thermal vibrations of the iodine atoms were also observed along **c**. These facts indicate that the structure of the crystal has no strong intermolecular force in the **c** direction.

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Relationships among Structure Factors due to Identical Molecules in Different Crystallographic Environments

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Restraints on phases are imposed when a molecule crystallizes in different crystal forms or occurs more than once per asymmetric unit. These restrictions are expressed by the equations

$$|F_p| \exp\{i\alpha_p\} = \frac{U}{V} \sum_{h=-\infty}^{+\infty} |F_h| \exp\{i\alpha_h \sum_{n=1}^{N} G_{hpn} \exp\{i\varphi_{hpn}\}.$$

Here $|F_p|$, α_p, $|F_h|$, and α_h are the structure factors and their phases at the reciprocal lattice points **p** and **h** in either the same or different crystals. G_{hpn} and φ_{hpn} are simple functions of the rotation and translation parameters relating the molecules in the structures concerned. These equations have been tested in both one and three dimensions. In the one-dimensional case the same arbitrary electron density distribution was repeated several times at irregular intervals within the unit cell. All chosen distributions led to equations that could be solved correctly, suggesting that in general there is a unique solution. Refinement of initial approximate translation parameters during phase solution was also successful.

Introduction

When there are chemically identical molecules in different crystallographic environments, the phase problem may be approached in three distinct stages. The first stage involves determining the three rotation parameters that relate any two molecules. The rotation fuction (Rossmann & Blow, 1962; Sasada, 1964) has proved successful for this purpose in a number of cases (Blow, Rossmann & Jeffery, 1964; Prothero & Rossmann, 1964; Dodsen, Harding, Hodgkin & Rossmann, 1966; Palmer, Palmer & Dickerson, 1964). The second stage involves determining the translation parameters that relate these molecules. A method of determining these parameters has been worked out in a special situation when the independent molecules are within the same crystal, related by a non-crystallographic two-fold rotation axis (Rossmann, Blow, Harding & Coller, 1964). This was used in the case of chymotrypsin (Blow *et al.*, 1964) and in insulin (Dodsen *et al.*, 1965).

The third and final stage is to determine the phases, given the results of the first two stages. Equations have been derived for this purpose in the case of two independent molecules within the same crystal (Rossmann & Blow, 1963). These equations were solved in a two-dimensional problem for the innermost 35 reflections, but success was probably partly due to the somewhat linear shape of the molecule giving rise to a large low order reflection. The method is also exceedingly expensive in terms of computer time, but a simpler and more powerful method of solution was given by Rossmann & Blow (1964). Application of the latter to improving the phases of the two independent α-chymotrypsin molecules (Blow *et al.*, 1964) showed that in this case the method did not give a unique answer.

The present paper derives a set of equations for the third stage which are perfectly general. We show that a method based on that of Rossmann & Blow (1964), interlaced with refinement procedures, produces unique solutions, and that a general solution to the translation problem may be obtained simultaneously.

The equations

The structure factor $\mathbf{F}_p$ at the reciprocal lattice point $\mathbf{p}$ may be expressed as

$$\mathbf{F}_p=\sum_{n=1}^{N}\int_U \varrho_1(\mathbf{x}_n)\exp\{2\pi i\mathbf{p}\,.\,\mathbf{x}_n\}d\mathbf{x}_n \tag{1}$$

where there are N identical molecules in the unit cell of the crystal, each molecule being enclosed within a volume U, and $\varrho_1(\mathbf{x}_n)$ is the electron density at the point $\mathbf{x}_n$ in the nth molecule. Let

$$\mathbf{x}_n=[\mathbf{C}_n]\mathbf{x}_1+\mathbf{d}_n \tag{2}$$

where $[\mathbf{C}_n]$ is the rotation matrix and $\mathbf{d}_n$ the translation vector that relate the equivalent points $\mathbf{x}_1$ and $\mathbf{x}_n$ in the first and nth molecules repectively. Thus $[\mathbf{C}_1]=[\mathbf{I}]$, the identity matrix, and $\mathbf{d}_1=0$. If there is only one molecule per asymmetric unit then $[\mathbf{C}_n]$ and $\mathbf{d}_n$ are purely space group operators.

Since $\varrho_1(\mathbf{x}_n)=\varrho_1(\mathbf{x}_1)$ by definition, we have from (1) and (2)

$$\mathbf{F}_p=\sum_{n=1}^{N}\int_U \varrho_1(\mathbf{x}_1)\exp\{2\pi i\mathbf{p}\,.\,([\mathbf{C}_n]\mathbf{x}_1+\mathbf{d}_n)\}d\mathbf{x}_1\,. \tag{3}$$

Now let $\varrho(x)$ be the electron density at a point $\mathbf{x}$ in a second crystal which contains the same molecule so that $\varrho(\mathbf{x})=\varrho_1(\mathbf{x}_1)$ within the molecular volume U. If the 'second' crystal is the same as the first then ϱ and ϱ_1 are identical. Expressing $\varrho(\mathbf{x})$ in terms of a Fourier summation we get

$$\varrho(\mathbf{x})=\frac{1}{V}\sum_{h=-\infty}^{+\infty}\mathbf{F}_h\exp\{-2\pi i\mathbf{h}\,.\,\mathbf{x}\} \tag{4}$$

where $\mathbf{F}_h$ is the structure factor at the reciprocal lattice point $\mathbf{h}$ and V is the volume of the unit cell.

Let

$$\mathbf{x}=[\mathbf{C}]\,.\,\mathbf{x}_1+\mathbf{d} \tag{5}$$

where $[\mathbf{C}]$ is the rotation matrix and $\mathbf{d}$ the translation vector relating the equivalent points $\mathbf{x}_1$ and $\mathbf{x}$ in the 'p' and 'h' crystals respectively.

We can eliminate $\mathbf{x}$ from (4) by using (5), and this gives us $\varrho(\mathbf{x}_1)$ which, by definition, is identical with $\varrho_1(\mathbf{x}_1)$ within the volume U. Putting this into (3) we obtain

$$\mathbf{F}_p=\sum_{n=1}^{N}\int_U\frac{1}{V}\sum_{h=-\infty}^{+\infty}\mathbf{F}_h\exp\{-2\pi i\mathbf{h}\,.\,([\mathbf{C}]\,.\,\mathbf{x}_1+\mathbf{d})\}$$
$$\exp\{2\pi i\mathbf{p}\,.\,([\mathbf{C}_n]\,.\,\mathbf{x}_1+\mathbf{d}_n)\}d\mathbf{x}_1$$

which, after rearrangement, becomes

$$\mathbf{F}_p=\frac{1}{V}\sum_{h=-\infty}^{+\infty}\sum_{n=1}^{N}\mathbf{F}_h\exp\{2\pi i(\mathbf{p}\,.\,\mathbf{d}_n-\mathbf{h}\,.\,\mathbf{d})\}$$
$$\int_U\exp\{2\pi i(\mathbf{p}\,.\,[\mathbf{C}_n]-\mathbf{h}\,.\,[\mathbf{C}])\,.\,\mathbf{x}_1\}d\mathbf{x}_1\,. \tag{6}$$

The integral part of the expression is the same as that described by Rossmann & Blow (1962) and is the Fourier transform of the volume U. It may be represented by a magnitude UG_{hpn} and a phase Ω_{hpn}. In the case of a sphere or a parallelepiped, the two most commonly used 'molecular envelopes', the phase is given by

$$\Omega_{hpn}=2\pi(\mathbf{p}\,.\,[\mathbf{C}_n]-\mathbf{h}\,.\,[\mathbf{C}])\,.\,\mathbf{S}_1 \tag{7}$$

where $\mathbf{S}_1$ is the position of the geometric center of the first molecular envelope in the 'p' crystal.

$$\therefore\ \mathbf{F}_p=\frac{U}{V}\sum_{h=-\infty}^{+\infty}\sum_{n-1}^{N}\mathbf{F}_h\exp\{2\pi i(\mathbf{p}\,.\,\mathbf{d}_n-\mathbf{h}\,.\,\mathbf{d})\}G_{hpn}$$
$$\exp\{2\pi i(\mathbf{p}\,.\,[\mathbf{C}_n]-\mathbf{h}\,.\,[\mathbf{C}])\,.\,\mathbf{S}_1\}$$

$$i.e.\quad \mathbf{F}_p=\frac{U}{V}\sum_{h=-\infty}^{+\infty}\sum_{n=1}^{N}\mathbf{F}_hG_{hpn}\exp\{2\pi i$$
$$[\mathbf{p}\,.\,(\mathbf{d}_n+[\mathbf{C}_n]\,.\,\mathbf{S}_1)-\mathbf{h}\,.\,(\mathbf{d}+[\mathbf{C}]\,.\,\mathbf{S}_1)]\}\,. \tag{8}$$

Let $\mathbf{S}_n$ be the nth position of the centre of the volume U in the 'p' crystal and let $\mathbf{S}$ be a corresponding point in the 'h' crystal, then from (2) and (5) we get

$$\mathbf{S}_n=[\mathbf{C}_n]\,.\,\mathbf{S}_1+\mathbf{d}_n \quad\text{and}\quad \mathbf{S}=[\mathbf{C}]\,.\,\mathbf{S}_1+\mathbf{d}\,. \tag{9}$$

By writing the structure factors in terms of magnitude and phase and from (8) and (9) we arrive at the final equations

$$|\mathbf{F}_p|\exp\{i\alpha_p\}=\frac{U}{V}\sum_{h=-\infty}^{+\infty}|\mathbf{F}_h|\exp\{i\alpha_h\}\sum_{n=1}^{N}G_{hpn}$$
$$\exp\{2\pi i(\mathbf{p}\,.\,\mathbf{S}_n-\mathbf{h}\,.\,\mathbf{S})\}\,. \tag{10}$$

As an example of an expression for G_{hpn} we can take the case of a sphere of radius R,

$$G_{hpn}=\frac{3(\sin 2\pi HR-2\pi HR\cos 2\pi HR)}{(2\pi HR)^3}\,, \tag{11}$$

where H is the length of the vector $\mathbf{p}\,.\,[\mathbf{C}_n]-\mathbf{h}\,.\,[\mathbf{C}]$. The shape of this function is shown in Fig. 1 of Rossmann & Blow (1962). In general, as H increases G_{hpn} decreases, so only those values of **h** which make H small need be included in equation (10), the remaining **h** values giving rise to negligible values for G_{hpn}.

Once the rotation and translation parameters relating all molecules in every crystal have been determined, the only unknowns in (10) are the phases α_h and α_p.

It must be pointed out that (10) refers only to a single set of equations, whereas several such sets of equations may generally be obtained for a single problem. If we have two crystals A and B, then making A the 'h' crystal and B the 'p' crystal will produce a different set of equations than when A is the 'p' and B is the 'h' crystal. In addition, (10) refers to only one molecule in crystal 'h' – that located within the envelope centered on **S** – but generally there will be more than one molecule in the unit cell of this crystal. Different sets of equations result by taking **S** at each *independent* molecule in turn, but the same set of equations is obtained when the different positions of **S** are related by space-group symmetry. This is shown in the Appendix. It should also be noted that the 'h' and 'p' crystals can be identical, though if there is only one molecule per asymmetric unit, the equations reduce to $\mathbf{F}_p = \mathbf{F}_p$ and give no phase information. With more than one independent molecule, however, a legitimate set of equations is obtained.

Clearly, the more crystals and independent molecules there are, the more equations can be set up in relation to the number of unknown phases. The problem therefore becomes progressively more over-determined as the number of independent molecules increases.

Accuracy of the equations

In a practical case, it will be difficult to define an envelope of volume U within which a single molecule is completely contained without any part of any other molecule. Our experiments have not allowed for this type of error. It is hoped that if only a small amount of electron density is present in the envelope in additon to the molecule, or if only a small part of the molecule is left outside the envelope, then the accuracy with which the equations are satified will not be greatly affected. Subsequent refinement of the structure should reveal the molecule more accurately. This, in turn, will lead to more accurate satisfaction of the equations.

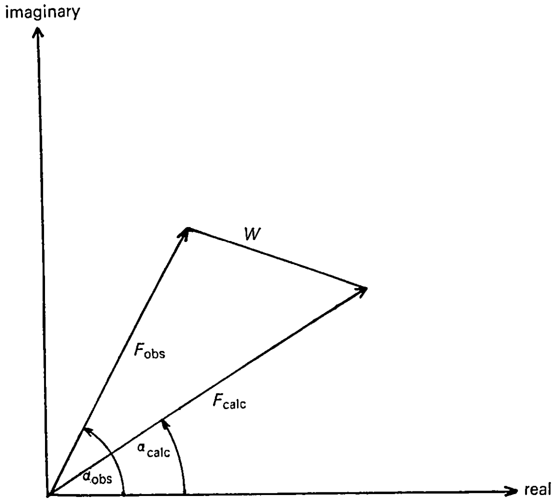

Fig. 1. W is the distance between the end of the vector F_o or left hand side of the equations, and the end of the vector F_c, or sum of the right hand side terms.

The accuracy of the equations may be defined by the usual crystallographic R index. If $\mathbf{F}_o$ is the left hand side of an equation, $\mathbf{F}_c$ the resultant of the right hand side sum and W is the magnitude of the vector difference btweeen them, as in Fig. 1, we can define

$$R = \frac{\Sigma W}{\Sigma|\mathbf{F}_o|}\,.$$

The equations have been set up in a three-dimensional case (to be published) in which one crystal consisted of four identical molecules in the unit cell of space group $P2_1$ and another crystal of four molecules in the unit cell of space group $P2_12_12_1$. The magnitude of G_{hpn} was assumed to be negligible for arguments greater than 1·75 and only the fifty largest terms were considered in each equation. In this case the residual was 18%. In every one-dimensional case for which 'observed' structure factors were calculated and the known phases used for substitution in the equations, a residual of less than 3% was obtained. Even after introducing a 4% random error on the $|\mathbf{F}_o|$ values, R was less than 5%.

Solutions of the equations

We have solved these equations for the phases of unknown structures under certain limited conditions, using methods similar to those described by Rossmann & Blow (1963, 1964) in conjunction with iterative refinement procedures. In practice, however, only rough values of **S** and $\mathbf{S}_n$ in equation (10) will be known from packing considerations, so these were also refined during the solution of the equations. Fig. 2 shows a hypothetical one-dimensional structure in which there are three identical 'molecules' per asymmetric unit and which was used to test the equations. After imposing a 4% random error on the $|\mathbf{F}_o|$ values and starting with approximate relative positions of the molecules, all phases out to $h=44$ were determined with an average error of 31°. These are shown in Table 1 together with the structure amplitudes and the correct phases. Other structures, with three or four identical molecules in the asymmetric unit were also solved using the same techniques. However, when a one-dimensional structure with two molecules in the asymmetric unit was used, the phase determination was only satisfactory to $h=10$. The breakdown of phase determination in this case can be attributed to the fact that the two molecule structure contained less information than the three or four molecule structures.

Conclusions

The equations presented in this paper are completely general. They relate the structure factors of any number of crystal forms of the same molecule, or of only one crystal form if there is more than one molecule per asymmetric unit. The fact that the equations are satisfied has been demonstrated and their ability to solve one-dimensional structures indicates the possibility of using them for phase determination with real structures.

APPENDIX

We wish to show that equation (10) reproduces the correct Laue symmetry and phase relationships for the structure factors $\mathbf{F}_p$ regardless of the symmetry of crystal 'h'.

Centric reflections

The N rotation matrices associated with the crystal 'p' may be divided into pairs $[\mathbf{C}_n]$, $[\mathbf{C}_{N-n+1}]$ $(n=1, 2\ldots N/2)$ such that the operation $[\mathbf{C}_n][\mathbf{C}_{N-n+1}]^{-1}$ is a space-group rotation which gives rise to centric reflections in certain zones of the reciprocal lattice. It can be shown that, for a centric reflection

$$\mathbf{p}\,.\,[\mathbf{C}_n]=-\mathbf{p}\,.\,[\mathbf{C}_{N-n+1}] \quad (n=1,2\ldots N/2)\,. \qquad (1A)$$

Therefore

$$\mathbf{p}\,.\,[\mathbf{C}_n]-\mathbf{h}\,.\,[\mathbf{C}]=-\mathbf{p}\,.\,[\mathbf{C}_{N-n+1}]+\bar{\mathbf{h}}\,.\,[\mathbf{C}]\,. \qquad (2A)$$

As the magnitude of G_{hpn} is unaltered when the direction of the argument is reversed, we have from (2A)

$$G_{hpn}=G_{\bar{h}p(N-n+1)}\,. \qquad (3A)$$

From equation (9) we have

$$\mathbf{S}_n=[\mathbf{C}_n]\mathbf{S}_1+\mathbf{d}_n\,. \qquad (4A)$$

Therefore, using (1A) it follows that

$$\mathbf{p}\,.\,\mathbf{S}_n=-\mathbf{p}\,.\,\mathbf{S}_{N-n+1}+\mathbf{p}\,.\,\mathbf{d}_n+\mathbf{p}\,.\,\mathbf{d}_{N-n+1}\,.$$

Therefore

$$\exp\{2\pi i\mathbf{p}\,.\,\mathbf{S}_n\}=\exp\{-2\pi i\mathbf{p}\,.\,\mathbf{S}_{N-n+1}\}\,, \qquad (5A)$$

since $\mathbf{d}_n+\mathbf{d}_{N-n+1}$ is a space group translation and for centric reflections $2\pi\mathbf{p}\,.\,(\mathbf{d}_n+\mathbf{d}_{N-n+1})$ will be equal to $2\pi m$, where m is an integer.

Now, rewriting (10) as

$$|\mathbf{F}_p|\exp\{i\alpha_p\}=\frac{U}{V}\sum_{h=-\infty}^{+\infty}\sum_{n=1}^{N/2}[|F_h|G_{hpn}\exp\{i(2\pi\mathbf{p}\,.\,\mathbf{S}_n-2\pi\mathbf{h}\,.\,\mathbf{S}+\alpha_h)\}+|\mathbf{F}_{\bar{h}}|G_{\bar{h}p(N-n+1)}\exp\{i(2\pi\mathbf{p}\,.\,\mathbf{S}_{N-n+1}-2\pi\bar{\mathbf{h}}\,.\,\mathbf{S}+\alpha_h)\}]$$

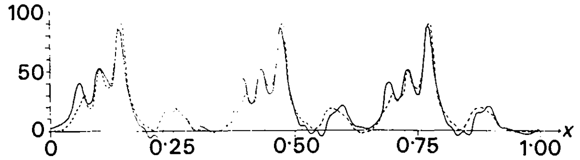

Fig. 2. Structure determination with three identical molecules per unit cell. The dashed line is the true structure, and the continuous line is the structure determined with an approximate knowledge of the position of the molecular centers and also $|\mathbf{F}_o|$ amplitudes which contained a 4 % experimental error.

Table 1. *Phase determination of structure shown in Fig.* 2

h is the index of the correct structure amplitude $|F_o|$ and phase $\alpha^0{}_0$. A random set of errors $\pm\varepsilon$ has been added to each $|F_o|$. Solution of the set of equations using coefficients based on the magnitudes ($|F_o|\pm\varepsilon$) gave the phase angles α^0.

h	$\lvert\mathbf{F}_o\rvert$	$\lvert\mathbf{F}_o\rvert\pm\varepsilon$	α^0	$\alpha^0{}_0$	h	$\lvert\mathbf{F}_o\rvert$	$\lvert\mathbf{F}_o\rvert\pm\varepsilon$	α^0	$\alpha^0{}_0$
0	18·92	18·92	0	0	23	0·95	0·97	359	351
1	1·31	1·27	173	169	24	2·43	2·53	166	148
2	2·05	1·99	247	236	25	0·86	0·82	130	107
3	9·91	10·56	244	228	26	0·50	0·54	281	261
4	2·32	2·37	78	62	27	2·00	1·85	69	29
5	2·43	2·50	157	145	28	0·29	0·29	359	308
6	5·81	5·43	129	123	29	0·29	0·28	232	200
7	3·21	2·91	290	295	30	1·21	1·24	299	273
8	2·70	2·55	323	343	31	0·26	0·27	126	124
9	3·11	3·26	259	282	32	0·16	0·16	88	118
10	2·98	3·02	76	98	33	0·25	0·24	78	142
11	2·20	2·31	148	157	34	0·03	0·03	265	251
12	1·24	1·14	101	90	35	0·09	0·09	353	222
13	1·72	1·86	320	315	36	0·33	0·33	7	223
14	1·14	1·08	71	40	37	0·43	0·43	191	63
15	0·61	0·61	327	286	38	0·28	0·28	232	116
16	1·32	1·26	202	188	39	0·33	0·33	195	94
17	0·96	1·01	255	257	40	0·68	0·68	19	303
18	0·97	1·05	63	86	41	0·26	0·26	68	15
19	1·52	1·58	258	24	42	0·18	0·18	344	307
20	1·14	1·07	87	111	43	0·50	0·50	191	195
21	1·99	1·92	277	285	44	0·20	0·20	267	286
22	1·57	1·42	246	242					

Translation parameters

Initial values $S_1=0{\cdot}150$; $S_2=0{\cdot}520$; $S_3=0{\cdot}800$
Refined values $S_1=0{\cdot}169$; $S_2=0{\cdot}500$; $S_3=0{\cdot}800$
Correct values $S_1=0{\cdot}170$; $S_2=0{\cdot}500$; $S_3=0{\cdot}800$

we see from (3A) and (5A) that the above simplifies to

$$|F_p| \exp\{i\alpha_p\} = \frac{U}{V} \sum_{h=-\infty}^{+\infty} \sum_{n=1}^{N/2} |\mathbf{F}_h| G_{hpn} \cos[2\pi(\mathbf{p}\,.\,\mathbf{S}_n - \mathbf{h}\,.\,\mathbf{S}) + \alpha_h] \quad (6A)$$

and the right hand side is completely real. The result is independent of the nature of crystal 'h'.

A similar argument can be produced for any phases which are restricted to particular discrete values by space group symmetry, such as those produced by zonal reflections in space group $P2_12_12_1$. whose values must be $\pi/2$ or $3\pi/2$.

Systematic absences

If $\mathbf{S}_1$ and $\mathbf{S}_n$ in (4A) are related by a Bravais type translation (giving rise to systematic absences) then $[\mathbf{C}_n]=[\mathbf{I}]$. Also since systematic absences due to screw axes or glide planes lie on an axis or in a plane respectively, it is clear that, in this case,

$$\mathbf{p}\,.\,[\mathbf{C}_n] = \mathbf{p}$$

where $\mathbf{p}$ is the reciprocal lattice vector corresponding to a systematic absence. Hence, in all cases

$$\mathbf{p}\,.\,\mathbf{S}_n = \mathbf{p}\,.\,\mathbf{S}_1 + \mathbf{p}\,.\,\mathbf{d}_n\,. \quad (7A)$$

Now, a factor in the summation over n in (10) is $\sum_{n=1}^{N} \exp(2\pi i\mathbf{p}\,.\,\mathbf{S}_n)$, which, from (7$A$), becomes

$$\sum_{n=1}^{N} \exp(2\pi i\mathbf{p}\,.\,\mathbf{S}_n) = \exp(2\pi i\mathbf{p}\,.\,\mathbf{S}_1) \sum_{n=1}^{N} \exp(2\pi i\mathbf{p}\,.\,\mathbf{d}_n)\,. \quad (8A)$$

But, if $\mathbf{p}$ is systematically absent we have

$$\sum_{n=1}^{N} \exp(2\pi i\mathbf{p}\,.\,\mathbf{d}_n) = 0$$

since $\mathbf{d}_n$ represented the Bravais, glide or screw translation element. Hence, from (8A)

$$\sum_{n=1}^{N} \exp(2\pi i\mathbf{p}\,.\,\mathbf{S}_n) = 0$$

and it is clear that the sum over n for each value of h in (10) will be zero, when $\mathbf{p}$ corresponds to a space-group systematic absence.

The effect of changing p to a Laue-symmetry related position

The structure factor $\mathbf{F}_p$ is defined as

$$|\mathbf{F}_p| = \int_v \varrho(\mathbf{x}) \exp\{2\pi i\mathbf{p}\,.\,\mathbf{x}\} dV\,. \quad (9A)$$

Now, if $[\mathbf{C}_m]$ and $\mathbf{d}_m$ are space group operators, we have

$$\mathbf{x} = [\mathbf{C}_m]\mathbf{x}' + \mathbf{d}_m \quad (10A)$$

where $\mathbf{x}$ and $\mathbf{x}'$ are equivalent positions. Eliminating $\mathbf{x}$ between (9A) and (10A) we obtain

$$\mathbf{F}_p = \int_v \varrho(\mathbf{x}') \exp\{2\pi i\mathbf{p}\,.\,([C_m]\mathbf{x}' + \mathbf{d}_m)\} dV$$

Therefore

$$\mathbf{F}_p = \exp\{2\pi i\mathbf{p}\,.\,\mathbf{d}_m\} \int_v \varrho(\mathbf{x}') \exp\{2\pi i\mathbf{p}[\mathbf{C}_m]\mathbf{x}'\} dV\,.$$

If we now let

$$\mathbf{p}' = \mathbf{p}\,.\,[\mathbf{C}_m] \quad (11A)$$

then

$$\mathbf{F}_p = \exp\{2\pi i\mathbf{p}\,.\,\mathbf{d}_m\} \mathbf{F}_{p'}$$

or, after rearrangement,

$$\mathbf{F}_{p'} = \mathbf{F}_p \exp\{-2\pi i\mathbf{p}\,.\,\mathbf{d}_m\}\,. \quad (12A)$$

That is, the effect on the left hand side structure factor, when the point $\mathbf{p}$ is changed to the symmetry related position $\mathbf{p}'$, is to rotate the phase by $2\pi\mathbf{p}\,.\,\mathbf{d}_m$.

From (10), the right hand side of the equation for $\mathbf{F}_{p'}$ may be written

$$\frac{U}{V} \sum_{h=-\infty}^{+\infty} |\mathbf{F}_h| \exp\{i(\alpha_h - 2\pi\mathbf{h}\,.\,\mathbf{S})\} \sum_{n=1}^{N} G_{hpn} \exp\{2\pi i\mathbf{p}'\,.\,\mathbf{S}_n\} \quad (13A)$$

and it is clear that the only changes are in the summation over n. But the argument of $G_{hp'n}$ is $(\mathbf{p}'\,.\,[\mathbf{C}_n] - \mathbf{h}\,.\,[\mathbf{C}]$ or $(\mathbf{p}\,.\,[\mathbf{C}_m][\mathbf{C}_n] - \mathbf{h}\,.\,[\mathbf{C}])$ from (11A). Since $[\mathbf{C}_m]$ is a space group rotation, $[\mathbf{C}_m][\mathbf{C}_n]$ are also space group rotations and merely reproduce the set $[\mathbf{C}_n]$ in a different order. Let this new set be $[\mathbf{C}_l]$, then the argument of G becomes $(\mathbf{p}\,.\,[\mathbf{C}_l] - \mathbf{h}\,.\,[\mathbf{C}])$ and the set of $G_{hp'n}$ for all n is reproduced by the set G_{hpl} for all l in a different order.

Let us now apply the operators $[\mathbf{C}_m]$ and $[\mathbf{d}_m]$ to each $\mathbf{S}_n$ in turn. We then obtain $[\mathbf{C}_m]\,\mathbf{S}_n \pm \mathbf{d}_m$ which from (6) becomes

$$[\mathbf{C}_m][\mathbf{C}_n]\,\mathbf{S}_1 + [\mathbf{C}_m]\,\mathbf{d}_n + \mathbf{d}_m\,.$$

If we now define $[\mathbf{C}_m]\mathbf{d}_n \pm \mathbf{d}_m$ to be $\mathbf{d}_l$ and $[\mathbf{C}_m][\mathbf{C}_n]$ as $[\mathbf{C}_l]$ as before, we then obtain $[\mathbf{C}_l]\mathbf{S}_1 + \mathbf{d}_l$ which, by analogy with (4A), is clearly the set of equivalent positions $\mathbf{S}_l$. That is ,we can write

$$\mathbf{S}_l = [\mathbf{C}_m]\mathbf{S}_n + \mathbf{d}_m\,. \quad (14A)$$

We can now deal with the product $\mathbf{p}'\,.\,\mathbf{S}_n$ in the expression (13A) above.

From (11A),

$$\mathbf{p}'\,.\,\mathbf{S}_n = \mathbf{p}\,.\,[\mathbf{C}_m]\mathbf{S}_n\,.$$

Then from (14A)

$$\mathbf{p}'\,.\,\mathbf{S}_n = \mathbf{p}\,.\,(\mathbf{S}_l - \mathbf{d}_m)$$

and we can now rewrite (13A) as

$$\exp\{-2\pi i\mathbf{p}\,.\,\mathbf{d}_m\} \frac{U}{V} \sum_{h=-\infty}^{+\infty} |F_h| \exp\{i(\alpha_h - 2\pi\mathbf{h}\,.\,\mathbf{S})\} \sum_{l=1}^{N} G_{hpl} \exp\{2\pi i\mathbf{p}\,.\,\mathbf{S}_l\}\,,$$

which from (10) is clearly equal to $\exp\{-2\pi i\mathbf{p}\,.\,\mathbf{d}_m\}\mathbf{F}_p$. Thus the equations are unchanged by moving to Laue-symmetry related lattice points, apart from the application of the factor exp $\{-2\pi i\mathbf{p}\,.\,\mathbf{d}_m\}$ which, from (12*A*), is necessary to preserve the symmetry in the phases.

The effect of changing S *to a space-group symmetry related position*

The argument of the exponential term in (10) involving $\mathbf{h}$ and S is

$$\varphi=\alpha_h-2\pi\mathbf{h}\,.\,\mathrm{S}\,.$$

Let us now use, instead of S, the space-group symmetry related position S′, where

$$\mathrm{S}=[\mathbf{C}']\mathrm{S}'+\mathbf{d}'$$

and $[\mathbf{C}']$ and $\mathbf{d}'$ are the space group operators. This space group operation has the effect in reciprocal space of producing symmetry related structure factors $\mathbf{F}_h$ and $\mathbf{F}_{h'}$ such that $\mathbf{h}'=\mathbf{h}[\mathbf{C}']$ and $\alpha_{h'}=\alpha_h-2\pi\mathbf{h}\,.\,\mathbf{d}'$ [see equations (11*A*) and (12*A*)]. If we sum the right hand side of (10) over $\mathbf{h}'$ instead of $\mathbf{h}$, φ' will be given by

$$\varphi'=\alpha_{h'}-2\pi\mathbf{h}'\,.\,\mathrm{S}'$$

i.e. $$\varphi'=\alpha_h-2\pi\mathbf{h}\,.\,\mathbf{d}'-2\pi\mathbf{h}\,.\,[\mathbf{C}'][\mathbf{C}']^{-1}(\mathrm{S}-\mathbf{d}')\,.$$

Therefore $\varphi'=\alpha_h-2\pi\mathbf{h}\,.\,\mathrm{S}=\varphi\,.$

Since φ is unchanged, it is clearly immaterial which of the equivalent positions of S is used in setting up the equations.

A corollary is that if S is changed to a molecular equivalent position, but one without any crystallographic equivalence, we form a different set of equations.

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The Crystal and Molecular Structure of Methyl 1-Thio-β-D-xylopyranoside

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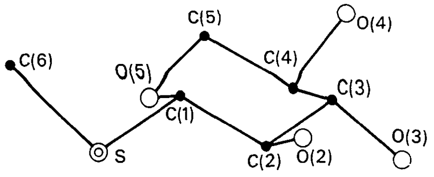
Methyl 1-thio-β-D-xylopyranoside crystallizes in the triclinic system: space group $P1$. Cell dimensions at −150°C are $a=4.320$, $b=7.611$, $c=13.285$ Å, $\alpha=92.3$, $\beta=92.4$, $\gamma=112.1°$. There are two molecules in the asymmetric unit. Both molecules are present in the $C1$ chair conformation with normal bond lengths and angles, although there appears to be some shortening of the anomeric carbon–sulphur bond and the ring angle C(2)C(3)C(4) is significantly larger than tetrahedral.



The ring oxygen atom, O(5), does not participate in the hydrogen bonding system which is confined to the hydroxyl groups on C(2), C(3), and C(4). Data were recorded at a low temperature (−150°C) and atom coordinates refined to $R=0.105$.

Introduction

Xylan, the main chain of the acidic non-cellulosic polysaccharides found in higher plant tissues, is a polymer of (1→4) linked β-D-xylose residues. Although normally found with attached side chains whose number, point of attachment to the main chain and constituent monosaccharide residues vary with the source and method