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Experience with the Method of Systems of Linear Structure-Factor Equations

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Dedicated to Professor K. Dornberger-Schiff on her 60*th birthday*

Five cases, two of them acentric, in which the use of the method of systems of linear structure-factor equations facilitates the determination of the approximate structure are discussed. Starting from the atomic positions known in one projection, the method gives the values of the third coordinates using the data from only one level of reciprocal space, and proves successful especially in cases where projections along other axes turn out to be badly resolved due to overlapping. The method may also be used to distinguish between those maxima of a minimum function which correspond to atomic positions and those which do not. All calculations needed for this method can be performed on a small computer which is not sufficient for three-dimensional Fourier or least-squares calculations. On a large computer the computer time required for the method is about half the time needed for one least-squares cycle.

Introduction

The method of systems of linear structure-factor equations (SFE) (Kutschabsky & Höhne, 1965; Kutschabsky, 1965) has been applied to various problems arising in the course of structure determinations of several substances. The experience gained is to be discussed in this paper. Starting from the atomic positions known in one projection, the method gave the values of the third coordinates with a comparatively small amount of computing time – hardly longer than needed for the calculation of an electron density projection and the preceding structure factor calculation. The method proved useful in rationalizing the procedures of structure determination especially in cases where generalized Patterson projections and projections along other axes turned out to be badly resolved due to overlapping. As experience shows, the data from few levels or even one level of reciprocal space suffice to obtain values of the coordinates in the third direction. The accuracy of these values is higher than the accuracy obtainable from the same data by Fourier methods. The SFE method may help to shorten the time needed for structure determination by giving relatively accurate atomic parameters even before full three-dimensional data are available for refinement.

The SFE method may also be used to distinguish between those maxima of a minimum function which correspond to atomic positions and those which do not. In some cases information decisive for the determination of the approximate structure has been obtained with the help of this method, information which would have been difficult to obtain by other methods. All calculations needed for this method can be performed on a small computer which is not sufficient for three-dimensional Fourier or least-squares calculations.

Determination of the real structure from an average structure (acetamide hemihydrobromide)

Crystal data of $(CH_3CONH_2)_2HBr$ (Reck 1969):

$a=6{\cdot}51$ Å $\quad P2_1/c$
$b=8{\cdot}64$
$c=8{\cdot}24 \quad Z=2$
$\beta=113{\cdot}1°$

In this structure the bromine atoms lie at centres of symmetry forming, taken by themselves, an *A*-centred lattice. With the help of the contributions of the bromine atoms most of the signs of the $F(h0l)$ could be determined and the x and z coordinates of all atoms except the hydrogen atoms were obtained from the electron density projection $\Delta\varrho(xz)$ (Fig. 1), but it was impossible at this stage to distinguish between C, N and O. Therefore the atoms are denoted by numbers. Three methods were tried for the determination of the y coordinates at a time when full three-dimensional data were not yet available:

(*a*) Fourier synthesis $\varrho(yz)$ using the signs of the Br contribution.
(*b*) Generalized Patterson projection using the $|F(h1l)|^2$.
(*c*) The SFE method.

(*a*) The bromine atoms contribute only to the $0kl$ with $k+l=2n$ and these structure factors were used for the calculation of an average structure $\hat{\varrho}(yz)$ (Fig. 2). But the projection is so badly resolved that the atomic positions could not be determined, even if the known configuration of the molecule was taken into account.

(*b*) Neither was it possible to determine the y coordinates from a generalized Patterson projection.

(*c*) For the SFE method two sets of equations were obtained:

$$F(h1l)_{l=2n+1}= \alpha\sum_j 4f_j \cos 2\pi(hx_j+lz_j) \cos 2\pi y_j \qquad (1)$$

and

$$F(h1l)_{l=2n}= -\alpha\sum_j 4f_j \sin 2\pi(hx_j+lz_j) \sin 2\pi y_j \qquad (2)$$

where α is the scaling factor. The expressions $\cos 2\pi(hx_j+lz_j)$ and $\sin 2\pi(hx_j+lz_j)$ may be calculated because x_j and z_j are known, whereas $\alpha \cos 2\pi y_j$ and $\alpha \sin 2\pi y_j$ are the unknown variables. With the help of the bromine atom most of the signs of the $F(h1l)$ with $l=2n+1$ could be determined and a system of equations of the first type (1) with a twelve-fold redundancy could be set up

$$F(h1l)_{l=2n+1}=\sum_j a_j(h1l)\, C'_j \qquad (3)$$

with the abbreviations $a_j(h1l)=4f_j \cos 2\pi(hx_j+lz_j)$ and $C'_j=\alpha \cos 2\pi y_j$. As in the following cases this system of equations was solved by a least-squares method. Because the $F(h1l)$ are on a relative scale, the solutions C'_j and S'_j were multiplied with a constant $1/\alpha$ so that $|(1/\alpha)\, C'_{\rm Br}|=1$ holds. Two values $y_j=y_{j0}$ and $y_j=1-y_{j0}$, say, are in keeping with the solutions $C_j=(1/\alpha)C'(y_{j0})$ obtained. In order to find out which of these values is correct, equations of the type (2) were used

$$F(h1l)_{l=2n}=\sum_j b_j(h1l)S'_j \qquad (4)$$

with $b_j(h1l)=-4f_j \sin 2\pi(hx_j+lz_j)$ and $S'_j=\alpha \sin 2\pi y_j$.

The bromine atoms give no contributions to the $F(h1l)$ with $l=2n$. Therefore the signs of these structure factors were unknown and the unobserved reflexions and one strong structure factor with an arbitrary sign were used for setting up the system of equations. The $S_j=(1/\alpha)S'_j$ were less accurate than the C_j because the system for computing the S_j had only a twofold redundancy. Therefore the y coordinates were calculated from the C_j but the ambiguity was eliminated by the S_j. The results are shown in Table 1 and Fig. 2. In Fig. 2 the atomic positions obtained from the systems of equations and marked by crosses are compared with the refined values marked by squares.

Determination of small deviations of light atoms from a pseudo mirror plane

In the course of the structure determination of 3-*N*-dimethylaminomethylpinene 2(10)-hydrobromide (Kutschabsky, 1969) we came acros ssuch a problem. Lattice constants:

$a=11{\cdot}373$ Å
$b=\ 8{\cdot}620$
$c=\ 7{\cdot}476$
$\beta=97{\cdot}42°$.

The unit cell contains two units of $C_{13}H_{24}BrN$. The space group is $P2_1$. The x and z parameters of the bromine atom were determined from the Patterson projection $P(uw)$ and refined by Fourier syntheses. The y coordinate of the bromine atom was chosen equal to $\frac{1}{4}$ and thus the Br atoms lie centrosymmetrically to the origin.

The three-dimensional electron density distribution based on the phases of the $F_{\rm obs}(hkl)$ derived from the bromine contributions had therefore a pseudo mirror plane at $y=\frac{1}{4}$. For the calculation of this synthesis only $F_{\rm obs}(hkl)$ with $0\le k\le 4$ were available. The three-dimensional electron density revealed the positions of all atoms except hydrogen atoms, most of them clearly resolved in the x and z directions. Nearly all these atoms are, however, located so closely to the pseudo mirror plane that the maximum corresponding to one atom and its mirrored mate were not separated but formed an elliptical maximum with its highest value lying on the mirror plane (Fig. 3). The determination of the deviations from the mirror plane by analysing the shape of the maxima gave rather inaccurate values.

Since all atoms are resolved in the x,z projection the attempt was made to obtain the y parameters by the SFE method. To start with, the positions of all

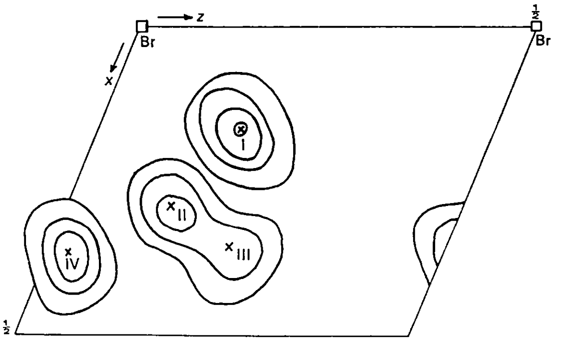

Fig. 1. Electron density projection $\Delta\varrho(xz)$ of acetamide hemihydrobromide.

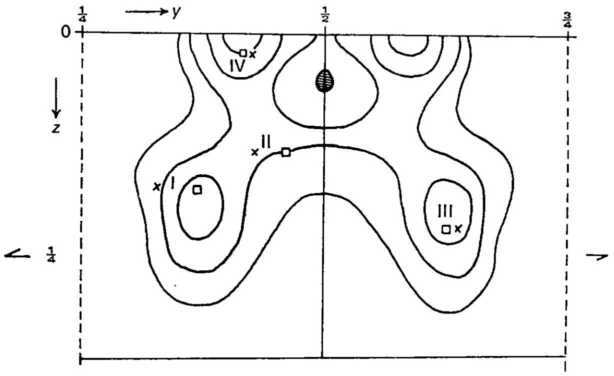

Fig. 2. The average structure $\bar{\varrho}(yz)$ of acetamide hemihydrobromide calculated only with $F_{\rm obs}(0kl)$ for $k+l=2n$. Atomic positions obtained with the help of SFE are marked by crosses, the refined positions are marked by squares.

atoms were refined by difference Fourier syntheses in the x,z projection (Fig. 4) to an R value of 0·16. Using the formulae

$$A_{\text{obs}}(h2l)=\alpha \sum_j 2f_j \cos 2\pi(hx_j+lz_j) \cos 2\pi 2y_j \quad (5)$$

and

$$A_{\text{obs}}(h3l)=\beta \sum_j -2f_j \sin 2\pi(hx_j+lz_j) \sin 2\pi 3y_j \quad (6)$$

where α and β are the scaling factors, two systems of equations were obtained taking $|A_{\text{obs}}(hkl)|$ equal to $|F_{\text{obs}}(hkl)|$. This may be done without creating large errors since the $B_{\text{obs}}(hkl)$ are expected to be small for nearly all structure factors because the Br atoms do not contribute to them. In the systems of equations only those $A_{\text{obs}}(hkl)$ were used, whose signs could be deduced from the contributions $\text{F}_{\text{Br}}(hkl)$ of the bromine atom.

With the abbreviations

$$\begin{aligned} 2f_j \cos 2\pi(hx_j+lz_j) &= a_j(h2l) \\ -2f_j \sin 2\pi(hx_j+lz_j) &= b_j(h3l) \\ \alpha \cos 2\pi 2y_j &= C_j^{(2)\prime} \\ \beta \sin 2\pi 3y_j &= S_j^{(3)\prime} \end{aligned}$$

the systems of equations have the form

$$F_{\text{obs}}(h2l)=\sum_j a_j(h2l)C_j^{(2)\prime} \quad (7)$$

$$F_{\text{obs}}(h3l)=\sum_j b_j(h3l)S_j^{(3)\prime} \quad (8)$$

Because $F_{\text{obs}}(h2l)$ and $F_{\text{obs}}(h3l)$ are on a relative scale, the solutions $C_j^{(2)\prime}$ and $S_j^{(3)\prime}$ obtained by a least-squares method were multiplied by constants $1/\alpha$ and $1/\beta$ so that $|(1/\alpha)C_{\text{Br}}^{(2)\prime}|=|(1/\beta)S_{\text{Br}}^{(3)\prime}|=1$ holds. Four values for the coordinate y_j of each atom are in keeping with $C_j^{(2)}=(1/\alpha)C_j^{(2)\prime}(y_{j0})$ namely $y_j=\pm y_{j0}$, $y_j=\pm y_{j0}+\frac{1}{2}$. Two of these values for each atom could be excluded by comparison with the positions of the maxima in the three-dimensional Fourier synthesis. The remaining values for the y coordinates are listed in column 4 of Table 2. Using a model of the structure and under the assumption that the molecule has a conformation similar to that of 3-*N*-methylaminomethylpinane hydrobromide (Reck & Kutschabsky, 1970) one of the two remaining y coordinates could be excluded for most of the atoms. The remaining possible values are marked with an asterisk in column 4 of Table 2. The accuracy of the y coordinates obtained from the $C_j^{(2)}$ was improved using the values obtained from $S_j^{(3)}=(1/\beta)S_j^{(3)\prime}(y_{j0})$. Compatible with these are six values: $y_j=\frac{3}{12}\pm(\frac{1}{4}-y_{j0})$; $y_j=\frac{7}{12}\pm(\frac{1}{4}-y_{j0})$; $y_j=\frac{11}{12}\pm$

Table 1. *Values for C_j and S_j obtained from* SFE *and the deduced y coordinates*

	C_j	y_j possible	S_j	y_j realized	y_j final
I=N	−0·290	0·326 or 0·674	0·480	0·326 (30)	0·367 (8)
II=C(1)	−0·583	0·423 or 0·577	0·392	0·423 (30)	0·459 (8)
III=C(2)	−0·865	0·411 or 0·589	−0·368	0·589 (30)	0·620 (8)
IV=O	−0·960	0·415 or 0·585	0·460	0·415 (30)	0·415 (8)

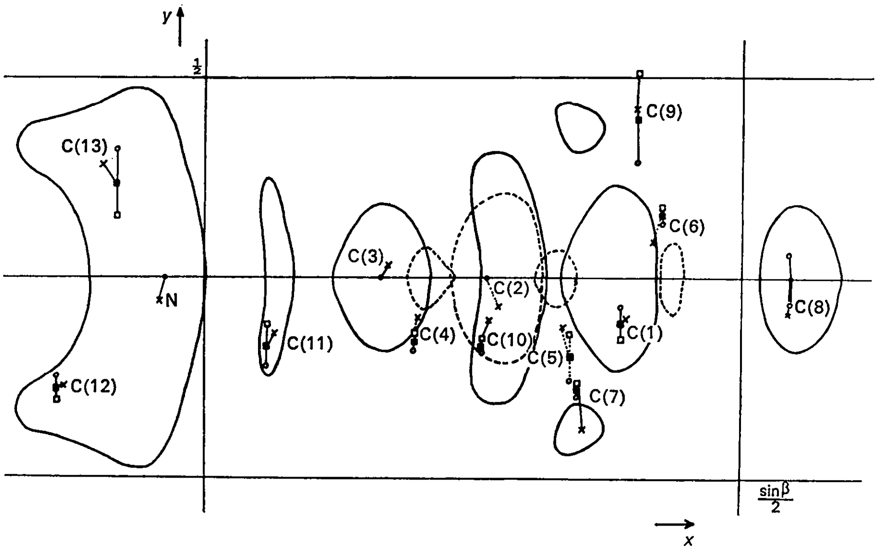

Fig. 3. Comparison of the composite three-dimensional electron density projected along [001] (only one full or dashed contour of the same height at arbitrary level is drawn) of atomic positions obtained by SFE (results from $F(h2l)$ are marked by open circles, from $F(h3l)$ by open squares, average values solid) and of the positions obtained by least-squares refinement marked by crosses.

$(\frac{1}{4}-y_{j0})$. For each atom those two values for the y coordinates are given (Table 2, column 5) which deviate least from the approximate coordinates derived from $C_j^{(2)}$ (Table 2, column 4). The values deviating least from the italicized values of the preceding column 4 are also italicized and used together with the italicized values of column 4 to obtain the mean values $\langle y_j \rangle$. Only for atom C(9) has the value with the larger deviation been italicized and used for the calculation of the mean value because otherwise an impossible bond length would have resulted. The atomic positions in the x,y projection obtained by the SFE-method are shown in Fig. 3. The mean values $\langle y_j \rangle$ and the x and z coordinates determined from the x,z projection were used as starting point for an isotropic least-squares (LS) refinement by a block-diagonal program. Whereas the discrepancy factor for the Br atoms only was $R_{hkl}^{(\mathrm{Br})}=0{\cdot}32$, it was $R_{hkl}^{(\mathrm{SFE})}=0{\cdot}18$ for all atoms with coordinates $\langle y_j \rangle$ and dropped to $R_{hkl}^{\mathrm{LS}}=0{\cdot}106$ during the refinement. 360 reflexions (unobserved included) were used. The final y coordinates are listed in the last column of Table 2.

Application of the method of systems of linear structure factor equations for the first stages of refinement

In the course of the determinations of the structures of three organic dyes we came across the following situation. In all three cases one of the lattice constants, chosen as a, is less than 4 Å, b and c are between 7 and 12 Å (Table 3). Accordingly in the y,z projections all atoms (except hydrogen atoms which will be left out of account in the following) are well resolved and these projections of the structures had been solved and fairly good y and z coordinates of the atoms obtained by conventional Fourier methods. Approximate x coordinates of the atoms had been obtained from Patterson and electron density projections on the xy or xz plane. However, owing to overlapping of most of the atoms in these projections, the x coordinates were rather inaccurate, (Table 4). For reasons of economy of time and expense we used the SFE method to determine x coordinates of the atoms with higher accuracy (to be used as a starting point for least-squares refinement) even while the collection of three-dimensional data was still in progress. In all three cases the systems of equations were derived from structure factor formulae written as follows:

$$F_{\mathrm{obs}}(Hkl)=\sum_j \left[a_j(ky_j,lz_j)\cos 2\pi Hx_j + b_j(ky_j,lz_j)\sin 2\pi Hx_j\right]. \quad (9)$$

The coefficients a_j and b_j were calculated using the known y,z coordinates while $\cos 2\pi Hx_j$ and $\sin 2\pi Hx_j$ were taken as independent variables. For each $F_{\mathrm{obs}}(Hkl)$ with vanishing intensity and for each $F_{\mathrm{obs}}(Hkl)$ for which the sign could be determined using the approximate x coordinates, an equation was set up. The scaling was performed by comparison of the values F_{calc} with the F_{obs} values. In this way systems of equations were obtained. Each of the systems of equations consists of equations with H=constant. From the solutions $C_j^{(H)}=\cos 2\pi Hx_j$ and $S_j^{(H)}=\sin 2\pi Hx_j$ for $H=1,2,3,4$ (structure I), $H=1,2$ (structure II), and $H=1,2,3$ (structure III) improved x coordinates were obtained. These coordinates were used together with the y,z coordinates to determine the signs of more $F_{\mathrm{obs}}\neq 0$. These F_{obs} were used in addition to the struc-

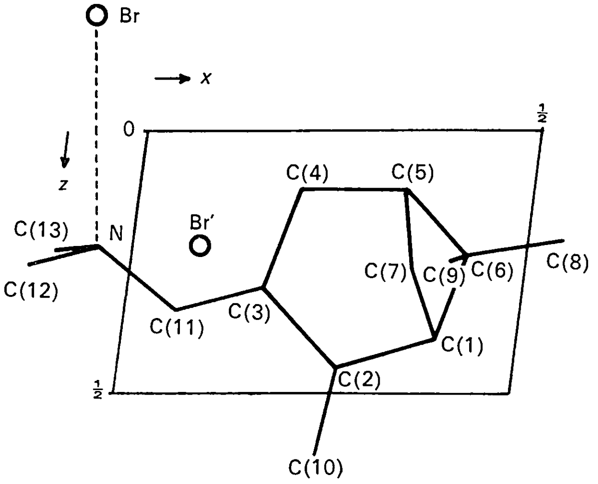

Fig. 4. Crystal structure of 3-*N*-dimethylaminomethylpinene 2(10)-hydrobromide looking down the [010] axis.

Table 2. *Comparison of fractional positional coordinates obtained from* SFE *and least-squares refinement*

	$C_j^{(2)}$	$S_j^{(3)}$	y_j from $C_j^{(2)}$	y_j from $S_j^{(3)}$	$\langle y_j \rangle$	y_j from LS
N	−1·033	0·210	*0·250*	0·155 or 0·345	0·250 (25)	0·216 (6)
C(1)	−0·878	−0·134	*0·210* or 0·290	*0·174* or 0·326	0·192 (16)	0·197 (7)
C(2)	−1·229	−0·660	*0·250*	0·205 or 0·295	0·250 (28)	0·211 (8)
C(3)	−1·320	−0·253	*0·250*	0·180 or 0·320	0·250 (24)	0·263 (9)
C(4)	−0·392	−0·205	*0·158* or 0·342	*0·178* or 0·322	0·168 (20)	0·196 (7)
C(5)	0·027	−0·214	*0·123* or 0·377	*0·178* or 0·322	0·151 (20)	0·185 (6)
C(6)	−0·654	0·125	0·182 or *0·318*	0·160 or *0·340*	0·329 (24)	0·290 (10)
C(7)	0·292	0·800	*0·103* or 0·398	0·049 or *0·117*	0·110 (28)	0·056 (13)
C(8)	−0·916	−0·360	*0·217* or *0·283*	*0·186* or *0·314*	0·250 (30)	0·220 (9)
C(9)	0·223	−0·206	0·107 or *0·393*	0·322 or *0·511*	0·452 (25)	0·461 (10)
C(10)	−0·387	−0·110	*0·156* or 0·344	*0·172* or 0·328	0·164 (22)	0·192 (8)
C(11)	−0·132	−0·420	*0·136* or 0·364	*0·190* or 0·310	0·163 (15)	0·179 (5)
C(12)	0·003	1·200	*0·125* or 0·375	*0·086*	0·105 (15)	0·108 (9)
C(13)	0·414	−0·160	0·091 or *0·409*	*0·325* or 0·511	0·367 (20)	0·385 (9)

ture factors used in the previous calculations. In this way the redundancy of the systems of equations was increased and thereby the accuracy of the values for the third coordinates was still further improved. The final values obtained by averaging after two or three cycles are listed in Table 4 (denoted by x_{SFE}). These parameters were much more accurate than the values obtained by Fourier methods (Table 4). The standard

Table 3. *Crystal data of three organic dyes*

I.	3,6-Dichloro-2,5-diamino-1,4-benzoquinone	Kulpe (1969*a*); Kulpe, Leupold & Dähne (1966)
II.	3,6-Dichloro-2,5-bis(methylamino)-1,4-benzoquinone	Kulpe (1969*b*)
III.	Dipotassium salt of 2,5-dihydroxy-1,4-benzoquinone	Kulpe & Dähne (1968)

	Substance	Space group	a	b	c	α	β	γ	Z
I.	$C_6O_2Cl_2(NH_2)_2$	$P2_1/n$	3·787 Å	10·771 Å	9·305 Å	90°	97·2°	90°	2
II.	$C_8N_2O_2Cl_2H_8$	$P\bar{1}$	3·892	9·404	7·514	89·32	117·12	105·86	1
III.	$C_6O_4H_2K_2$	$P2_1/n$	3·922	11·239	9·922	90	104·36	90	2

Table 4. *Comparison between the x coordinates obtained by Fourier methods, by* SFE *and by least-squares refinement*

Standard deviations are given in parentheses.

x	Fractional positional coordinates
F	Fourier methods
SFE	Systems of structure factor equations
LS	Least squares
R_{LS}	Final discrepancy index after least-squares refinement
Number of $F_{\mathrm{obs}}(hkl)$	Number of independent $F_{\mathrm{obs}}(hkl)$ including $F_{\mathrm{obs}}(hkl)=0$.

Substance (Table 3)		x_{F}	x_{SFE}	x_{LS}	R_{LS}	Number of $F_{\mathrm{obs}}(hkl)$
I	Cl	0·216	0·192 (2)	0·1905 (4)	0·076	740
	O	0·178	0·131 (4)	0·1317 (10)		
	N	0·334	0·314 (4)	0·3123 (13)		
	C(1)	0·122	0·097 (4)	0·0674 (13)		
	C(2)	0·085	0·149 (4)	0·1572 (14)		
	C(3)	0·101	0·078 (4)	0·0879 (13)		
II	Cl	0·000	−0·020 (2)	−0·0220 (4)	0·102	880
	O	0·000	−0·010 (5)	−0·0218 (13)		
	N	0·000	0·019 (5)	0·0273 (14)		
	C(1)	0·000	0·003 (5)	−0·0073 (15)		
	C(2)	0·000	−0·012 (5)	−0·0125 (14)		
	C(3)	0·000	0·008 (5)	0·0120 (14)		
	C(4)	0·000	0·065 (5)	0·0468 (19)		
III	K	0·265	0·276 (2)	0·2781 (3)	0·082	770
	O(1)	−0·165	−0·145 (5)	−0·1463 (10)		
	O(2)	0·225	0·222 (5)	0·2292 (11)		
	C(1)	−0·123	−0·095 (6)	−0·0861 (13)		
	C(2)	0·170	0·143 (6)	0·1327 (13)		
	C(3)	0·215	0·206 (6)	0·2039 (14)		

Table 5. *The values G_j obtained from* SFE *for the atomic positions gained from $M_2(xyz)$*

The refined parameters are also listed.

		Parameters from $M_2(xyz)$			Refined parameters		
Position	G_j	x_j	y_j	z_j	x_j	y_j	z_j
0′	1	0·015	0·080	0·976	0·0405	0·0794	0·9846
0″	1	0·985	0·920	0·024	0·9595	0·9206	0·0154
1′	0·68	0·904	0·252	0·195	—	—	—
1″	—	0·096	0·748	0·805	0·0944	0·7488	0·8117
2′	0·64	0·998	0·303	0·760	—	—	—
2″	—	0·002	0·697	0·240	0·0067	0·6960	0·2478
3′	0·65	0·477	0·404	0·301	—	—	—
3″	—	0·523	0·596	0·699	—	—	—
4′	0·45	0·571	0·456	0·864	—	—	—
4″	—	0·429	0·544	0·136	—	—	—
5′	0·91	0·567	0·369	0·899	0·5340	0·3724	0·9180
5″	—	0·433	0·631	0·101	—	—	—
6′	0·81	0·536	0·208	0·936	0·5706	0·2142	0·9573
6″	—	0·464	0·792	0·064	—	—	—

deviations of the x_F and the x_{SFE} are given in Table 4. For each structure the computer time required for the calculation of the atomic coordinates in the x direction by the SFE method was about half the time needed for one least-squares cycle.

Determination of the positions of an unknown number of heavy atoms (*trans*-8,8-dibromo-1,4,4-trimethyltricyclo-[5,1,0,0^{3,5}]octane)

Unit-cell dimensions and space group (Reck, 1969):

$$\begin{array}{lll} a = 7{\cdot}25\ \text{Å} & \alpha = 96{\cdot}7^\circ & \\ b = 19{\cdot}38 & \beta = 91{\cdot}3 & P1 \\ c = 6{\cdot}38 & \gamma = 93{\cdot}0 & \end{array}$$

The number of molecules $C_{11}H_{16}Br_2$ and thus of heavy atoms per unit cell could not be deduced from the density which was too difficult to obtain. Each molecule contains two bromine atoms attached to one and the same carbon atom.

The three-dimensional Patterson-synthesis showed quite a number of strong maxima which could possibly be Br–Br vectors. To start with, a minimum function $M_2(xyz)$ was prepared (Fig. 5). A shift vector was selected which, judging from its length, could be assumed to link two bromine atoms attached to the same carbon atom. This minimum function contained, apart from the pair 0′,0″ across the shift vector three further pairs of strong maxima with a distance corresponding to the distance between bromine atoms attached to the same carbon atom, as well as their centrosymmetric mates.

This relatively small number of prominent peaks indicated that the shift vector chosen was indeed a Br–Br vector. On the other hand, it was suspected that not all these pairs of maxima actually correspond to bromine atoms. The SFE method was used in order to find at least one more bromine position to make a minimum function of higher order. Thus, neglecting the contribution of all atoms except the Br atoms, and using only reflexions too weak to be observed, a system of equations was obtained of the form

$$\frac{F_{\text{obs}}(hkl)}{f_{\text{Br}}} = \sum_j \exp\{2\pi i(hx_j + ky_j + lz_j)\} G_j = 0 \qquad (10)$$

where x_j, y_j, z_j denote the coordinates of positions which, according to the minimum function, could possibly be atomic positions, G_j denotes a variable of value 1 or 0 depending on whether the position j is occupied by a Br atom or not, respectively. The two positions (0′) and (0″) coinciding with the origins of the two Patterson projections were taken to be occupied with certainty and the corresponding G_j values were taken as equal to 1. The set of equations (10) was then used to obtain G_j values for the positions for which it was uncertain whether they correspond to atomic positions or not. The positions of three pairs were numbered 1′ to 6′ and the corresponding G values denoted by G'_j, the positions related to them by the artificial centre of symmetry of the minimum function are denoted by 1″ to 6″ and the corresponding G values denoted by G''_j. Then from (10)

$$\begin{aligned} \frac{F_{\text{obs}}(hkl)}{f_{\text{Br}}} &= 2\cos 2\pi(hx_0 + ky_0 + lz_0) \\ &+ \sum_{j=1}^{6} G'_j \exp\{2\pi i(hx_j + ky_j + lz_j)\} \\ &+ \sum_{j=1}^{6} G''_j \exp\{-2\pi i(hx_j + ky_j + lz_j)\} = 0. \qquad (11) \end{aligned}$$

Because of the approximate nature of the equations (only approximate values of coordinates, neglect of light atoms, structure factors only approximately equal to zero) G_j values obtained from these equations may only be expected to be approximately equal to zero or one. The real part and the imaginary part must vanish separately. Using the real part

$$\begin{aligned} &\sum_{j=1}^{6} G_j \cos 2\pi(hx_j + ky_j + lz_j) \\ &\qquad = -2\cos 2\pi(hx_0 + ky_0 + lz_0) \qquad (12) \end{aligned}$$

where $G_j = G'_j + G''_j$. The G_j values obtained for the positions of the $M_2(xyz)$ are shown in Table 5. For comparison the refined positional parameters are also listed in the Table 5. The maxima 0′,0″; 1′,2′; 3′,4′; and 5′,6′ form pairs with a distance corresponding to pairs of bromine atoms attached to a carbon atom and so do the corresponding double-dashed positions. The largest G_j values were obtained for the maxima 5′ and 6′, *i.e.* for one of these pairs. Therefore it was assumed that the maxima 0′,0″, 5′ and 6′ (or 0′,0″, 5″ and 6″, *i.e.* the enantiomorphous arrangement) correspond to relative positions of four bromine atoms. An $M_4(xyz)$ was then constructed corresponding to these four Br atoms in which the following pairs of Br atoms show up: (0′,0″), (1″,2″), (5′,6′). Neither of the maxima 4′ and 4″ was visible. Therefore it was

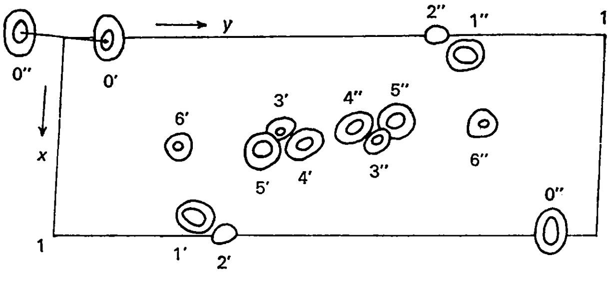

Fig. 5. Composite drawing of the minimum function $M_2(xyz)$ of *trans*-8,8-dibromo-1,4,4-trimethyltricyclo[5,1,0,0^{3,5}]octane.

expected, that the maxima 4′, 4″, 3′ and 3″ which form two pairs might not correspond to bromine atoms. This is not astonishing in view of the fact that the value G_4 is the smallest of all G_j values. The six bromine atoms found were taken as a starting point for a three-dimensional Fourier synthesis with cycles of refinement following. These confirmed the correctness of the conclusions arrived at by the SFE method.

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Application of the Hankel Transform Method in Small-Angle X-ray Scattering for the Study of the Internal Structure of Tobacco Mosaic Virus

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A method developed earlier [Fedorov & Aleshin (1966) *Vysokomol. Soed.* **8**, 5016; translated into English in *Polymer Sci. USSR* (1967) **8**, 1657] which permits the determination of the radial electron density distribution function of cylinders on the basis of the small-angle scattering curve, is applied to the study of the tobacco mosaic virus structure. The results obtained are in good agreement with the X-ray structural analysis of TMV. Questions concerning the extrapolation of the experimental curve, the estimation of the obtained resolution of electron density as well as the possibilities of this method are also considered.

Introduction

Over a period of some years different authors have analysed the angle distribution of intensity of small-angle X-ray diffuse scattering by cylindrical unoriented particles. From some peculiarities of the scattering curve a number of methods of treating small-angle X-ray data were suggested to obtain the main parameters characterizing the cylinder. The most widely known methods are Kratky's method (Kratky & Porod, 1948; Porod, 1948) based on the use of a 'point' collimation and Luzzati's method (Luzzati, 1960; Luzzati, Mathis, Masson & Witz, 1964) which suggests the existence of an 'infinitely' high collimation slit. Both techniques analyse the same section of the scattering curve by a long rigid particle and give similar information on its structure (the electronic radius of gyration of the cylinder with respect to its axis R_q). Kratky's method consists of rearranging the experimental curve into coordinates of log $[I(\theta)\theta]$ *vs* θ^2 ($I(\theta)$ being the scattering intensity at an angle of 2θ) having, as was shown, a linear dependence in some region of the θ^2 change, and in finding R_q from the slope of this curve. Luzzati's method is based on superposing the experimental curve plotted in a double logarithmic scale on a set of theoretical curves calculated (with some approximations) for long rigid uniform cylinders, the same parameter, R_q, being determined by the coincidence of the curves.

Besides these two well-known methods for study of the structure of unorientated cylindrical particles (macromolecules) it is necessary to mention a simple method suggested by Fedorov & Ptitsyn (1963) for determining the diameter of the cross section of a uniform cylinder by the position of a maximum of the dependence of $I(\theta)\theta^2$ *vs* θ, as well as Kirste's (1964) method which, within the framework of a concrete model of a non-uniform cylinder, allows the evaluation of two of its parameters. In the latter work a form factor of the particle cross section is replaced by the form factor of a uniform sphere surrounded by a vacuum spherical layer. The technique suggested permits the determination of R_q and the relation of the diameter of the sphere with a shell to the diameter of the sphere itself. Of course, this model may have a rather limited application.

If we add to the method mentioned above the usual