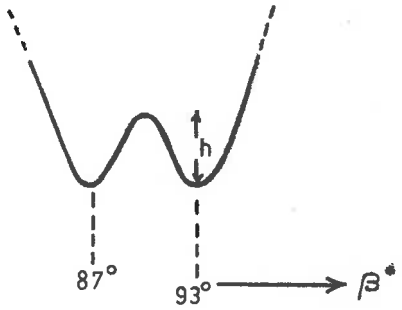
of the bond from 44° to 55° is therefore implied. This is consistent with Bolton's electrostatic interpretation of the contact (section 4.4.3.1), although similar decreases in the length of C = O are only observed when C = O and C′ = O′ are equivalent (by symmetry).

Of the six examples of the contact, parabanic acid alone has all its carbonyl groups equal in length. The symmetry of the molecule (mm2) implies that an orthorhombic unit cell would be more likely to satisfy the least energy condition (Medlin (1955)). The only asymmetry in the structure is in the hydrogen bond lengths and the apparent uniqueness of O1 and C2 (the contact atoms). The least squares solutions for the carbonyl groups were

C1 = O1	1·212Å	(·004)
C2 = O2	1·216Å	(·003)
C3 = O3	1·208Å	(·003)

and although these differences are not statistically significant, the fact that O3 is involved in a longer hydrogen bond than O2 supports the hypothesis in section 4.2.2.1. On the other hand, the physical significance of C2 = O2 being longer than the other groups is contrary to the usual shortness of C′ = O′.

Medlin (1955) has observed a strange property of parabanic acid which may be related to the contact formation. When thin sections of the crystal are cut (perpendicular to b) and left to stand on a glass slide, they will, on occasions, change their morphology from a form in which β is obtuse to one in which β is acute. This was observed in small sections under the polarising microscope. The angle involved in this change is 6° and the evidence favours an energy function as follows:-



The height of the barrier (h) is apparently greater than kT at room temperature since this morphological change occurs only once after cleavage. Evidently cleaving has generated a metastable energystate and the phonon energy in the lattice is released by the transition described.

Such a transition will interchange the environments of all atoms related by the mirror plane; in particular the lengths of the hydrogen bonds are reversed and the contact atom C' is now C3 and not C2. The preference for a monoclinic cell is therefore a direct result of

the extra stability acquired by the structure when the contact forms.

An observation unique to UPBA and barbituric acid is the lengthening of C-N adjacent to C = O (and C' = O'), and a mechanism for this lengthening is given in section 4.4.3.2. Molecular symmetry in the other examples prevents a comparison. In fact, in barbituric acid and UPBA the equivalence of C = O and C' = O' may be related to the asymmetrical environments of the carbonyl groups.

The striking anomaly in the data is the contact angle in UPBA whilst three general trends are indicated;

(i) C' = O' is always short,

(ii) there are never hydrogen bonds on O, and

(iii) the contact is always collinear with the C' p_z orbital.

4.4.3 Mechanisms for the Contact

4.4.3.1 Previous Conceptions

Bolton (1964(b)) has suggested two possible mechanisms for the contact,

(1) electrostatic attraction between C = O dipoles and C' positive charge centres, and

(2) involvement of the sp^2 hybrid orbitals of oxygen.

These will be considered in turn.

(1) The postulate that there are centres of positive residual charge on C' is well founded in each case. The force of attraction or repulsion between this charge and a dipole is a function of cosθ, where θ is the angle between the dipole axis and the line joining the charge to the centre of this axis. The greater the overlap of Van der Waals' radii the stronger is the intermolecular binding force and therefore it should be possible to correlate contact lengths and angles, the shorter contacts being the more linear. The table on page 137 illustrates that the data has an incorrect qualitative content. The longest contact (anhydrous barbituric acid) is in fact the most linear.

Hamilton (1968) has pointed out that it is not clear that the energetically most favored configuration for the hydrogen bond is the linear one. It is likely that the proton should be directed towards the centre of density of the lone pair orbital of the acceptor atom rather than towards the nucleus of this atom. In this respect, non-linearity of C = O...C' atoms may be the result either of

displacement of the dipole axis of C = O or of a weakening of the dipole field through some other effect (see section 4.4.3.2). It is important to realise here that the C = O group has little freedom to direct itself towards the charge centre at C', since its orientation is primarily determined by the orientation of the molecule.

It is customary to assert the influence of crystal field forces when the crystal data is in slight conflict with the predicted geometry of the system. Although the influence of the crystal field is not readily estimated, the number and direction of other intermolecular bonds in the six compounds does correlate to some degree with the contact angles. Parabanic acid has no other intermolecular bonds in the b-direction and, in fact, it appears that packing of the molecules in the cell could be arranged with no overlap of Van der Waals radii between screw related sheets. On the other hand, one of the hydrogen bonds in barbituric acid is between centre related molecules and the contact (between glide related molecules) is therefore affected. Of the six hydrogen bonds in UPBA, four will affect the geometry of the contact and this may explain the anomalous angle in this case. Nevertheless, if the dipole-charge attraction in UPBA is weakened by the crystal field in this way, a significantly longer

contact should be observed.

(2) The involvement of sp^2 orbitals of oxygen is said to give marginally worse agreement with the data than the electrostatic interaction. Angles of 120° are predicted by Bolton with this mechanism but it is the author's opinion that the angle should still be 180° since two of the three sp^2 orbitals are involved in the double bond.

4.4.3.2 A Modified Mechanism

The observed shortening of C' = O' (and in some cases of C = O) has been related to an increase in ionic character of the bond, and this in turn may be related to an increase in electronegativity difference between the carbon and oxygen atoms. The review of Bent (1961) indicates that an increase in the electronegativity of oxygen may be effected by increasing the s character of the bonding orbitals, and similarly a decrease in electronegativity of carbon will result from an increase in p character of the orbitals which bind it to the oxygen atom. This rehybridisation will shorten the carbonyl bond.

In the ground state the parabanic acid ring bonds are pure single bonds. There is no delocalisation of π

electrons as is found in benzene and other aromatic compounds. The four π electrons in the parabanic acid ring system are the two unshared pairs contributed by the hetero-atoms in the ring. The geometry of the bonds at the carbon atoms is consistent with an sp^3 hybridisation state, for these atoms (Pauling 1960) and the bonding orbitals for the carbonyl oxygen atoms are $2p_x$ and $2p_y$. The carbonyl bond is secured by two bent sp^3-p bonding orbitals and these orbitals are in a plane containing the double bond and perpendicular to the parabanic acid molecule.

Carbonyl shortening may therefore be explained by a change in $2p_x$ and $2p_y$ (of oxygen) towards sp^3 hybrids and a change in the sp^3 orbitals (of carbon) towards pure p orbitals. The effect of these changes on the other atomic orbitals of carbon and oxygen may be inferred from the conservation of angular momentum about these atoms. An increase in p character of the 2s lone pair of oxygen must occur although no change in the $2p_z$ lone pair is required. An increase in s character of the two remaining sp^3 carbon orbitals will increase the electronegativity of this atom relative to the two other atoms to which it is bonded. In anhydrous barbituric acid and UPBA this will decrease the electronegativity difference between C and N

and corresponding lengthening of C-N has been observed in both cases. The fact that C-C undergoes no shortening indicates that most of the increase in s character has gone into C-N.

When discussing intermolecular contacts involving oxygen it is necessary to examine the state of the valence shell lone pair orbitals of the atom. There is experimental evidence to support the following changes in the oxygen valence shell:-

$$2s \rightarrow s + \lambda_1 p,$$

$$2p_x \rightarrow s + \lambda_2 p,$$

and $$2p_y \rightarrow s + \lambda_2 p.$$

Consider the effect of

$$2p_z \rightarrow s + \lambda_3 p,$$

i.e. an increase in s character of the lone pair electrons. When the mixing constants (λ_i) are equal, the atom is tetrahedrally hybridised with two of the orbitals containing lone pairs (formerly 2s and $2p_z$). The bonding orbitals (derived from $2p_x$ and $2p_y$) are bent to secure the carbonyl bond and this forces the lone pair orbitals into the plane of the ring in such a way that each makes an angle of $125^{\circ}16'$ with the direction of the double bond. Electro-

static attraction between the positive charge centre at C' and the centre of density of one of the lone pair orbitals of O will account for contact angles between $125^{o}16'$ and 180^{o}, the exact value of the angle depending on the hybridisation state of O.

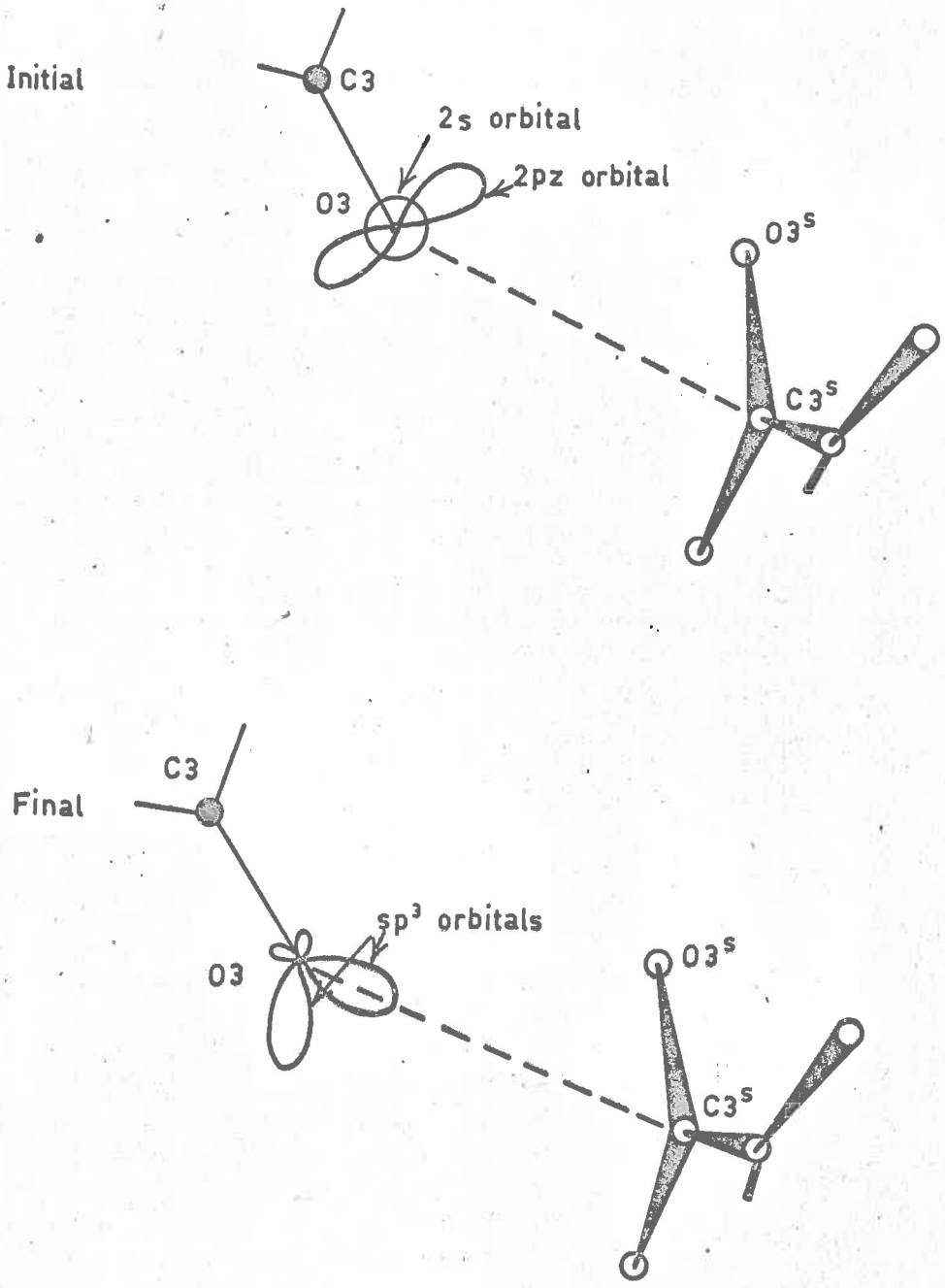
The condition of coplanarity of the lone pair orbitals with the parabanic acid molecule is only enforced when sp^3 hybridisation of O has occurred, and it is interesting to note that the displacement of C' from the parabanic acid plane of O is $\cdot 54\mathring{A}$ in UPBA (where sp^3 hybridisation has apparently occurred) and $\approx 1\mathring{A}$ in parabanic acid (where the contact angle is $157\cdot 4^{o}$). When no mixing of s and p wave functions has occurred the lone pair orbitals 2s and $2p_z$ are respectively spherically symmetrical about the oxygen nucleus and dumb-bell shaped in the parabanic acid plane (perpendicular to C = O). The probability densities in each lobe of the $2p_z$ orbital are equal and less than that in the main lobe of an sp^3 lone pair orbital. When no change has occurred in the lone pair orbitals of oxygen, C' is attracted to the time averaged centre of density of the 2s and $2p_z$ orbitals.

The UPBA data therefore is best explained by a simple charge-charge (rather than a dipole-charge) mechanism, and

under these conditions an account must be given for the apparent weakening of the field of the carbonyl dipole.

Bolton (1964(b)) has observed that in all examples of the contact C' is in a stable position relative to the C = O dipole, but he has not remarked upon the instability of O relative to the C' = O' dipole. (Angle O' = C' ...O is always near 90°). Apparently the C' = O' dipole field has been weakened and, when O and O' are equivalent, this may be a result of hybridisation of O. In particular the asymmetry of the 2s lone pair in its new hybrid state could account for this. The field of the point change at C' dominates over the weakened dipole field and interacts with the field of one of the lone pair orbitals.

The three dimensional geometry of the contact and, in particular, the near coplanarity of the contact with the parabanic acid plane in UPBA is shown in figure 3.8. The asserted redistribution of atomic s and p character is shown in figure 4.3, this being part of figure 3.7. The apparent error in the angle between the sp^3 lone pair orbitals (theoretically 109°28') arises from the small angle each makes to the plane of the figure.



Hybridisation of oxygen atom in contact.

Fig. 4.3

4.4.3.3 Further Discussion of Bonding Mechanisms

The possible interpretation of the TUPBA contact as a weak covalent bond has been discussed in section 4.3.2.2. However, the final difference map for UPBA shows no significant density along the line O3...C3^{8}. Itis worth noting here that the bond order for typical contact lengths is only ·01 and this is negligibly small (Pauling, in a private communication to Bolton (1964(b))). Difference peak heights at C3 and O3 are positive and negative respectively and these are contrary to the predicted values for a $C^{\delta+} - O^{\delta-}$ dipole.

The interpretation of difference maps for small redistributions of bonding electrons is only possible when very accurate diffraction data has been collected and, in fact, the separation of thermal smearing of the electronic wave function from redistribution of the probability density due to bonding is best achieved by the compilation of both X-ray and neutron data. Neutron data would yield the thermal motion of the nuclei, and when this is subtracted from the electron density distribution, the bonding density information remains.

Whilst these remarks may seem contrary to the conclusions drawn in section 4.3.2.2, the difference density

in that case was significant in two respects. The peaks were well above the background level for sections of the cell between molecular layers, and the geometry of the peaks was consistent with the density being a real bonding density. In UPBA the peaks in question are only of the level of other spurious peaks in the cell and are therefore of doubtful significance.

The value of the Van der Waals' radius of carbon used throughout this work is 1·7Å. This value derives from the half-thickness of an aromatic molecule (benzene) and, as such, is relevent to carbon in the sp^2 state. The dependence of atomic radius on hybridisation has been discussed by Coulson (1956). From packing considerations alone, the contact radius of carbon (when approached from above the plane of the molecule) is less when the atom is tetrahedrally hybridised than when it is in the trigonal state. In the latter case, the π electron orbital will restrict this particular approach.

Bolton (1964(b)) has considered the problem of reduction of the Van der Waals' radius and concluded that it is not likely to occur. This result is based upon X-ray data from nonaromatic compounds in which there are non-hydrogen bonded carbonyl groups yet no contacts

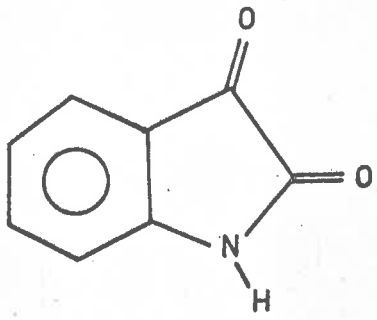
(e.g. succinimide). Theoretical predictions and bond length data are in conflict over this issue.

4.4.3.4 The Fundamental Criterion for the Contact

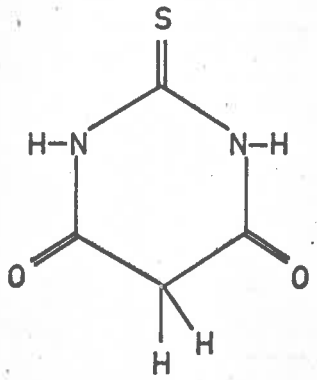
In all substances which exhibit the contact there is a preponderance of carbonyl groups associated with a ring molecule and in all but two cases there are at least two carbonyl groups on adjacent ring atoms. (In chloranil and barbituric acid the carbonyl groups are separated by ring carbon atoms). The inductive effects of the carbonyl groups (Bolton (1964(b))) will be strongest when the groups are adjacent to each other and under these conditions the residual positive charge on C' will be greatest. The absence of contacts in succinimide is explained by this reasoning.

Other compounds which might be expected to exhibit the contact are isatin, thiobarbituric acid, croconic acid and cholestrophane (see fig. 4.4). The melting points of these compounds are 204°C, 235°C, 100°C (sublimation) and 155°C, and this data supports the existence of contacts in both isatin and thiobarbituric acid.

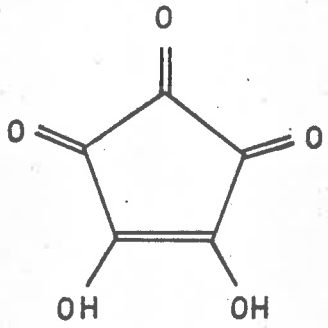
No contacts are found in the isatin structure (Goldschmidt and Llewellyn (1950)) which is planar in



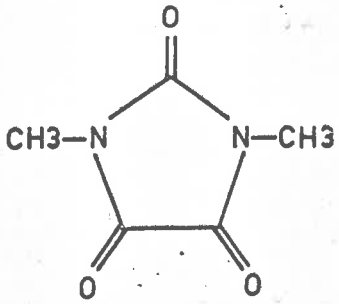
Isatin (2,3 Indolinedione)



thiobarbituric acid



croconic acid



cholestrophane
(dimethyl parabanic acid)

Fig. 4.4 Prediction Compounds.

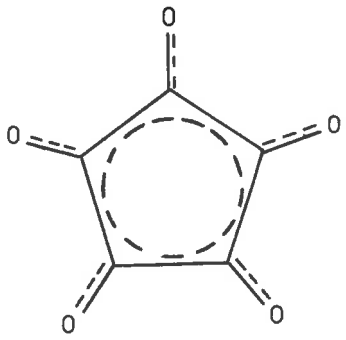
the $P2_1/c$ unit cell with

$$a = 6{\cdot}19\text{Å}$$
$$b = 14{\cdot}46\text{Å}$$
$$c = 7{\cdot}17\text{Å}$$
$$\text{and} \quad \beta = 94^{\circ}49' .$$

The spacing between the molecular planes, $(10\bar{2})$, is 3·12Å, and therefore no carbon-oxygen approaches less than 3·1Å are allowed.

A preliminary report on the unit cell data of thiobarbituric acid has been given by Parry and Strachan (1958), but apparently the structure has not yet been determined.

Croconic acid is not as stable as the known contact compounds and the presence of the ring double bond in the valence structure is also unusual if contacts are to occur. The structure of this compound has already created some interest, but not for the reason in question. Yamada et al. (1958) have shown that the structure is principally the one given in fig. 4.4, i.e. the hydroxyl groups are bound to adjacent ring atoms. However, the croconate ion is symmetrical



and the structures of two ammonium salts of croconic acid have been determined (Baenziger, Hegenbarth and Williams (1963) and Baenziger and Williams (1966)). The ion was found to be planar and pentagonal to the accuracy of the data, but no contacts were found.

The structure of cholestrophane is apparently stabilised by some intermolecular forces (M.P. = 155°C) and it is unlikely that these forces are hydrogen bonds since the methyl group is a very weak hydrogen bond donor. The possibility exists that the stabilising mechanism is the carbon-oxygen contact, especially in light of the contacts in parabanic acid and UPBA.

Owing to the variety of scientific journals in which reports of crystal structure analyses may be published, it is possible to overlook a recently determined structure. However, to the best of the author's knowledge the structures of thiobarbituric acid, croconic acid and cholestrophane have not been studied by diffraction methods.

4.4.4 Conclusions

When attempting to explain a phenomenon such as the contacts described in this thesis, it is necessary to find an underlying consistency throughout both the data itself and the environment in which the phenomenon may occur.

Of the two criteria suggested by Bolton for the formation of the contact, the second is apparently redundant. The UPBA data illustrates that contacts will occur in an environment of excess protons. It is apparently the absence of suitable hydrogen bond acceptors which influences the contact formation. The existence of several carbonyl groups in a ring molecule remain important. The inductive effects of such groups on the ring atoms are vital to an electrostatic interpretation of the contact.

The two most consistent items of data are the shortness of C' = O' and the absence of hydrogen bonds on O. (In fact in only one case does O' participate in a hydrogen bond and that is in parabanic acid). Analysis of the data has shown that hybridisation of the oxygen atom in the contact will account for contact angles between $125^{\circ}16'$ and 180°. This assumes that the dipole fields

of the carbonyl groups are weakened and that the interaction is essentially between oppositely charged centres in the structure.

The observed contact in TUPBA can also be explained by this mechanism. In the contact C = S...C′ = O′, C′ = O′ is again the shortest carbonyl group in the structure. The electrostatic attraction of the residual positive charge on C′ for the lone pair orbital of S is consistent with the contact angle in this case. However, the significant difference density peaks in this structure suggest a real bonding density between S and C′ atoms. Similar peaks are not found in UPBA.

APPENDIX A

A MODIFIED DOUBLE SLIT WEISSENBERG TECHNIQUE

The following is the text of a note (by the author) in the press of the Journal of Scientific Instruments.

Stadler (1950) has reported a method for simultaneously recording more than one reciprocal lattice layer about a given axis. This is made possible by inserting a ring of width $2r\tan\mu - s$ between the conventional layer line screens. In order to overcome the necessity of making a different ring for every pair of layers to be recorded, three screens have been constructed for use with the Unicam 335 X-ray goniometer. S_1 and S_2 are cut away cylinders and S_3 a cylinder which slides over S_2. S_2 has the same diameter as S_4 (a conventional screen) whilst S_1 fits snugly over S_4.

Referring to plates A1 and A2 and figure A1, the zero layer, defined by S_2 and S_4 and the nth layer, by S_1 and S_3, are recorded on the lower and upper halves of the film respectively. Corrections for contraction and elongation of reflections can be made by rotating the screens through 180°. Such a photograph is shown in plate A3.

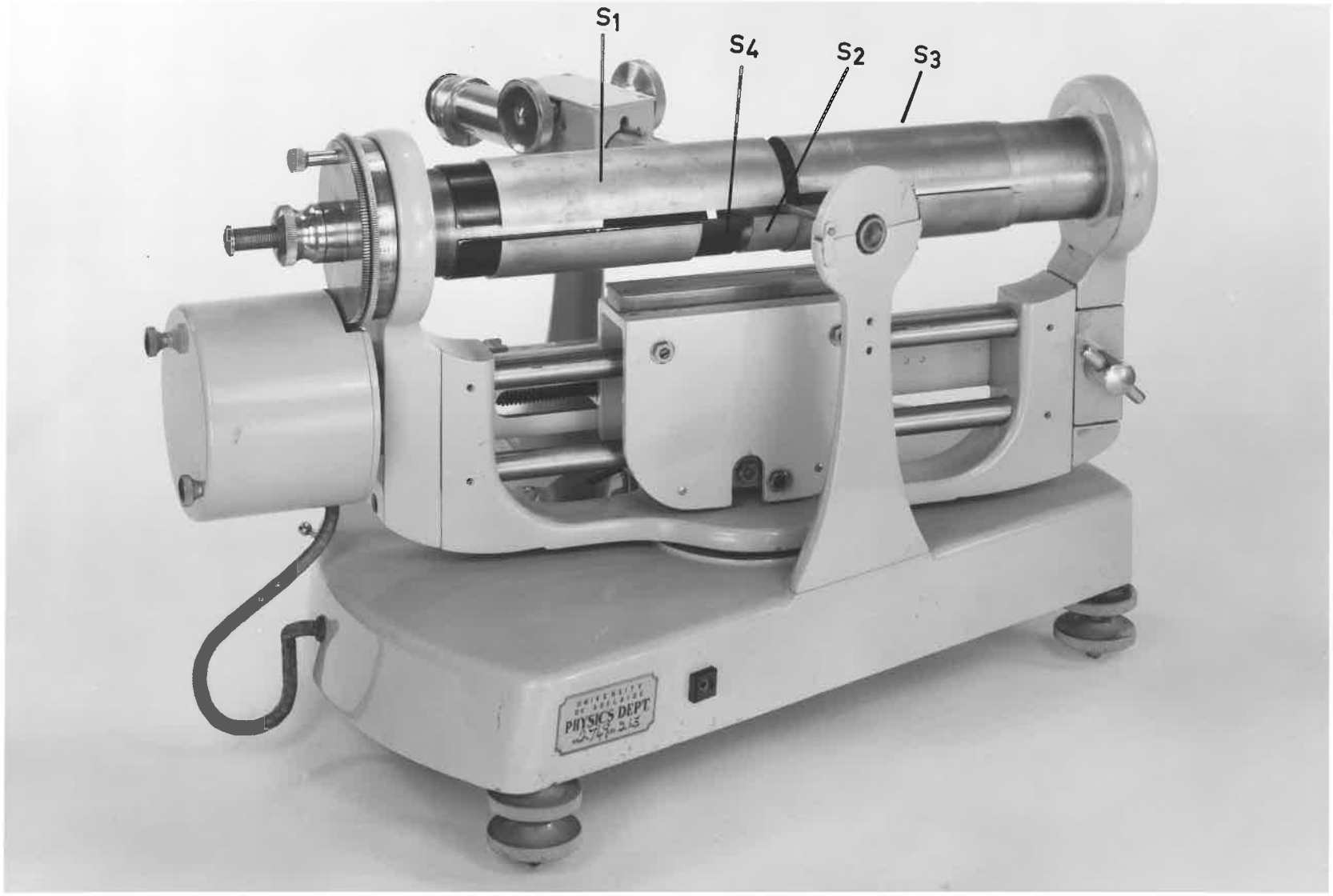


Plate A1 The arrangement of the screens on the goniometer.

Plate A2 The arrangement of the screens on the goniometer.

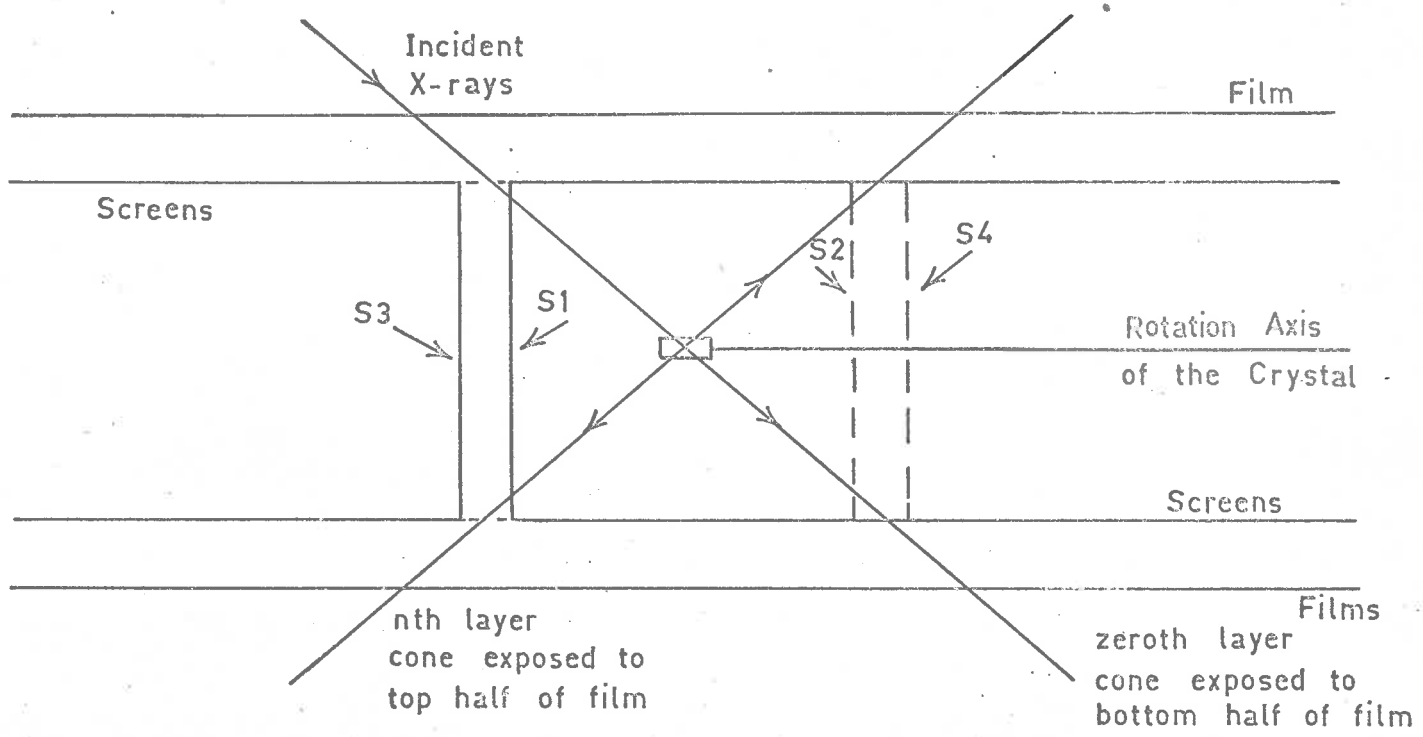


Fig. A1 The modified double slits and their relation to the zeroth and nth reciprocal lattice layers as seen from above the goniometer.

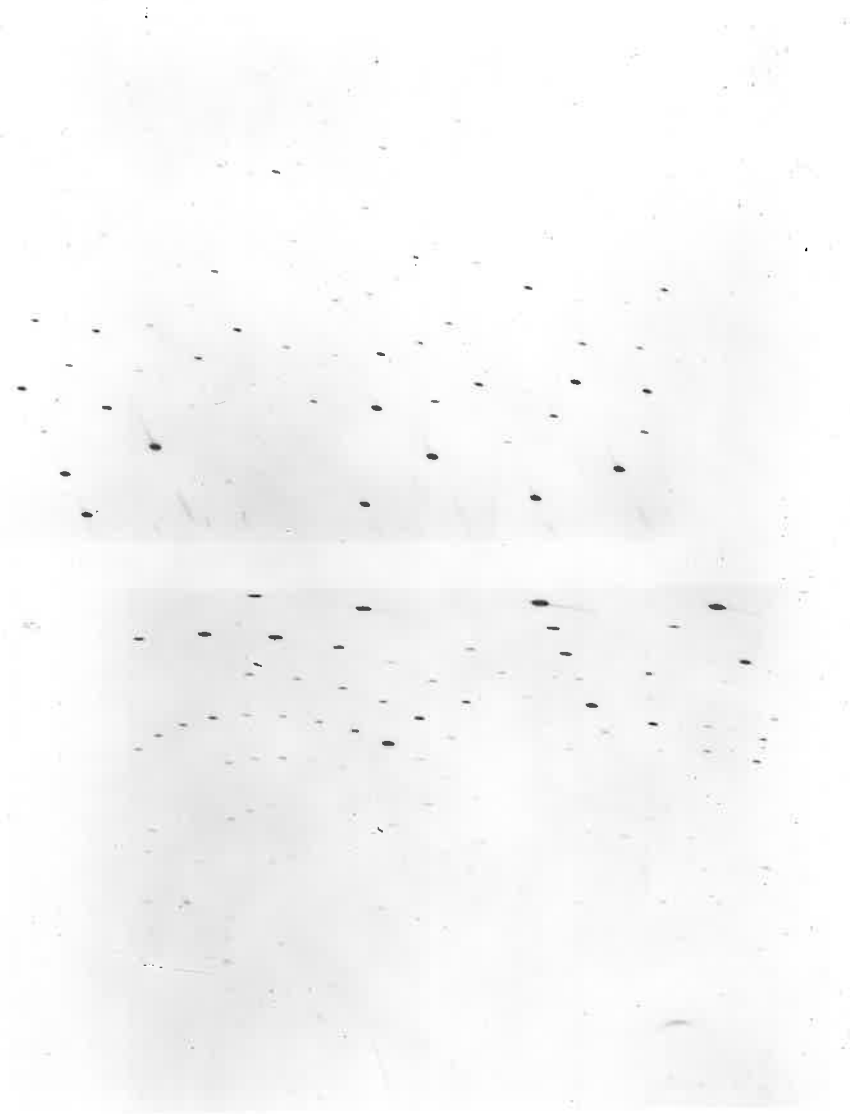


Plate A 3 The (h0l) and (h2l) reciprocal lattice sections of urea parabanate (zero layer above the equator).

The method may be further improved by making S_1 and S_2 identical. The need for S_3 is thereby obviated since a conventional screen serves its purpose.

The screens were constructed in the department workshop by Mr. T. Spurr.

Reference

Stadler (1950) Acta Cryst. 3, 262.

Appendix B

UPBA Structure factor tables

* unobserved

h	k	l	F_o	F_c
1	0	0	24.235	24.880
2	0	0	28.280	28.345
3	0	0	13.928	12.918
4	0	0	40.347	38.029
5	0	0	33.433	32.252
6	0	0	33.435	31.183
7	0	0*	.509	.821
8	0	0	10.435	10.402
9	0	0	7.804	8.333
10	0	0	6.628	7.556
11	0	0	3.950	3.814
0	0	2	21.210	21.250
1	0	2	6.711	6.593
-1	0	2	37.729	37.884
2	0	2	113.001	100.989
-2	0	2	51.584	58.824
3	0	2	30.050	30.153
-3	0	2	16.025	16.682
4	0	2	23.344	21.487
-4	0	2	31.640	34.534
5	0	2	30.903	29.059
-5	0	2	23.019	21.703
6	0	2	7.281	7.035
-6	0	2	16.905	16.248
7	0	2	11.774	11.399
-7	0	2	1.753	1.973
8	0	2*	.509	.072
-8	0	2	16.501	16.362
9	0	2	1.143	1.823
-9	0	2	3.246	2.766
10	0	2	3.757	4.926
-10	0	2	9.349	9.352
-11	0	2*	.509	.739
0	0	4	1.064	1.232
1	0	4	5.917	6.567
-1	0	4	52.829	53.743
2	0	4	8.671	7.947
-2	0	4	10.962	10.926
3	0	4	13.077	13.633
-3	0	4	21.508	19.869
4	0	4	29.414	28.986
-4	0	4	41.948	45.901
5	0	4	7.064	6.408
-5	0	4	25.724	24.798
6	0	4	.908	1.138
-6	0	4	14.008	14.918
7	0	4	16.119	16.536
-7	0	4	2.885	2.641
8	0	4	6.174	6.695
-8	0	4	17.811	16.599
9	0	4	.987	1.623
-9	0	4*	.509	.401
-10	0	4	6.444	6.339
-11	0	4	9.568	9.235
0	0	6	17.469	18.466
1	0	6	10.916	10.511
-1	0	6	52.959	50.409
2	0	6	25.561	22.929
-2	0	6	19.727	19.135
3	0	6	19.129	17.794
-3	0	6	30.612	30.148
4	0	6	9.194	8.329
-4	0	6	5.798	5.445
5	0	6	2.391	2.260
-5	0	6	10.558	10.150
6	0	6	8.067	7.828
-6	0	6	37.877	41.316
7	0	6	9.806	10.059
-7	0	6	2.671	2.304
8	0	6	4.941	6.505
-8	0	6	5.369	5.113
9	0	6	7.089	7.489
-9	0	6	1.821	2.199
-10	0	6	6.481	6.361
-11	0	6	14.990	12.819
0	0	8	20.310	19.721
1	0	8	33.570	33.251
-1	0	8	13.021	12.617
2	0	8	12.452	10.597
-2	0	8	30.042	29.155
3	0	8	12.479	9.853
-3	0	8	21.127	19.168
4	0	8	17.605	16.666
-4	0	8	24.118	24.136
5	0	8	13.384	13.188
-5	0	8	1.761	1.520
6	0	8*	.509	.395
-6	0	8	21.761	23.439
7	0	8	1.520	1.552
-7	0	8*	.509	.529
8	0	8	3.227	4.393
-8	0	8	13.977	14.414
-9	0	8	22.055	22.572
-11	0	8	12.538	10.460
0	0	10	3.861	2.734
1	0	10	31.934	27.038
-1	0	10	3.175	2.351
2	0	10	4.633	3.661
-2	0	10	23.357	20.976
3	0	10	4.776	3.673
-3	0	10	20.464	20.875
4	0	10	9.515	9.852
-4	0	10	17.135	17.002
5	0	10	2.732	2.766
-5	0	10	29.933	30.459
6	0	10	1.483	2.005
-6	0	10	5.654	6.206
7	0	10*	.509	1.796
-7	0	10	15.053	15.712

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-8	0	10	15.974	17.957
-9	0	10	11.353	10.237
-10	0	10	12.306	11.453
-11	0	10	7.309	5.962
0	0	12	6.232	5.805
1	0	12	5.471	3.856
-1	0	12	4.412	4.329
2	0	12	3.153	2.557
-2	0	12	20.914	19.996
3	0	12	3.484	3.156
-3	0	12	2.527	2.275
4	0	12	5.811	5.309
-4	0	12	11.225	11.034
5	0	12	6.697	9.327
-5	0	12	27.132	26.872
-6	0	12	11.215	11.039
-7	0	12	27.248	29.231
-8	0	12	13.525	14.767
-9	0	12	2.635	2.539
-10	0	12	1.302	1.771
0	0	14	12.874	12.850
1	0	14	13.059	12.919
-1	0	14	22.515	23.213
2	0	14	6.434	7.161
-2	0	14	15.322	15.151
3	0	14*	.509	.182
-3	0	14	35.997	36.357
4	0	14	4.081	6.420
-4	0	14	17.844	19.501
-5	0	14	4.762	2.957
-6	0	14	14.926	15.748
-7	0	14	7.716	8.324
-8	0	14*	.509	.990
-9	0	14	8.734	9.067
0	0	16	7.555	4.789
1	0	16	11.939	9.150
-1	0	16	7.692	6.038
2	0	16	2.794	2.361
-2	0	16	7.687	7.038
3	0	16	4.594	5.758
-3	0	16	3.517	2.621
-4	0	16	7.007	5.586
-5	0	16	5.140	4.341
-6	0	16	2.059	2.041
-7	0	16	5.153	4.199
-8	0	16	8.848	5.327
0	0	18	2.381	2.755
1	1	0	40.449	34.091
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2	1	0	89.282	94.364
-2	0	18	2.694	2.642
3	1	0	13.479	13.485
-3	0	18	7.200	5.177
4	1	0	6.590	6.170
-4	0	18	8.924	7.076
5	1	0	14.129	12.781
-5	0	18	7.570	6.391

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6	1	0	17.910	15.918
7	1	0	3.709	3.525
8	1	0	10.772	10.606
9	1	0	4.355	4.027
10	1	0	12.110	10.122
0	1	1	29.246	23.434
1	1	1	13.960	12.689
-1	1	1*	.533	.813
2	1	1	105.217	100.888
-2	1	1	13.361	14.259
3	1	1	41.757	40.135
-3	1	1	37.318	44.767
4	1	1	5.995	5.814
-4	1	1	37.836	39.329
5	1	1	18.741	17.767
-5	1	1	6.204	5.736
6	1	1	5.562	4.668
-6	1	1	3.529	2.784
7	1	1	8.608	8.109
-7	1	1	9.856	10.094
8	1	1	4.516	4.448
-8	1	1	5.188	4.304
9	1	1	4.754	5.009
-9	1	1	1.286	1.396
10	1	1	1.221	1.157
-10	1	1	4.610	3.572
-11	1	1	4.639	4.133
0	1	2	91.268	80.294
1	1	2	3.057	2.107
-1	1	2	5.416	5.649
2	1	2	97.206	106.883
-2	1	2	25.108	24.822
3	1	2	1.996	2.216
-3	1	2	27.875	30.915
4	1	2	6.867	6.549
-4	1	2	12.344	12.616
5	1	2	7.882	7.249
-5	1	2	3.012	2.999
6	1	2	10.630	10.615
-6	1	2	21.104	21.759
7	1	2	2.782	2.235
-7	1	2	5.499	4.821
8	1	2	9.022	9.336
-8	1	2	6.999	6.571
9	1	2*	.533	.898
-9	1	2	1.306	1.221
10	1	2	2.683	2.184
-10	1	2	9.558	7.673
-11	1	2	7.426	7.214
0	1	3	26.262	23.655
1	1	3	19.993	21.207
-1	1	3	7.889	8.482
2	1	3	28.325	30.959
-2	1	3	24.482	26.108
3	1	3	4.121	3.164
-3	1	3	34.479	38.351
4	1	3	31.906	31.345

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-4	1	3	14.090	14.999
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-5	1	3	4.894	4.256
6	1	3	2.963	2.151
-6	1	3	7.088	7.247
7	1	3	3.553	3.326
-7	1	3	9.009	8.628
8	1	3	4.926	5.342
-8	1	3	12.124	11.742
-9	1	3	1.318	1.561
9	1	3	7.147	5.516
10	1	3	2.739	2.550
-10	1	3	7.995	6.374
-11	1	3	5.346	4.118
0	1	4	11.834	10.662
1	1	4	21.656	21.431
-1	1	4*	.533	.723
2	1	4	5.356	5.670
-2	1	4	20.365	19.663
3	1	4	9.608	9.893
-3	1	4	18.991	19.074
4	1	4	25.833	25.019
-4	1	4	14.709	16.429
5	1	4	21.866	21.702
-5	1	4	9.661	11.075
6	1	4	14.732	14.370
-6	1	4	23.539	25.307
7	1	4	3.733	3.137
-7	1	4	1.291	1.253
8	1	4	1.753	1.613
-8	1	4	11.513	11.098
9	1	4	5.914	4.519
-9	1	4	7.328	6.891
-10	1	4	4.767	3.539
-11	1	4	4.180	3.066
0	1	5	30.726	28.457
1	1	5	3.586	3.371
-1	1	5	19.530	19.413
2	1	5	7.351	7.427
-2	1	5	35.560	39.129
3	1	5	8.941	9.222
-3	1	5	40.764	45.840
4	1	5	5.174	4.558
-4	1	5	2.259	1.692
5	1	5	10.153	9.117
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6	1	5	3.359	2.690
-6	1	5	12.495	14.017
7	1	5*	.533	.861
-7	1	5	3.146	3.316
8	1	5*	.533	1.161
-8	1	5	16.460	18.542
9	1	5	3.906	3.579
-9	1	5	9.005	8.925
-10	1	5*	.533	.033
-11	1	5	5.849	4.637
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2	1	6	21.797	21.808
-2	1	6	24.657	25.185
3	1	6	10.782	11.022
-3	1	6	3.933	4.578
4	1	6	3.567	3.210
-4	1	6	4.060	3.594
5	1	6	9.195	8.482
-5	1	6	7.413	7.802
6	1	6	2.753	2.523
-6	1	6	2.968	1.950
7	1	6	8.655	10.111
-7	1	6	1.846	1.307
8	1	6	4.283	5.537
-8	1	6	3.221	3.295
9	1	6	2.179	2.183
-9	1	6	3.131	2.817
-10	1	6*	.533	1.268
-11	1	6*	.533	.745
0	1	7	15.166	14.358
1	1	7	3.825	3.511
-1	1	7	10.230	10.109
2	1	7	22.557	23.265
-2	1	7	8.763	8.649
3	1	7	6.652	6.381
-3	1	7	6.614	5.502
4	1	7	5.390	3.828
-4	1	7	36.030	41.175
5	1	7	5.405	4.550
-5	1	7	2.198	2.081
6	1	7	6.750	5.271
-6	1	7	6.109	6.085
7	1	7*	.533	1.595
-7	1	7	1.319	1.683
8	1	7*	.533	.378
-8	1	7	10.232	10.145
-9	1	7	7.358	7.609
-10	1	7	6.888	5.004
-11	1	7	4.275	3.875
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-1	1	8	35.210	35.993
2	1	8	4.195	3.398
-2	1	8	6.043	5.637
3	1	8	1.565	1.710
-3	1	8	7.965	8.010
4	1	8*	.533	.363
-4	1	8	3.920	3.952
5	1	8*	.533	.018
-5	1	8	14.950	17.273
6	1	8	2.521	2.571
-6	1	8	10.595	10.598
7	1	8	1.085	1.020
-7	1	8	13.136	15.458
-8	1	8	.533	.067
-9	1	8	2.938	2.815

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-10	1	8	13.558	11.101
-11	1	8	14.506	12.132
0	1	9	9.076	7.852
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-1	1	9	14.199	13.762
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-2	1	9	13.423	13.699
3	1	9	4.520	4.241
-3	1	9	3.713	3.957
4	1	9	2.154	1.783
-4	1	9	3.443	3.584
5	1	9	2.956	2.309
-5	1	9	5.826	6.327
6	1	9	1.185	.932
-6	1	9	12.920	14.425
-7	1	9	4.420	5.113
-8	1	9*	.533	.414
-9	1	9	7.840	8.049
-10	1	9	5.462	3.634
0	1	10	9.813	8.333
1	1	10	5.338	4.845
-1	1	10	18.566	16.775
2	1	10	3.000	.875
-2	1	10	2.237	2.178
3	1	10	15.814	15.168
-3	1	10	5.920	5.705
4	1	10	5.340	4.018
-4	1	10	14.646	16.734
5	1	10	7.194	7.836
-5	1	10	4.403	3.910
6	1	10	3.867	4.924
-6	1	10*	.533	.194
-7	1	10	22.523	27.029
-8	1	10	11.379	12.348
-9	1	10	16.226	21.341
-10	1	10*	.533	.848
0	1	11	12.267	11.606
1	1	11	6.220	5.671
-1	1	11	4.970	4.531
2	1	11	5.109	4.158
-2	1	11	4.567	4.239
3	1	11	1.655	1.611
-3	1	11	14.881	15.636
4	1	11	6.366	5.605
-4	1	11	11.466	11.719
5	1	11	4.185	4.427
-5	1	11	14.213	14.575
-6	1	11	15.943	17.531
-7	1	11	8.808	9.053
-8	1	11	2.763	3.178
-9	1	11	5.852	5.231
-10	1	11	5.151	2.524
0	1	12	2.765	2.236
1	1	12	3.630	3.325
-1	1	12	7.844	7.618
2	1	12	5.506	5.387
-2	1	12	6.837	7.177
3	1	12	12.935	14.029
-3	1	12	26.246	29.864
4	1	12*	.533	.110
-4	1	12	12.658	12.759
5	1	12	2.607	2.450
-5	1	12	23.617	28.398
6	1	12	5.774	5.487
-7	1	12	3.849	4.041
-8	1	12*	.533	.384
-10	1	12	4.393	3.299
0	1	13	13.970	14.102
1	1	13	2.620	2.646
-1	1	13	7.383	7.822
2	1	13	7.068	7.693
-2	1	13	8.136	8.049
3	1	13	9.520	10.344
-3	1	13	5.948	6.497
4	1	13	2.302	2.345
-4	1	13	14.581	16.095
5	1	13	3.150	2.953
-5	1	13	1.668	2.248
-6	1	13	15.680	17.303
-7	1	13	1.599	1.959
-8	1	13	6.328	6.465
-10	1	13	5.348	3.442
0	1	14	7.709	7.913
1	1	14	1.560	.952
-1	1	14	17.355	18.588
2	1	14	1.447	1.614
-2	1	14	10.415	10.787
3	1	14	7.547	8.606
-3	1	14	7.422	7.405
4	1	14	3.790	2.971
-4	1	14	.957	1.404
-5	1	14	17.850	20.169
-6	1	14	1.307	1.678
-7	1	14*	.533	.676
-8	1	14	3.132	3.534
-9	1	14	6.708	5.511
0	1	15*	.533	.205
1	1	15	14.252	10.589
-1	1	15	6.849	7.041
2	1	15	9.794	7.325
-2	1	15	5.966	6.388
3	1	15	2.620	1.910
-3	1	15*	.533	.458
-4	1	15	12.533	10.042
-5	1	15	2.528	2.781
-6	1	15	1.508	1.536
-7	1	15	9.599	7.185
0	1	16*	.533	1.359
1	1	16*	.533	.021
-1	1	16	11.466	13.777
2	1	16	5.961	5.110
-2	1	16	5.863	6.257
-3	1	16	5.724	5.077
-4	1	16	7.008	7.640

h	k	l	F_o	F_c	h	k	l	F_o	F_c
-5	1	16	2.044	2.928	9	2	2	7.508	6.357
0	1	17	6.640	5.108	-9	2	2	5.842	6.058
-1	1	17	1.821	1.803	10	2	2	5.561	5.561
-2	1	17	1.932	.958	-10	2	2*	.513	.503
-3	1	17	4.857	3.829	0	2	3	20.536	21.555
-4	1	17	2.794	1.594	1	2	3	14.347	13.060
-5	1	17	1.354	.362	-1	2	3	14.199	13.575
-6	1	17	9.367	6.262	2	2	3	16.755	15.406
-7	1	17	5.961	4.648	-2	2	3	5.069	4.666
1	2	0	16.707	16.389	3	2	3	33.860	35.601
2	2	0	30.843	32.251	-3	2	3	4.759	3.959
3	2	0	14.896	13.318	4	2	3	15.808	13.552
4	2	0	19.777	19.870	-4	2	3	22.916	25.940
5	2	0	12.959	10.874	5	2	3	17.786	18.709
6	2	0	3.547	3.749	-5	2	3	15.641	14.785
7	2	0	5.636	5.187	6	2	3	9.981	9.605
8	2	0	9.727	10.099	-6	2	3	2.287	2.120
9	2	0*	.513	.619	7	2	3*	.513	.004
10	2	0	3.446	2.857	-7	2	3	1.756	1.522
0	2	1	45.355	38.697	8	2	3	1.155	.939
1	2	1	28.771	29.111	-8	2	3	4.768	4.534
-1	2	1	10.443	10.396	9	2	3	6.362	5.747
2	2	1	21.328	20.291	-9	2	3	9.748	11.406
-2	2	1	30.687	32.355	10	2	3	.988	2.328
3	2	1	17.663	17.419	-10	2	3	4.728	3.782
-3	2	1	16.994	15.013	-11	2	3	4.934	5.176
4	2	1	23.403	24.447	0	2	4	24.526	25.494
-4	2	1	17.424	15.873	1	2	4	12.668	13.086
5	2	1	4.136	3.912	-1	2	4	1.421	1.854
-5	2	1	8.645	9.221	2	2	4	24.979	23.172
6	2	1	14.996	15.690	-2	2	4	28.843	30.879
-6	2	1	9.948	8.948	3	2	4	16.274	15.416
7	2	1	7.872	8.496	-3	2	4	9.201	7.634
-7	2	1	5.898	5.671	4	2	4	11.555	10.102
8	2	1*	.513	.078	-4	2	4	20.515	19.711
-8	2	1	8.984	8.465	5	2	4	5.741	4.856
9	2	1	2.182	2.557	-5	2	4	17.547	18.048
-9	2	1	5.721	6.199	6	2	4	13.380	15.054
10	2	1	1.770	1.700	-6	2	4	10.530	9.949
-10	2	1	3.140	2.996	7	2	4	4.112	4.101
0	2	2	63.190	58.089	-7	2	4	6.841	6.848
1	2	2	6.101	4.027	8	2	4	4.897	6.320
-1	2	2	36.675	37.319	-8	2	4	4.346	4.429
2	2	2	11.564	10.626	9	2	4	4.734	3.995
-2	2	2	19.647	19.201	-9	2	4	4.883	5.911
3	2	2	18.428	17.232	-10	2	4	7.292	6.088
-3	2	2*	.513	.863	0	2	5	13.365	12.556
4	2	2	51.763	60.102	1	2	5	9.695	8.569
-4	2	2	15.673	14.948	-1	2	5	19.105	17.428
5	2	2	4.311	4.204	2	2	5	4.067	4.055
-5	2	2	19.649	19.314	-2	2	5	9.450	8.295
6	2	2	9.234	7.873	3	2	5	3.749	3.010
-6	2	2	10.508	10.332	-3	2	5	2.085	2.293
7	2	2	10.670	9.552	4	2	5	14.163	13.178
-7	2	2	1.247	1.423	-4	2	5	22.687	22.189
8	2	2	6.203	7.594	5	2	5	13.189	13.547
-8	2	2	13.883	16.102	-5	2	5	1.191	1.163

h	k	l	F_o	F_c	h	k	l	F_o	F_c
6	2	5	3.833	3.878	4	2	8	4.365	3.794
-6	2	5	15.513	16.253	-4	2	8	2.161	1.695
7	2	5	3.408	3.112	5	2	8	5.810	4.923
-7	2	5	12.524	11.775	-5	2	8	4.557	4.204
8	2	5*	.513	.469	6	2	8	6.216	7.305
-8	2	5*	.513	1.792	-6	2	8	3.935	3.859
9	2	5	3.517	3.695	7	2	8	1.304	1.881
-9	2	5	5.627	6.012	-7	2	8	5.147	5.316
-10	2	5	3.375	2.813	8	2	8*	.513	.160
-11	2	5	3.681	3.771	-8	2	8	3.625	3.013
0	2	6	37.400	41.702	-9	2	8	9.565	9.577
1	2	6	6.851	6.091	-10	2	8	6.092	4.834
-1	2	6	8.181	7.425	0	2	9	9.757	9.845
2	2	6	4.391	3.160	1	2	9	6.510	6.146
-2	2	6	8.307	7.323	-1	2	9	5.370	4.253
3	2	6	6.529	6.797	2	2	9	11.158	11.076
-3	2	6	16.829	16.805	-2	2	9	3.072	2.786
4	2	6	6.310	5.667	3	2	9	6.252	5.906
-4	2	6	20.793	20.751	-3	2	9*	.513	.763
5	2	6	5.178	5.141	4	2	9	14.833	13.730
-5	2	6	2.997	2.174	-4	2	9	9.829	9.653
6	2	6	5.528	5.280	5	2	9	2.229	2.477
-6	2	6	16.291	17.884	-5	2	9	17.456	19.430
7	2	6	3.874	4.017	6	2	9	3.075	3.571
-7	2	6	12.527	14.263	-6	2	9	12.227	12.803
8	2	6*	.513	.179	7	2	9	3.368	3.070
-8	2	6	6.905	7.594	-7	2	9	4.042	3.725
-9	2	6	5.608	5.803	-8	2	9	10.543	12.327
-10	2	6	6.306	5.203	-9	2	9	1.608	1.889
-11	2	6	2.750	2.780	-10	2	9*	.513	.227
0	2	7	15.863	15.996	0	2	10	12.228	10.871
1	2	7	13.557	12.296	1	2	10	15.085	15.664
-1	2	7	30.122	33.643	-1	2	10	2.944	3.145
2	2	7	7.769	7.030	2	2	10	1.548	1.868
-2	2	7	17.240	17.130	-2	2	10	4.714	4.888
3	2	7	3.183	2.661	3	2	10	7.753	7.663
-3	2	7	22.733	23.099	-3	2	10	5.702	4.011
4	2	7	4.180	3.547	4	2	10	3.540	3.891
-4	2	7*	.513	1.488	-4	2	10	6.640	5.545
5	2	7	10.440	11.278	5	2	10	3.842	4.305
-5	2	7	9.398	9.779	-5	2	10	15.299	16.113
6	2	7*	.513	.108	6	2	10	3.655	3.067
-6	2	7	3.909	3.958	-6	2	10	1.787	1.747
7	2	7	4.156	5.544	7	2	10*	.513	.417
-7	2	7	9.677	9.941	-7	2	10	11.466	12.502
8	2	7*	.513	1.607	-8	2	10	3.956	4.183
-8	2	7	7.466	7.171	-9	2	10	15.283	12.823
-9	2	7	4.832	5.114	-10	2	10	2.945	2.642
-10	2	7*	.513	.900	0	2	11	9.705	9.658
-11	2	7	6.044	5.013	1	2	11	11.541	12.651
0	2	8	8.431	7.413	-1	2	11	12.351	13.133
1	2	8	9.618	8.663	2	2	11	9.281	9.340
-1	2	8	11.572	10.826	-2	2	11	8.116	7.783
2	2	8	2.968	2.983	3	2	11	6.048	6.225
-2	2	8	19.527	19.330	-3	2	11	2.561	.790
3	2	8	5.256	4.893	4	2	11	5.418	6.393
-3	2	8	24.378	25.676	-4	2	11	11.280	10.929

h	k	l	F_o	F_c
-5	2	11	4.273	3.693
6	2	11	3.596	3.351
-6	2	11	20.744	25.079
-7	2	11	10.098	11.597
-8	2	11	5.570	6.918
-9	2	11	4.007	2.724
0	2	12	3.292	2.747
1	2	12	17.010	19.219
-1	2	12	13.112	13.230
2	2	12	7.115	6.905
-2	2	12	10.021	10.157
3	2	12	4.684	5.474
-3	2	12	22.598	24.514
4	2	12	4.059	4.415
-4	2	12	14.089	14.168
5	2	12	8.171	7.917
-5	2	12	15.371	15.851
-6	2	12	1.787	1.772
-7	2	12	14.992	18.744
-8	2	12	4.255	4.348
-9	2	12	7.534	6.007
-10	2	12	6.037	4.475
0	2	13	3.993	3.780
1	2	13	9.629	9.850
-1	2	13	14.865	15.806
2	2	13	1.413	1.890
-2	2	13*	.513	1.132
3	2	13	3.371	3.802
-3	2	13	8.339	7.264
4	2	13	5.265	4.413
-4	2	13	1.796	2.065
-5	2	13	11.283	11.686
-6	2	13	.871	.898
-7	2	13	6.954	8.695
-8	2	13*	.513	.527
-9	2	13	11.215	9.106
0	2	14	2.850	2.964
1	2	14	4.636	4.801
-1	2	14	.868	.528
2	2	14	4.536	5.609
-2	2	14*	.513	.350
3	2	14	1.734	2.085
-3	2	14	15.916	18.507
-4	2	14	6.388	6.627
-5	2	14	4.017	3.683
-6	2	14	2.374	2.407
-7	2	14	6.611	5.071
-8	2	14	5.851	4.111
-9	2	14	4.500	2.345
0	2	15	4.571	4.519
1	2	15	7.045	6.343
-1	2	15*	.513	.108
2	2	15	6.220	5.553
-2	2	15	6.808	7.800
-3	2	15	1.667	1.994
-4	2	15	5.332	5.845
-5	2	15	3.341	3.511
-6	2	15	5.446	3.814
-7	2	15	7.030	5.740
0	2	16	9.491	8.288
1	2	16	10.016	8.213
-1	2	16	5.318	3.709
-2	2	16	8.710	7.122
-3	2	16	9.169	7.245
-4	2	16	3.205	2.697
-5	2	16	7.365	5.219
-6	2	16	3.182	2.450
-7	2	16	5.216	3.530
-2	2	17	2.922	2.562
-3	2	17	7.002	5.746
-6	2	17	6.105	4.398
1	3	0	24.761	24.832
2	3	0	35.856	38.661
3	3	0	7.868	7.653
4	3	0	1.631	1.560
5	3	0	12.822	13.548
6	3	0	4.535	4.784
7	3	0	6.857	6.672
8	3	0	4.228	4.655
9	3	0	5.839	5.107
10	3	0	3.329	3.902
0	3	1	17.444	20.095
1	3	1	30.301	28.233
-1	3	1	10.853	10.197
2	3	1	7.456	6.159
-2	3	1	8.847	7.518
3	3	1	14.464	12.016
-3	3	1	7.421	6.474
4	3	1	15.161	14.144
-4	3	1	4.991	4.329
5	3	1	3.881	3.683
-5	3	1	12.062	11.651
6	3	1	1.752	1.222
-6	3	1	13.831	13.860
7	3	1	9.200	8.893
-7	3	1	6.872	6.519
8	3	1	5.073	6.840
-8	3	1	2.527	2.894
9	3	1	5.657	4.855
-9	3	1	9.025	8.564
-10	3	1*	.535	.919
0	3	2	5.058	4.468
1	3	2	30.130	29.247
-1	3	2	22.055	21.228
2	3	2	14.366	11.488
-2	3	2	17.266	15.576
3	3	2	10.214	9.145
-3	3	2	3.349	3.201
4	3	2	4.318	3.745
-4	3	2	17.752	15.331
5	3	2	12.004	10.748
-5	3	2	5.638	5.635
6	3	2	23.189	24.034
-6	3	2	15.140	14.811

h	k	l	F_o	F_c
7	3	2	4.929	5.759
-7	3	2	9.718	10.960
8	3	2	5.513	5.657
-8	3	2	3.496	4.017
9	3	2	3.846	3.674
-9	3	2	5.707	5.830
-10	3	2	1.671	2.018
0	3	3	16.864	16.487
1	3	3	5.105	4.391
-1	3	3	9.432	9.671
2	3	3	6.528	5.485
-2	3	3	15.342	13.685
3	3	3	2.172	2.439
-3	3	3*	.535	.223
4	3	3	11.257	10.563
-4	3	3	1.930	1.746
5	3	3	.859	1.394
-5	3	3	3.957	3.301
6	3	3	11.266	10.522
-6	3	3	18.480	20.023
7	3	3	2.235	2.745
-7	3	3	8.922	8.776
8	3	3*	.535	.090
-8	3	3*	.535	1.119
9	3	3*	.535	.535
-9	3	3	6.131	4.650
-10	3	3	3.093	2.800
0	3	4	2.725	2.637
1	3	4	20.191	19.757
-1	3	4	10.801	9.758
2	3	4	25.063	24.160
-2	3	4	34.688	39.509
3	3	4	16.578	15.594
-3	3	4	21.745	20.941
4	3	4	15.624	15.776
-4	3	4	.984	.428
5	3	4	8.719	8.488
-5	3	4	2.203	1.855
6	3	4	13.181	14.045
-6	3	4	9.199	8.282
7	3	4	10.344	11.845
-7	3	4	15.762	17.366
8	3	4	10.451	10.847
-8	3	4	4.703	4.220
-9	3	4	7.234	6.553
-10	3	4*	.535	.682
0	3	5*	.535	.391
1	3	5	.503	.789
-1	3	5	9.641	9.389
2	3	5	14.484	13.375
-2	3	5	6.593	5.785
3	3	5	5.525	4.523
-3	3	5	6.023	5.218
4	3	5	.854	.844
-4	3	5	12.368	12.275
5	3	5	3.167	3.423
-5	3	5	4.231	3.779
6	3	5	1.722	2.070
-6	3	5	3.542	3.542
7	3	5	3.845	4.036
-7	3	5	.686	.467
8	3	5	3.305	3.446
-8	3	5	3.175	2.970
-9	3	5	2.822	2.572
-10	3	5	8.042	7.226
0	3	6	13.605	12.570
1	3	6	6.027	5.330
-1	3	6	8.645	7.524
2	3	6	.975	.798
-2	3	6	16.394	16.451
3	3	6	13.999	12.682
-3	3	6	25.106	24.058
4	3	6	1.239	1.420
-4	3	6	12.028	11.072
5	3	6	3.415	3.232
-5	3	6	29.187	29.979
6	3	6	5.169	6.298
-6	3	6	7.515	7.354
7	3	6	6.499	7.155
-7	3	6	2.857	2.770
8	3	6	3.589	4.629
-8	3	6	3.736	3.917
-9	3	6	7.135	6.762
-10	3	6	3.461	3.316
0	3	7	8.099	7.131
1	3	7	12.037	11.797
-1	3	7	3.779	3.464
2	3	7*	.535	1.070
-2	3	7	14.066	12.889
3	3	7	10.645	10.587
-3	3	7	12.387	12.031
4	3	7	10.570	10.969
-4	3	7	6.785	6.009
5	3	7	2.280	2.620
-5	3	7	1.049	.943
6	3	7	.601	.987
-6	3	7*	.535	.326
7	3	7	3.962	3.658
-7	3	7	9.088	9.437
-8	3	7	1.471	1.532
-9	3	7	5.330	4.922
-10	3	7	3.993	3.535
0	3	8	19.451	20.405
1	3	8	2.171	2.199
-1	3	8	8.311	7.501
2	3	8	22.729	23.957
-2	3	8	2.158	3.055
3	3	8	6.095	5.623
-3	3	8	5.641	5.023
4	3	8	1.961	2.433
-4	3	8	9.908	9.154
5	3	8	3.871	4.263
-5	3	8	1.903	2.453
6	3	8*	.535	.564

h	k	l	F_o	F_c
-6	3	8	7.386	6.550
7	3	8*	.535	.202
-7	3	8	7.260	6.991
-8	3	8	9.043	9.942
-9	3	8	4.507	3.339
-10	3	8	7.142	6.230
0	3	9	1.120	1.045
1	3	9	12.248	12.503
-1	3	9	9.960	9.336
2	3	9	9.187	8.281
-2	3	9*	.535	.539
3	3	9	2.497	3.607
-3	3	9	7.051	6.286
4	3	9	2.394	2.506
-4	3	9*	.535	1.092
5	3	9	4.019	4.508
-5	3	9	6.809	7.532
6	3	9*	.535	.808
-7	3	12	7.619	8.967
-8	3	12*	.535	.894
0	3	13	3.748	3.786
1	3	13	6.281	6.160
-1	3	13	6.064	6.159
2	3	13	5.920	6.313
-2	3	13	10.036	11.047
3	3	13*	.535	1.213
-3	3	13*	.535	.597
4	3	13*	.535	4.357
-4	3	13	9.387	10.498
-5	3	13*	.535	.006
-6	3	13*	.535	.940
-7	3	13	4.309	6.096
0	3	14	3.542	4.011
1	3	14	6.561	7.453
-1	3	14	11.148	11.842
2	3	14*	.535	2.880
-2	3	14*	.535	.729
3	3	14*	.535	.489
-3	3	14	4.935	5.253
-4	3	14	5.779	7.108
-5	3	14	7.134	8.362
-6	3	14	4.084	4.503
0	3	15	2.914	3.122
1	3	15*	.535	.217
-1	3	15	4.908	5.813
2	3	15*	.535	1.574
-2	3	15	5.503	7.059
-3	3	15	1.494	1.658
-4	3	15	2.333	3.038

Appendix C

TUPBA Structure factor tables

* unobserved

h	k	l	F_o	F_c
0	2	0	123.172	131.500
0	4	0	64.519	58.111
0	6	0	26.961	25.445
0	8	0	10.860	10.849
1	0	0	11.401	9.955
1	1	0	8.657	8.491
1	2	0	8.352	8.830
1	3	0	3.939	3.958
2	0	0	23.339	29.245
2	1	0	19.605	21.799
2	2	0	20.990	23.729
2	3	0	11.859	11.574
2	4	0	16.169	15.979
2	6	0	9.980	9.967
3	0	0*	1.253	.960
3	1	0	10.278	10.992
3	2	0*	.767	1.047
3	3	0	9.666	8.757
3	5	0	7.167	6.351
4	0	0	28.317	30.103
4	1	0	12.834	10.767
4	2	0	22.753	23.093
4	3	0	6.601	5.896
5	0	0	20.959	18.293
5	1	0*	1.583	3.510
5	2	0	17.246	15.861
5	3	0*	1.193	6.894
6	0	0	25.311	13.309
6	1	0	2.547	3.331
6	2	0	12.986	12.113
6	3	0*	1.332	4.331
7	0	0	30.807	28.485
7	1	0	3.569	4.532
7	2	0	24.786	24.524
7	3	0*	1.441	1.881
8	0	0*	2.399	3.372
8	1	0	21.512	20.686
8	2	0*	1.401	2.839
8	3	0	16.919	16.348
9	0	0*	2.496	3.597
9	1	0	16.212	15.743
9	2	0*	1.417	2.333
9	3	0	12.648	12.207
10	0	0	6.528	6.208
10	1	0	16.285	15.592
10	2	0	6.512	5.678
10	3	0	12.754	13.385
11	0	0	13.949	13.051
11	1	0*	1.905	1.313
11	2	0	10.890	11.364
11	3	0*	1.050	3.375
12	1	0	6.393	5.306
12	2	0*	.808	.937
12	3	0*	.417	4.277
0	0	1	16.737	18.785
0	0	-1	18.041	18.785
0	1	1	26.152	32.774
0	1	-1	28.174	32.774
0	2	1	15.415	16.028
0	2	-1	16.628	16.028
0	3	1	16.183	16.056
0	3	-1	16.326	16.056
0	4	1	12.722	12.437
0	5	1	9.110	7.028
0	6	1	8.879	8.843
1	0	1	11.343	10.239
1	0	-1	15.151	15.145
1	1	1	7.379	7.114
1	1	-1	15.022	15.089
1	2	1	9.904	9.215
1	2	-1	12.531	12.031
1	3	1*	.776	1.751
1	3	-1	7.162	7.210
1	4	1	6.683	5.783
1	4	-1	5.416	8.244
2	0	1	13.518	11.039
2	0	-1	38.125	54.253
2	1	1	29.146	32.870
2	1	-1	5.262	5.048
2	2	1	11.714	12.404
2	2	-1	28.960	38.665
2	3	1	20.018	19.637
2	3	-1	4.382	4.654
2	4	-1	20.419	20.471
2	6	-1	12.721	10.944
2	8	-1	4.684	5.389
3	0	1*	1.508	2.290
3	0	-1	24.451	31.143
3	1	1	33.009	36.320
3	1	-1	33.349	40.530
3	2	1*	.921	1.620
3	2	-1	21.878	24.347
3	3	1	24.485	23.186
3	3	-1	23.404	26.359
3	4	-1	13.266	14.410
3	5	-1	13.266	14.401
4	0	1	19.666	18.109
4	0	-1	6.209	4.694
4	1	1	21.869	23.529
4	1	-1	24.210	27.503
4	2	1	16.605	15.577
4	2	-1	3.333	3.335
4	3	1	16.743	16.020
4	3	-1	16.796	17.184
4	5	-1	7.622	9.573
5	0	1	17.966	15.544
5	0	-1	25.999	26.510
5	1	1*	1.792	1.938
5	1	-1	14.548	13.972

h	k	l	F_o	F_c
5	2	1	15.063	13.621
5	2	-1	21.172	21.536
5	3	1	3.791	3.927
5	3	-1	11.532	10.446
5	4	-1	13.198	13.173
5	5	-1	7.321	7.048
5	6	-1	6.161	7.235
6	0	1	24.345	22.888
6	0	-1	27.257	25.094
6	1	1	9.847	8.417
6	1	-1	7.941	7.843
6	2	1	20.404	20.037
6	2	-1	21.194	20.044
6	3	1	8.467	6.603
6	3	-1	2.805	3.269
7	0	1*	2.383	4.463
7	0	-1	14.733	13.036
7	1	1	23.210	21.998
7	1	-1	6.259	6.463
7	2	1*	1.395	3.406
7	2	-1	12.301	11.989
7	3	1	18.919	15.950
7	3	-1	5.178	5.333
8	0	1	20.192	18.832
8	0	-1	4.669	5.605
8	1	1	18.396	18.866
8	1	-1	10.612	9.875
8	2	1	16.269	16.452
8	2	-1	5.098	4.974
8	3	1	15.061	14.893
8	3	-1	9.836	7.746
9	0	1	4.966	6.235
9	0	-1	14.763	13.046
9	1	1*	2.189	.574
9	1	-1	13.718	15.315
9	2	1	5.423	5.390
9	2	-1	12.385	11.250
9	3	1*	1.333	.338
9	3	-1	11.187	11.630
10	0	1*	2.204	.255
10	0	-1	13.721	12.965
10	1	1	8.085	8.318
10	1	-1	18.058	16.801
10	2	1*	1.170	1.183
10	2	-1	12.039	11.743
10	3	1	7.033	6.601
10	3	-1	14.235	14.004
11	0	1	6.299	5.113
11	0	-1	4.821	1.519
11	1	1*	1.542	3.033
11	1	-1*	2.084	6.680
11	2	1	4.842	4.768
11	2	-1	2.544	1.875
11	3	1	4.068	2.741
11	3	-1	2.479	4.956
12	1	-1*	1.755	2.636
12	2	-1	3.256	3.466
12	3	-1	3.473	3.644
13	2	-1	8.676	9.387
0	0	2	29.316	37.290
0	0	-2	32.626	37.290
0	1	2*	1.278	2.669
0	1	-2*	1.378	2.669
0	2	2	25.811	28.734
0	2	-2	26.431	28.734
0	3	2*	.977	.333
0	3	-2*	.994	.333
1	0	2*	1.514	.135
1	0	-2	9.552	8.506
1	1	2	31.082	32.607
1	1	-2	18.950	18.937
1	2	2	2.037	3.173
1	2	-2	7.832	7.564
1	3	2	21.769	21.179
1	3	-2	13.389	13.241
1	4	-2	5.788	5.957
1	5	-2	8.453	8.062
2	0	2	16.849	15.810
2	0	-2	2.327	.558
2	1	2	5.040	4.329
2	1	-2	36.097	48.327
2	2	2	15.793	13.084
2	2	-2	1.866	2.493
2	3	2	3.702	3.475
2	3	-2	24.598	27.997
2	5	-2	14.548	13.411
3	0	2	22.893	19.589
3	0	-2	12.057	10.868
3	1	2	18.379	16.121
3	1	-2	32.814	38.755
3	2	2	17.641	15.328
3	2	-2	8.246	7.253
3	3	2	13.919	13.520
3	3	-2	21.642	23.324
3	5	-2	11.023	11.823
4	0	2	21.997	19.767
4	0	-2	13.207	12.623
4	1	2	11.589	12.454
4	1	-2	12.150	11.488
4	2	2	19.617	17.784
4	2	-2	10.125	9.833
4	3	2	8.074	8.439
4	3	-2	11.238	10.681
4	5	-2	8.919	8.606
4	7	-2	5.737	5.543
5	0	2	12.914	11.452
5	0	-2	2.422	1.367
5	1	2	15.703	14.231
5	1	-2	20.603	23.849
5	2	2	10.204	9.375
5	2	-2*	1.027	1.565
5	3	2	11.979	11.075
5	3	-2	15.804	16.089
5	5	-2	7.928	8.990

h	k	l	F_o	F_c
6	0	2	21.869	18.878
6	0	-2	5.753	6.357
6	1	2*	2.196	2.090
6	1	-2	32.367	37.365
6	2	2	18.412	16.986
6	2	-2	5.734	5.520
6	3	2*	1.492	3.919
6	3	-2	24.533	25.332
6	5	-2	14.969	14.407
7	0	2*	2.497	2.310
7	0	-2	5.324	2.855
7	1	2	3.428	3.881
7	1	-2	4.293	4.655
7	2	2	2.844	3.279
7	2	-2	5.445	5.619
7	3	2*	1.446	1.934
7	3	-2*	1.385	3.989
8	0	2*	2.423	.087
8	0	-2*	2.272	.437
8	1	2	4.480	5.489
8	1	-2	19.896	18.167
8	2	2*	1.329	3.370
8	2	-2*	1.347	.477
8	3	2	4.565	4.509
8	3	-2	15.944	15.524
9	0	2	10.305	8.625
9	0	-2	6.012	6.813
9	1	2	8.788	10.204
9	1	-2*	2.204	2.429
9	2	2	8.889	8.155
9	2	-2	4.923	5.267
9	3	2	6.708	7.654
9	3	-2*	1.492	3.839
10	0	2	6.145	3.798
10	0	-2	8.668	8.938
10	1	2	8.848	8.972
10	1	-2	22.217	19.682
10	2	2	4.427	4.590
10	2	-2	8.014	8.357
10	3	2	6.378	7.106
10	3	-2	16.879	15.291
11	0	-2	12.089	12.183
11	1	-2*	2.152	1.004
11	2	-2	9.629	10.505
11	3	-2*	1.289	2.246
12	1	-2	7.730	9.471
12	2	-2*	1.125	3.623
12	3	-2	8.065	8.243
13	1	-2	7.135	6.294
13	2	-2	6.498	6.433
0	0	3	32.265	34.763
0	0	-3	34.231	34.763
0	1	3	12.381	11.474
0	1	-3	13.386	11.474
0	2	3	27.762	28.709
0	2	-3	25.926	28.709
0	3	3	10.145	9.611
0	3	-3	10.415	9.611
1	0	3	20.517	18.593
1	0	-3*	1.744	1.761
1	1	3	2.506	3.579
1	1	-3	17.663	14.711
1	2	3	16.402	15.123
1	2	-3	2.335	1.564
1	3	3*	1.314	2.912
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2	0	3	24.432	21.914
2	0	-3	11.013	9.725
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2	1	-3	2.388	3.478
2	2	3	20.216	19.200
2	2	-3	9.776	9.218
2	3	3	6.945	6.375
2	3	-3	4.655	4.887
3	0	3	9.416	8.877
3	0	-3	23.168	21.725
3	1	3	10.251	9.873
3	1	-3	11.947	15.767
3	2	3	6.578	6.469
3	2	-3	18.625	17.265
3	3	3	8.852	8.653
3	3	-3	12.818	12.912
3	4	-3	10.672	10.024
3	5	-3	9.212	8.954
4	0	3	25.726	24.794
4	0	-3	11.789	10.973
4	1	3	3.299	3.603
4	1	-3	35.728	36.253
4	2	3	21.715	21.732
4	2	-3	8.942	8.059
4	3	3	2.981	3.624
4	3	-3	24.101	24.573
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5	0	3	9.353	8.814
5	0	-3	20.283	18.039
5	1	3	4.640	5.507
5	1	-3	4.058	5.119
5	2	3	8.663	8.887
5	2	-3	16.278	15.666
5	3	3	2.949	3.248
5	3	-3	4.030	4.066
5	4	-3	8.923	10.836
6	0	3	21.472	19.723
6	0	-3*	2.023	2.240
6	1	3	14.417	15.166
6	1	-3	12.064	11.036
6	2	3	18.067	17.771
6	2	-3*	1.218	3.014
6	3	3	10.483	11.385
6	3	-3	10.821	10.446
6	5	-3	8.114	8.157
7	0	3	13.076	11.364
7	0	-3	11.711	13.492
7	1	3	9.110	8.925

h	k	l	F_o	F_c
7	1	-3*	1.986	1.637
7	2	3	10.470	10.313
7	2	-3	10.907	11.541
7	3	3	7.294	6.927
7	3	-3*	1.430	3.275
8	0	3	15.247	13.374
8	0	-3	10.243	9.042
8	1	3	6.396	6.958
8	1	-3	24.824	25.705
8	2	3	11.336	11.851
8	2	-3	8.165	7.742
8	3	3	5.129	5.058
8	3	-3	19.972	19.279
8	5	-3	11.342	11.697
9	0	-3*	2.454	1.633
9	1	3	8.338	8.895
9	1	-3*	2.221	5.488
9	2	3	3.215	3.310
9	2	-3*	1.418	3.046
9	3	-3*	1.489	3.739
10	0	-3	5.069	3.009
10	1	-3	12.202	10.857
10	2	-3	4.453	3.584
10	3	-3	10.660	10.134
11	0	-3*	2.409	.246
11	1	-3	10.388	8.812
11	2	-3*	1.317	.437
11	3	-3	7.982	7.052
12	1	-3*	1.914	2.156
12	2	-3*	1.141	1.795
12	3	-3*	1.058	2.594
13	1	-3	7.894	8.259
13	2	-3	7.628	8.036
13	3	-3	6.899	7.770
0	0	4	23.919	20.793
0	0	-4	23.399	20.793
0	1	4	18.505	17.733
0	1	-4	20.014	17.733
0	2	4	19.048	17.865
0	2	-4	18.993	17.865
0	3	4	18.188	13.492
0	3	-4	15.367	13.492
1	0	4	12.277	10.586
1	0	-4	22.085	19.626
1	1	4	12.533	11.496
1	1	-4	5.052	5.841
1	2	4	10.747	11.087
1	2	-4	17.875	16.299
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2	0	4*	2.429	.894
2	0	-4	23.872	21.770
2	1	4*	2.202	2.284
2	1	-4	13.553	12.123
2	2	4*	1.411	1.277
2	2	-4	18.862	18.208
2	3	4*	1.492	3.577
2	3	-4	10.927	10.172
3	0	4	21.372	20.610
3	0	-4	13.824	11.077
3	1	4	7.389	5.961
3	1	-4	13.832	11.806
3	2	4	16.974	17.644
3	2	-4	11.743	10.374
3	3	4	5.614	4.833
3	3	-4	10.874	9.380
4	0	4	19.914	17.243
4	0	-4	19.004	17.024
4	1	4	11.200	11.513
4	1	-4*	1.939	4.762
4	2	4	15.292	15.539
4	2	-4	16.041	13.710
4	3	4	8.352	8.695
4	3	-4*	1.408	2.676
5	0	4	4.807	6.644
5	0	-4	13.223	11.183
5	1	4*	2.110	2.354
5	1	-4	14.016	14.073
5	2	4	5.951	5.681
5	2	-4	10.975	9.594
5	3	4	2.516	2.776
5	3	-4	9.503	9.339
5	4	-4	6.514	6.438
5	5	-4	6.161	4.613
6	0	4	12.618	11.838
6	0	-4*	2.257	.964
6	1	4	3.394	4.445
6	1	-4	9.425	6.429
6	2	4	9.698	10.930
6	2	-4*	1.340	1.119
6	3	4	2.775	3.059
6	3	-4	8.294	7.440
7	0	4	4.912	4.827
7	0	-4	20.528	18.699
7	1	4	5.841	4.689
7	1	-4	16.254	14.621
7	2	4	4.082	4.171
7	2	-4	18.080	16.891
7	3	4	2.271	3.825
7	3	-4	10.763	11.152
7	4	-4	10.928	12.549
8	0	-4	19.341	19.992
8	1	-4	4.577	2.644
8	2	-4	16.704	17.032
8	3	-4	3.012	3.704
8	4	-4	9.937	10.850
9	0	-4	13.374	13.041
9	1	-4*	2.249	2.841
9	2	-4	11.907	11.564
9	3	-4*	1.458	2.230
9	4	-4	7.928	8.315
10	0	-4	13.090	12.850
10	1	-4	16.078	16.333
10	2	-4	11.541	11.837

h	k	l	F_o	F_c
10	3	-4	12.958	13.203
10	4	-4	4.990	9.362
10	5	-4	5.762	9.038
11	0	-4	10.093	8.269
11	1	-4	7.472	4.107
11	2	-4	8.289	7.393
11	3	-4*	1.217	3.283
12	0	-4	6.673	5.669
12	1	-4*	1.830	1.699
12	2	-4	5.064	4.875
12	3	-4*	.980	2.030
13	1	-4	3.687	4.007
13	2	-4	8.988	8.913
13	3	-4*	.296	2.747
0	0	5	17.111	18.596
0	0	-5	17.300	18.596
0	1	5	11.139	9.661
0	1	-5	12.805	9.661
0	2	5	15.663	15.774
0	2	-5	15.320	15.774
0	3	5	9.708	8.986
0	3	-5	9.613	8.986
1	0	5	16.109	15.172
1	0	-5	4.328	4.843
1	1	5	18.809	19.299
1	1	-5*	2.238	.513
1	2	5	13.101	13.616
1	2	-5	4.043	3.299
1	3	5	15.133	14.979
1	3	-5*	1.480	.919
2	0	5	3.542	3.593
2	0	-5	6.057	5.141
2	1	5*	2.174	2.304
2	1	-5	27.013	27.392
2	2	5	2.687	2.943
2	2	-5	5.314	4.871
2	3	5*	1.315	4.566
2	3	-5	22.048	21.330
3	0	5*	2.296	2.082
3	0	-5	11.810	11.437
3	1	5	10.589	10.710
3	1	-5	12.252	12.119
3	2	5	2.494	2.305
3	2	-5	11.507	10.279
3	3	5	8.513	8.961
3	3	-5	8.555	9.082
4	0	5	6.652	5.567
4	0	-5	13.175	12.513
4	1	5*	1.824	2.703
4	1	-5	24.217	22.283
4	2	5	5.957	5.354
4	2	-5	11.500	10.907
4	3	5	1.949	2.400
4	3	-5	19.965	17.611
5	0	-5	9.218	8.066
5	1	5	10.006	10.637
5	1	-5	8.530	8.721
5	2	5	3.338	3.164
5	2	-5	8.758	7.544
5	3	-5	6.511	7.866
6	0	-5	7.085	6.231
6	1	-5	20.446	18.957
6	2	-5	6.369	5.522
6	3	-5	16.361	15.307
7	0	-5*	2.491	1.683
7	1	-5	5.340	2.974
7	2	-5*	1.420	2.565
7	3	-5	4.185	2.968
8	0	-5	11.097	9.218
8	1	-5	4.056	4.810
8	2	-5	8.841	7.376
8	3	-5	4.724	3.859
9	0	-5	7.857	4.798
9	1	-5	3.975	4.909
9	2	-5	6.367	4.856
9	3	-5	4.711	3.888
10	0	-5	19.779	18.441
10	1	-5*	2.091	3.366
10	2	-5	16.177	16.515
10	3	-5	2.476	2.657
10	4	-5	9.071	12.037
11	0	-5	8.588	1.964
11	1	-5*	1.900	1.341
11	2	-5	2.263	2.118
11	3	-5	2.091	2.126
12	1	-5*	1.613	.921
12	2	-5	6.437	6.437
12	3	-5*	.748	.880
13	0	-5	7.321	5.856
13	1	-5	6.315	6.524
13	2	-5	5.523	5.819
0	0	6	9.361	7.742
0	0	-6	9.747	7.742
0	1	6	7.918	7.606
0	1	-6	7.389	7.606
0	2	6	7.429	6.622
0	2	-6	7.290	6.622
0	3	6	6.869	6.369
0	3	-6	6.795	6.369
1	0	6	12.089	11.696
1	0	-6*	2.338	3.373
1	1	6	4.661	5.244
1	1	-6	9.541	10.270
1	2	6	9.473	10.466
1	2	-6	2.541	3.043
1	3	6	4.662	4.947
1	3	-6	7.972	7.866
2	0	6*	1.826	.407
2	0	-6*	2.402	3.250
2	1	6	9.435	10.079
2	1	-6	15.382	15.722
2	2	6*	.916	2.375
2	2	-6	3.252	3.577
2	3	6	7.439	8.484

h	k	l	F_o	F_c
2	3	-6	12.392	12.995
3	0	-6*	2.435	.584
3	1	6	2.527	3.681
3	1	-6*	2.178	4.112
3	2	6	5.108	5.593
3	2	-6*	1.339	1.453
3	3	-6*	1.319	3.039
4	0	-6	9.993	8.261
4	1	-6	11.498	9.525
4	2	-6	8.833	7.932
4	3	-6	9.437	8.136
5	0	-6	3.564	3.241
5	1	-6*	2.189	3.549
5	2	-6	2.713	2.989
5	3	-6*	1.334	2.996
6	0	-6	7.822	7.007
6	1	-6	11.129	10.824
6	2	-6	6.882	6.574
6	3	-6	10.147	9.436
7	0	-6	4.179	4.013
7	1	-6	14.434	13.553
7	2	-6	4.123	4.438
7	3	-6	11.036	10.361
8	0	-6*	2.317	.486
8	1	-6	12.820	12.751
8	2	-6*	1.249	2.364
8	3	-6	10.415	10.603
9	0	-6*	2.198	1.225
9	1	-6	10.941	11.446
9	2	-6	2.851	1.703
9	3	-6	9.392	9.642
10	0	-6*	2.077	.484
10	1	-6	5.420	.827
10	2	-6*	1.045	1.322
10	3	-6*	.930	1.989
11	1	-6	5.314	6.738
11	2	-6	5.163	4.650
11	3	-6	3.974	4.798
12	0	-6	4.684	4.926
12	2	-6	3.990	4.301
0	0	7*	1.246	4.474
0	0	-7*	1.284	4.474
0	1	7	7.633	8.852
0	1	-7	9.023	8.852
1	0	-7	8.114	7.804
1	1	-7	6.063	6.241
1	2	-7	6.529	7.011
2	0	-7	3.068	3.177
2	1	-7	5.427	5.176
2	2	-7	2.721	3.007
2	3	-7	4.171	4.886
3	0	-7	8.362	8.191
3	1	-7*	1.626	1.699
3	2	-7	7.239	7.516
3	3	-7*	.765	2.031
4	0	-7	6.174	7.198
4	1	-7	4.948	4.438
4	2	-7	6.213	6.043
4	3	-7	3.908	3.745
5	0	-7	14.669	14.774
5	1	-7	3.429	3.564
5	2	-7	11.042	13.039
5	3	-7	2.205	2.532
6	0	-7	6.182	6.583
6	1	-7*	1.699	1.518
6	2	-7	5.543	5.902
6	3	-7*	.849	.963
7	0	-7	8.871	8.174
7	1	-7	4.813	4.335
7	2	-7	6.819	7.403
7	3	-7	4.198	3.819
8	0	-7	3.588	4.005
8	1	-7*	1.544	1.128
8	2	-7	4.200	3.571
9	0	-7	9.492	8.274
9	1	-7	3.916	3.853
9	2	-7	7.090	7.312
10	2	-7	4.990	6.288

FIGURE INDEX

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