strong librations in their own planes as indicated by the elongation of the peripheral atoms. This is also supported by the temperature factors used in the molecular planes which are higher than those in the perpendicular direction. However, the presence in the X-ray photographs of some streaks, and the nearly identical orientations which either TMU or BP may adopt, indicate the possibility of disorder phenomena, not checked in this work, like those found in the indole–*s*-trinitrobenzene complex (Hanson, 1964). In fact the molecular arrangements corresponding to the four minima fill the available space equally well and are practically equivalent with respect to the Fourier transform.

Like the least-squares refinement with rigid groups (Scheringer, 1963), the method of analysis used in this work can be considered as a very convenient one, particularly when the ratio between the experimental data and the parameters is not too high. Moreover, it must be emphasized that, in the minimum residual search, convergence can be reached even if few reflexions are used.

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Minimum Residual Analysis of Crystal Structures

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When the approximate geometrical features of the molecule or molecules present in a unit cell of a crystal are known it is possible to utilize a few X-ray experimental intensities of low Bragg angle to scan systematically both the orientation and the positions in the cell with the help of the 'minimum residual' function *R*. The regions in which a reasonable agreement has been observed can subsequently be explored more carefully, increasing the number of reflexions and decreasing the rotational and translational increments. Then computation of intermolecular distances and potential energy as well as rigid-body least-squares techniques can be powerfully coupled together in the search for the true minimum. In this way it is possible to locate the individual molecules in the unit cell with such an accuracy as to allow the subsequent use of standard refinement techniques. The result of such an analysis in the case of a trimolecular complex (2:1 complex of 1,3,7,9-tetramethyluric acid and 3,4-benzpyrene) is discussed in detail.

Introduction

If the geometry of a molecule is known its Fourier transform can be evaluated as originally done by Knott (1940) or reproduced through the 'optical diffractometer' derived by Taylor, Hinde & Lipson (1951) from the X-ray microscope of Bragg (1939). Since the first application by Lipson & Taylor (1951) its usefulness has been widely recognized and exploited, stimulating many investigations to enlarge the field of its application (see *e.g.* Hanson, Lipson & Taylor, 1953; Taylor, 1954; Stokes, 1955; Liquori, 1956; Liquori & Ripamonti, 1956; Taylor & Morley, 1959; Harburn & Taylor, 1961).

Fourier transform methods, a modification of them (Giglio, Liquori & Ripamonti, 1958) and the 'optical diffractometer' have been among the most successfully used tools for crystal analysis of simple molecules and macromolecules carried out in our laboratory during the past few years. The increasing availability of electronic computers has opened up some possibilities for a more general approach to the solution of crystal structure, as already suggested by Milledge (1962).

Along the line of our past investigations we have therefore checked, through the systematic computation of three-dimensional Fourier transforms, the possibilities of convergence to the solution in some relatively complicated crystal structures (Damiani, Giglio, Liquori, Puliti & Ripamonti, 1966, 1967; Damiani, Giglio, Liquori & Ripamonti, 1967). Some investigations in this field have already been reported (Albano, Bellon, Pompa & Scatturin, 1963*a*,*b*; Bhuiya & Stanley, 1963, 1964; Stanley, 1964) but for less complicated systems and with a number of limitations that we have now removed.

The results obtained till now (Damiani, Giglio, Liquori, Puliti & Ripamonti, 1966, 1967) are encouraging and there is the possibility of handling, with a computer, rather complex structures in a reasonable time.

Moreover with this method, any further gain in our knowledge about the conformation of one molecule in a crystal, opening the way to the computation of its transform, can be directly utilized to solve related structures.

Outline of the method

To test a structure it is common practice to compute the value of the residual $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.

Looking at the residual as a continuous function, computation on net points in a multi-dimensional parametric space can be carried out to find the regions in which R reaches its minima. These regions, avoiding any physical and chemical consideration, can be assumed as defining possible structures, since generally the lower R is the more reliable the structure.

R can be written as $R(x_i,y_i,z_i,\varphi_i,\theta_i,\chi_i)$, i being the running index over the independent molecules (or atoms) in the unit cell, x_i,y_i,z_i crystal coordinates for some point* of the molecule and $\varphi_i,\theta_i,\chi_i$, three Eulerian angles defining the orientation of a unitary orthogonal framework fixed on the molecule in relation to a similar framework fixed on the crystal system.

The translational degrees of freedom can be reduced by using two- or one-dimensional X-ray data, but no reduction is possible for the rotational parameters. However, it must be noted that the minima are less well defined in cases of projections with increasing degree of overlap. On the other hand the ratio between the reciprocal space radius and the number of reflexions decreases when three-dimensional data are used and therefore the allowed translational increments increase (Stanley, 1964). The time required by a computer, to carry out a full analysis, increases rapidly with the number of independent molecules in the asymmetric unit and therefore it is important:

(*a*) to reduce as far as possible the regions to be scanned in the multidimensional space;

(*b*) to plan a suitable sequence of variation of the parameters.

Physical and chemical criteria are helpful for point (*a*) (Milledge, 1962). For point (*b*) it is well known that the structure factors modified by a translational movement of one molecule can be evaluated from the original ones through a 'modulation' with a suitable phase factor. Therefore it will be a good strategy to perform for each one of the rotational movements the relative full set of translations. The formulae for the modulation with three independent molecules in a unit cell, space group P_1, are derived in Appendix I. In Appendix II are derived the mathematical relationships used to perform the rotational movements.

Application

The strategy used in one of the two actual cases (Damiani, Giglio, Liquori, Puliti & Ripamonti, 1966, 1967) in which this technique has been found helpful will be discussed in some detail.

The 2:1 molecular complex between 1,3,7,9-tetramethyluric acid (TMU) and 3,4-benzpyrene (BP), space group P_1, is a system of three independent molecules. The following observations allowed a reduction of the theoretical degrees of freedom from fifteen to seven:

(i) Very strong X-ray diffraction amplitudes belonging to groups of hkl reflexions with $k=3n$ (n integer) indicated that the TMU and BP molecular planes are nearly parallel. These planes can be assumed to intersect the b axis at about 0, $\frac{1}{3}$ and $\frac{2}{3}$ b.

From the data with $k=3,6,9,12$ we derived the following equation for the mean molecular plane in the form $mx+ny+pz=1$:

$$0\cdot64x+3\cdot00y-1\cdot62z=1\ .$$

With the BP plane through the origin of the crystal system the TMU molecules turned out to be located on parallel planes about $+3\cdot4$ Å and $-3\cdot4$ Å away from the origin. In this way the degrees of freedom for the TMU molecule were reduced to two degrees of translation and one degree of rotation and for the BP molecule to only one degree of rotation.

(ii) (*a*) The transform of the hexagonal ring allowed us to fix the approximate orientation of the hexagons and therefore we had at first to check only rotations with increments of 60°. (*b*) The relatively broad regions

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* The centre of mass or an approximate geometrical centre can be conveniently used.

in which the maxima of the transform were spread out suggested a departure from a truly iso-orientation of the hexagonal rings of the different molecules.

(iii) From the intensity distribution near to the origin, the most reliable direction for the length of the BP molecule has been deduced in agreement with (ii). (This information was not fully utilized at the beginning, since the analysis was carried out also on models with the BP molecule rotated +60° and 120°.)

(iiii) The reduction of the degrees of freedom left some ambiguities in the selection of the models derived in agreement with Sutor (1963) for TMU and with constant lengths of 1·40 Å and bond angles of 120° for BP*. In fact it must be noted that because of the lack of a mirror plane in the individual molecules there are two possibilities, schematically indicated in Fig. 1(*a*), for the positions of BP on the molecular plane and two possibilities for each molecule of TMU [Fig. 1(*b*)]. Since the differences between the two orientations of the TMU are smaller than in BP, exchanging the pseudo mirror [Fig. 1(*b*)] two CH_3 groups and two N atoms with two O and two C atoms respectively, these possibilities were not taken into account at the beginning of the analysis.

Analysis

The models were fixed at the beginning as shown in Fig. 2 in the X,Z crystal plane. The BP was oriented on a plane parallel to the molecular one through the origin with the rotations of Table 1, where we report also the similar data for the TMU's and the translations to shift them +3·4 (TMU_+) and −3·4 Å (TMU_-) apart in a direction normal to the molecular plane. The different values of χ for the TMU molecules as compared to χ of BP represent an attempt to take into consideration point (*b*) of (ii). The results of the analysis for the 36 independent models, derived from the first one through independent rotations of $n\times 60°$ ($n=1,2,3,4,5$) for each TMU, utilizing 30 low Bragg angle reflexions and allowing the molecules to undergo cycles† of translational movements in the molecular

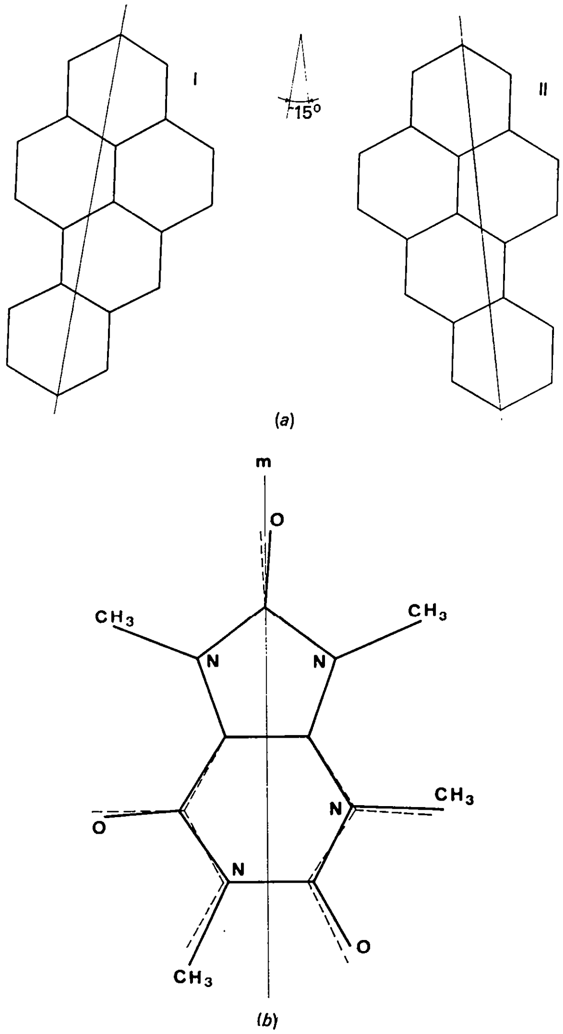

Fig. 1. (*a*) BP molecule. The direction of the pseudo binary axis existing in the Fourier transform at low sin θ/λ and the related approximate rotation in space are indicated. (*b*) The close similarity of space positions for two TMU molecules. Heavy lines: original position; dashed lines: position resulting from application of the pseudo twofold axis (vertical line).

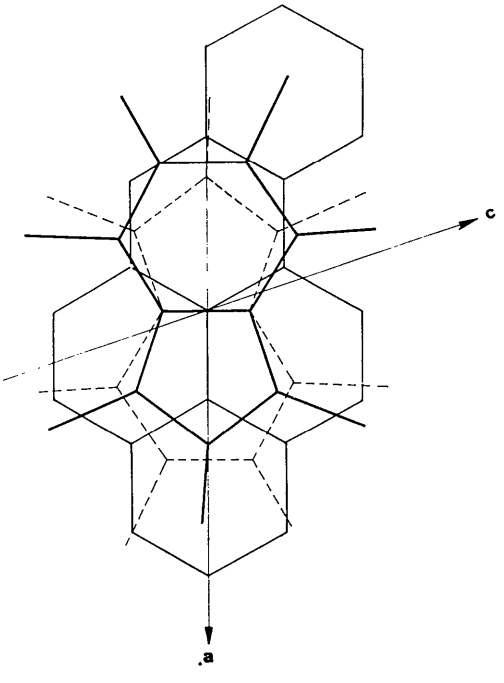

Fig. 2. The triplet of molecules on the *a*, *c* plane before application of rotation and translation ($X,Y,Z,\varphi,\theta,\chi$ coordinates all equal to 0).

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* These values are not far from the data of Iball & Young (1956).

† A cycle is defined through the following groups of operations: (*a*) translations of the first TMU molecule with computation of *R* in each point, (*b*) selection of the deepest minimum to define the new molecular position of the first TMU molecule, (*c*) repetition of the preceding operations for the second TMU molecule and then for the BP.

planes, are shown in Fig. 3(*a*). Similar plots for the other two orientations of the BP molecule 60° and 120° from the initial one are also shown in Fig. 3(*b*) and (*c*). φ, θ, χ, X, Y and Z coordinates of the molecules in the four minima are given in Table 2(*a*).

These plots fully support the preliminary remarks. The direction of elongation for BP was correctly derived and only ill defined minima appear for models with a wrong BP orientation. The long directions for the TMU molecules were also roughly correct, but no strong evidence supports one of the four possibilities [see minima of Fig. 3(*a*)] against the other.

To analyse this point further, rotation-translation cycles were carried out for all the models of Fig. 3 with $R < 0{\cdot}50$. For models with wrong BP orientation the 'minimum residual' never decreases to values lower than 0·40 and the analysis was henceforth restricted only to models in agreement with the preliminary deductions (ii). Rotations from −20° up to +20° with increments of 10° were allowed around the positions for each one of the three molecules of all the models. For all but one the improved value of R resulted in a rotational shift of the TMU toward the nearest of the four minima. The angular position of the BP remained

Table 1. *Rotations and translations of the* BP *and two* TMU *molecules*

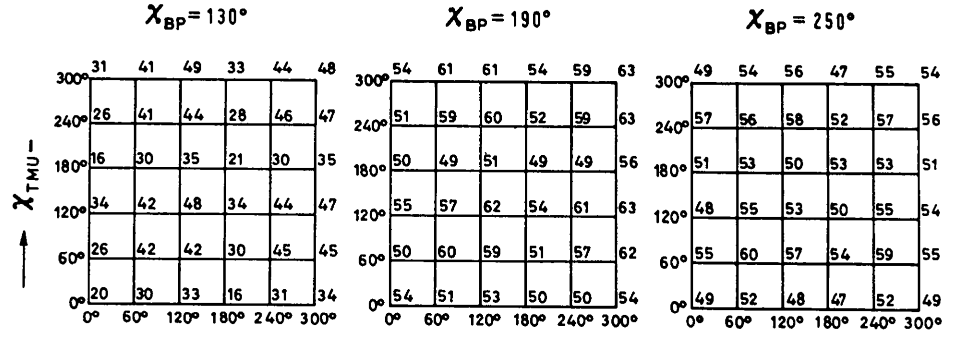
	φ	θ	χ	X	Y	Z
BP	300·0°	34·0°	130·0°	0·000	0·000	0·000
TMU₊	300·0	34·0	30·0	0·026	0·371	0·081
TMU₋	300·0	34·0	30·0	−0·026	−0·371	−0·081

Table 2. *Group parameters for the best models obtained with the use of* 60 *reflexions in each one of the four minima of Fig.* 4

Values of R correspond to the first computation with a group of 122 reflexions.

Part (*a*) refers to one of the orientations of the BP molecule of Fig. 1, (*b*) refers to the alternative orientation of Fig. 1. φ, θ, χ parameters in degrees. X, Y, Z crystal coordinates.

	(*a*)							(*b*)						
	φ	θ	χ	X	Y	Z	R	φ	θ	χ	X	Y	Z	R
BP	120·0	146·0	253·6	0·050	0·037	0·040		300·0	34·0	127·0	0·005	0·013	0·020	
TMU₊	118·7	147·4	149·0	0·010	0·402	0·119	0·230	120·0	146·0	152·0	−0·065	0·403	0·099	0·251
TMU₋	300·0	34·0	46·0	−0·124	−0·318	−0·019		120·0	146·0	310·0	−0·124	−0·319	−0·019	
BP	120·0	146·0	253·5	0·110	0·085	0·110		300·0	34·0	130·0	0·050	0·053	0·070	
TMU₊	300·0	34·0	46·0	0·040	0·388	0·089	0·259	118·2	149·2	309·5	−0·040	0·380	0·069	0·247
TMU₋	117·1	149·0	148·9	−0·154	−0·327	−0·049		120·0	146·0	150·2	−0·125	−0·318	−0·019	
BP	120·0	146·0	257·0	0·030	0·065	0·100		300·0	34·0	127·0	0·000	0·035	0·060	
TMU₊	297·8	33·1	51·9	0·010	0·365	0·059	0·300	297·7	35·7	54·9	0·010	0·364	0·059	0·295
TMU₋	120·8	148·5	325·8	−0·124	−0·319	−0·019		120·0	146·0	318·0	−0·114	−0·319	−0·019	
BP	120·0	146·0	253·7	0·050	0·085	0·130		300·0	34·0	130·0	0·000	0·045	0·080	
TMU₊	301·2	35·2	204·2	0·070	0·395	0·089	0·274	120·0	146·0	160·1	0·040	0·388	0·089	0·278
TMU₋	122·3	148·5	153·2	−0·094	−0·324	0·019		121·5	149·5	152·2	−0·094	−0·339	0·049	



$\chi_{BP} = 130°$

	0°	60°	120°	180°	240°	300°
300°	31	41	49	33	44	48
240°	26	41	44	28	46	47
180°	16	30	35	21	30	35
120°	34	42	48	34	44	47
60°	26	42	42	30	45	45
0°	20	30	33	16	31	34

$\chi_{BP} = 190°$

	0°	60°	120°	180°	240°	300°
300°	54	61	61	54	59	63
240°	51	59	60	52	59	63
180°	50	49	51	49	49	56
120°	55	57	62	54	61	63
60°	50	60	59	51	57	62
0°	54	51	53	50	50	54

$\chi_{BP} = 250°$

	0°	60°	120°	180°	240°	300°
300°	49	54	56	47	55	54
240°	57	56	58	52	57	56
180°	51	53	50	53	53	51
120°	48	55	53	50	55	54
60°	55	60	57	54	59	55
0°	49	52	48	47	52	49

(*a*) (*b*) (*c*)

Fig. 3. Two-dimensional nets of R values (computed by comparison with 30 reflexions) as a function of the rotational angles χ of the TMU molecules. The TMU on the plane at +3·4 Å from the origin is indicated with TMU₊, that on the plane −3·4 Å with TMU₋. Three orientations of the BP molecule are considered: $\chi_{BP} = 130°$(*a*), 190°(*b*), 250°(*c*). Translational coordinates are not indicated but correspond for all cases to the minimum reached after two translational cycles.

unmodified except in few cases where a rotation of +10° or −10° gave rise to better values of R. These models are indicated with + or − respectively in the level contour map of Fig. 4.

The R values for the four minima are so close that no conclusive deductions could be made at this stage; therefore we explored the alternative possibility for the BP molecule using the TMU of the four minima and modifying the BP through the variation of the Eulerian angles

$$\varphi'=\varphi+\pi;\ \theta'=\pi-\theta;\ \chi'=2\pi-\chi \qquad (1)$$

where φ,θ,χ are the first set and φ',θ',χ' the new one. Again we had four minima in a narrow range of R but with rotational shift of 20° in the orientations of BP [Table 2(*b*)]. This was in agreement with our expectation of an approximate coincidence of the long axes of the BP molecules. [Fig. 1(*a*)]. The last restriction made in the assumption of only one possibility for the TMU molecule was removed at this point, and the full set of 32 models thus generated from the preceding group of 8 was analysed allowing, in addition to the previous movements, oscillations around the axis normal to each molecular plane. In Table 3 are reported the number of reflexions used, the range of values of R, and the number of the models considered in the different steps of this second part of the analysis. From the last row of the Table it is possible to note that 15 models were clustered in the relatively restricted range from 0·28 to 0·36 and also if a difference of 0·08 in R could be considered meaningful a computation of intermolecular distances was estimated to be useful.

Table 3. *Range of R values and numbers of models using different possibilities for the* BP *molecule*

Number of reflexions	Range of R	Number of models	Upper limit of R*
60 (*t*)	0·17 − 0·24	32	
122 (*i*)	0·24 − 0·41	32	0·30
122 (*t*)	0·21 − 0·29	15	
742	0·28 − 0·36	15	

(*i*) Values at the beginning of the analysis.
(*t*) Values at the end of the analysis.
* Models with higher R values have not been analysed further.

This criterion allowed a further reduction in the possible number of models. Four models with a pseudo parallel arrangement of the TMU molecules had acceptable intermolecular contacts. Furthermore we considered also the possible effect of the H atoms on the low Bragg angle reflexions and introduced approximate anisotropic temperature factors for each one of the four kinds of atom. In this way the best R value decreased to 0·156, using the 103 reflexions now allowed by computer storage; with all the data the R value was 0·26 (Table 4). At this point of the analysis standard refinement techniques were introduced and the results obtained in this way are reported elsewhere (Damiani, Giglio, Liquori & Ripamonti, 1967).

Discussion

To understand this 'minimum residual' analysis and especially the permanence of 8 minima with small R differences we have to take the following into account.

The use of a mean isotropic temperature factor in the first stage of the analysis and, to a lesser extent, the exclusion of the H atoms, together with the low resolution of the experimental data and with the possibility of a large overlap for two TMU molecules centrosymmetrically arranged, contributed to a smeared picture of the minima and therefore increased the difficulty of the selection. Furthermore the reduced number of the collected data, less than 20% of the theoretically possible, can be interpreted as a consequence of strong thermal motion, as well as a consequence of some degrees of positional disorder within the molecular planes. This is further supported by the existence of large streaks corresponding to many strong reflexions of the molecular planes.

It seems to us that the results of this 'minimum residual' analysis with three-dimensional data are truly encouraging; not only can the analysis be carried out in a reasonable time with the use of few reflexions, but a more general comprehensive picture will eventually suggest possible alternatives to be taken into account.

In conclusion it is our opinion that this type of analysis to define the regions of minimum with very few reflexions can be successfully coupled with the computation of intermolecular distances and, at an advanced stage, of potential energy (Williams, 1965, 1966; Rabinovich & Schmidt, 1966; Giglio & Liquori, 1967). The allowed minima can then be explored with the 'rigid body refinement' of Scheringer (1963) to speed up the convergence procedure with an increased number of experimental data. Further work on this subject is now in progress.

APPENDIX I

Let m,n,p be running indices over the atoms of three (i,j,k) independent molecules in the unit cell of space group P_1.

The Fourier transform will be written:

$$F_{\mathrm{h}}=\Sigma_m f_m \exp 2\pi i(\mathbf{h}\,.\,\mathbf{r}_m) + \Sigma_n f_n \exp 2\pi i(\mathbf{h}\,.\,\mathbf{r}_n)+\Sigma_p f_p \exp 2\pi i(\mathbf{h}\,.\,\mathbf{r}_p)$$

Table 4. *φ,θ,χ, X,Y,Z values for the model with R*=15·6%

	φ	θ	χ	X	Y	Z
BP	120·8°	146·2°	255·6°	0·030	0·042	0·060
TMU_+	118·5	146·5	150·9	0·030	0·398	0·099
TMU_-	299·2	33·6	50·6	−0·124	−0·318	−0·019

where $\mathbf{r}_m \ldots$ are starting position vectors of the atoms in real space and $\mathbf{h}$ is a reciprocal space vector.

If i is the molecule undergoing translational movements with increments $\Delta\mathbf{r}$ we will reorganize the data as follows:

$$F_{\mathbf{h}} = F_{\mathbf{h},i} + F_{\mathbf{h},1}$$

with

$$F_{\mathbf{h},i} = \Sigma_m f_m \exp 2\pi i(\mathbf{h} \,.\, \mathbf{r}_m)$$

and

$$F_{\mathbf{h},1} = \Sigma_n f_n \exp 2\pi i(\mathbf{h} \,.\, \mathbf{r}_n) + \Sigma_p f_p \exp 2\pi i(\mathbf{h} \,.\, \mathbf{r}_p)\,.$$

After translation the new factors will be of the form:

$$F'_{\mathbf{h}} = F'_{\mathbf{h},i} + F_{\mathbf{h},1}$$

with

$$F'_{h,i} = F_{h,i} \exp 2\pi i(\mathbf{h} \,.\, \Delta\mathbf{r})\,,$$

where $\exp 2\pi i(\mathbf{h} \,.\, \Delta\mathbf{r})$ represents the fringe function.

APPENDIX II

We report the basic mathematical relationships used to perform the molecular movements

(*a*) *Definitions*

a Crystal system with axes $\mathbf{a}_1, \mathbf{a}_2, \mathbf{a}_3$ and interaxial angles $\alpha_1, \alpha_2, \alpha_3$.

$\mathbf{r}^{(n)}$ Vector defining the position of the nth atom in the system **a** (components $r_1^{(n)}, r_2^{(n)}, r_3^{(n)}$).

u Orthogonal unitary system with axes $\mathbf{u}_1, \mathbf{u}_2, \mathbf{u}_3$ rigidly connected to **a** as follows:

$\mathbf{u}_1 = \mathbf{a}_1$, $\mathbf{u}_2$ in the plane defined by $\mathbf{a}_1$ and $\mathbf{a}_2$,

$\mathbf{u}_3 = \mathbf{u}_1 \times \mathbf{u}_2$.

$\mathbf{x}^{(n)}$ Vector defining the position of the nth atom in the **u** system (components $x_1^{(n)}, x_2^{(n)}, x_3^{(n)}$).

v, **w** Orthogonal unitary systems with axes $\mathbf{v}_1, \mathbf{v}_2, \mathbf{v}_3$ and $\mathbf{w}_1, \mathbf{w}_2, \mathbf{w}_3$ rigidly connected to the molecule.

T Transformation matrix between the systems **a** and **u** through $\mathbf{a} = \mathbf{T}^{-1}\mathbf{u}$.

These rotation matrices are in agreement with the convention of Wilson, Decius & Cross (1955).

(*b*) No matrix transformation will be necessary for the translational movements, the coordinates being directly incremented in the crystal system. For a rigid rotation of the system **v** it is convenient to utilize **u** as a reference framework and therefore to express the rotations through the φ, θ, χ Eulerian angles.

The new crystal coordinates, except for a translational vector, are derived from the starting ones as:

$$\mathbf{r}^{(n)\prime} = (\mathbf{T}')(\mathbf{R})(\mathbf{T}')^{-1}\mathbf{r}^{(n)}$$

where the primed vector refers to the modified point in the crystal system and the primed matrix is the transpose of the given one.

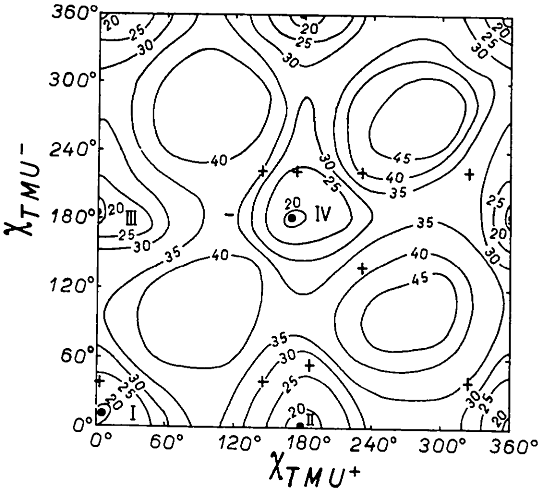


Fig. 4. Contour line map of R after a finer exploration of the positions of Fig. 3(*a*) ($\chi_{\rm BP} = 130°$). The values in the four minima are (I 18·1, II 15·7, III 16·4, IV 19·5). The − and + signs on the map correspond to $\chi_{\rm BP} = 120°$ and $\chi_{\rm BP} = 140°$ respectively. For these points better R values have been calculated than for the same TMU positions with $\chi_{\rm BP} = 130°$, but these points are generally far away from the minima.

$$\mathbf{T} = \begin{pmatrix} (a_1)^{-1} & 0 & 0 \\ -(a_1 \tan \alpha_3)^{-1} & (a_2 \sin \alpha_3)^{-1} & 0 \\ (a_1 \tan \alpha'_1 \tan \alpha_3)^{-1} - (a_1 \tan \alpha_2 \sin \alpha'_1)^{-1} & -(a_2 \sin \alpha_3 \tan \alpha'_1)^{-1} & (a_3 \sin \alpha_2 \sin \alpha'_1)^{-1} \end{pmatrix},$$

$$\mathbf{T}^{-1} = \begin{pmatrix} a_1 & 0 & 0 \\ a_2 \cos \alpha_3 & a_2 \sin \alpha_3 & 0 \\ a_3 \cos \alpha_2 & a_3 \cos \alpha'_1 \sin \alpha_2 & a_3 \sin \alpha'_1 \sin \alpha_2 \end{pmatrix}$$

where α'_1 is defined by

$$\cos \alpha'_1 = (\cos \alpha_1 - \cos \alpha_2 \cos \alpha_3)/(\sin \alpha_2 \sin \alpha_3)$$

R, **S** Eulerian matrices defining the transformation between the **u**, **v** and **v**, **w** systems through $\mathbf{u} = \mathbf{R}\mathbf{v}$ and $\mathbf{v} = \mathbf{S}\mathbf{w}$.

If it is desired to analyse a region in the neighbourhood of a group of parameters φ, θ, χ, this can be carried out by rotating the system **w** referred to the system **v** as fixed.

The Cartesian coordinates of the model are now fixed in the **w** system and with reference to the **u** system they will be $\mathbf{x}^{(n)\prime} = \mathbf{R}\mathbf{S}\mathbf{x}^{(n)}$ and therefore the new crystal coordinates are:

$$\mathbf{r}^{(n)\prime} = (\mathbf{T}')\mathbf{R}\mathbf{S}(\mathbf{T}')^{-1}\mathbf{r}^{(n)}\,.$$

$$\mathbf{R} = \begin{pmatrix} (\cos \varphi \cos \theta \cos \chi - \sin \varphi \sin \chi) & (\sin \varphi \cos \theta \cos \chi + \cos \varphi \sin \chi) & (-\sin \theta \cos \chi) \\ (-\cos \varphi \cos \theta \sin \chi - \sin \varphi \cos \chi) & (-\sin \varphi \cos \theta \sin \chi + \cos \varphi \cos \chi) & (\sin \theta \sin \chi) \\ (\cos \varphi \sin \theta) & (\sin \varphi \sin \theta) & (\cos \theta) \end{pmatrix}$$

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Seemann–Bohlin X-Ray Diffractometry. I. Instrumentation*

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The principles of using a counter tube diffractometer in the Seemann–Bohlin focusing arrangement are described. Simultaneous focusing of all reflections makes it possible to employ several detectors, and the stationary specimen simplifies the design of chambers to modify environmental conditions. Changing the specimen position to achieve a different angular range requires rotating the X-ray tube or goniometer around the X-ray tube focus. The diffracted intensity varies along the specimen length owing to the varying angle-of-view of the anode and the varying mean angle of incidence but does not affect the quality of the focusing. The resolution and intensity are dependent on the source and receiving apertures. The receiving slit may be pointed toward the middle of the curved specimen surface so that the aperture decreases with increasing θ, or toward the center of the goniometer to achieve a constant aperture.

Introduction

The principle of X-ray focusing, in which the incident divergent beam is reflected from a stationary curved specimen and all reflections occur simultaneously focused on the circumference of a focusing circle containing the source, specimen surface and cylindrical film, was first applied to X-ray powder cameras by Seemann (1919) and Bohlin (1920). In practice the advantage of the high intensities inherent in this focusing geometry was usually outweighed by the inaccessible low-angle region, the limited angular range that could be photographed with one setting and the broadening caused by inclination of the reflected beam to the film. Aside from occasional uses in metallurgical laboratories and the application to symmetrical back-reflection focusing cameras, the method was never as widely used as the Debye–Scherrer–Hull method. However, the use of a focusing crystal monochromator in conjunction with the Seemann–Bohlin (S–B) geometry has been used in a number of cameras, as for example, Guinier (1939), de Wolff (1948), Hofmann & Jagodzinski (1955).

The use of a counter tube detector in conjunction with the S–B geometry makes it possible to eliminate some of the difficulties of the S–B film methods and also offers some attractive new possibilities. The major potential advantages over the conventional diffractometer which prompted this study are: (*a*) simultaneous

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