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A Phase-Determining Procedure Related to the Vector-Coincidence Method

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It is shown that one form of the vector-coincidence method is approximately equivalent to a probable calculation of certain origin-invariant products of structure factors. Equations are developed in detail for space groups $P\overline{1}$ and $P1$, and their validity is investigated both theoretically and by a numerical test.

Introduction

At the present time, two general methods for solving crystal structures from diffraction intensities are undergoing rather extensive investigation. Methods are being developed by means of which the phases of structure factors might be found directly, and techniques for obtaining an approximate structure from the Patterson function are being used. Harker & Kasper (1948) derived a set of inequalities which has been extensively developed by later investigators and which can often be used for direct phase determination. A general method for sign determination which is based on probability theory has been presented by Hauptman & Karle (1953) and the results of these authors have also been derived by Bertaut (1955). General methods for solving the Patterson function seem to have occurred almost simultaneously to several crystallographers (Beevers & Robertson, 1950; Buerger, 1951; Clastre & Gay, 1950; Garrido, 1950; McLachlan, 1951). It is the purpose of this paper to show that the Patterson-superposition (vector-coincidence) procedure (Buerger, 1951) can be developed in a manner which yields probable phase-determining relations between certain products of structure factors and the set of structure-factor moduli. This general approach has been used by McLachlan & Harker (1951). However, the equations presented by these investigators require the initial location of one atom. It will be seen that this is not necessary in order to use the equations presented here.

Distribution functions

We introduce distribution functions defined by

$$D_n(\mathbf{u}_1, \mathbf{u}_2, \ldots, \mathbf{u}_n) = \int_{\text{cell}} \varrho(\mathbf{r})\varrho(\mathbf{r}+\mathbf{u}_1)\varrho(\mathbf{r}+\mathbf{u}_2)\ldots\varrho(\mathbf{r}+\mathbf{u}_n)\,dv_{\mathbf{r}}\,. \quad (1)$$

These functions are atomic distribution functions for $n+1$ atoms in the sense that they have maxima when $\mathbf{u}_1, \mathbf{u}_2, \ldots, \mathbf{u}_n$ are vectors connecting an atom with n other atoms. We can expand D_n in a Fourier series:

$$D_n(\mathbf{u}_1, \mathbf{u}_2, \ldots, \mathbf{u}_n) = \sum_{\mathbf{H}_1,\mathbf{H}_2,\cdots,\mathbf{H}_n} \left[\left(\prod_{j=1}^{n} F_{\mathbf{H}_j}\right) F_{-\mathbf{H}_1-\mathbf{H}_2-\cdots-\mathbf{H}_n}\right] \times \exp\left[-2\pi i(\mathbf{H}_1.\mathbf{u}_1+\mathbf{H}_2.\mathbf{u}_2+\ldots+\mathbf{H}_n.\mathbf{u}_n)\right] \quad (2)$$

in which $F_{\mathbf{H}_1}$ is the structure factor associated with the reciprocal-lattice point $\mathbf{H}_1$, etc. The volume unit is taken, for convenience, to be one unit cell.

It is obvious that $D_0 = F_{000}$ and that $D_1(\mathbf{u}_1)$ is the Patterson function. It should also be noted that the Fourier coefficients of all D_n are independent of the choice of origin of $\varrho(\mathbf{r})$, but that D_n for $n \geq 2$ is centrosymmetric only if $\varrho(\mathbf{r})$ is centrosymmetric.

Most vector-coincidence methods (Buerger, 1951) amount to the construction of a D_n (or sections through one of these functions) for $n \geq 2$ from the Patterson function. We will consider product functions for n superposed Patterson functions of the form

$$Q_n(\mathbf{u}_1, \mathbf{u}_2, \ldots \mathbf{u}_n) = \prod_{j=1}^{n} P(\mathbf{u}_j) \prod_{k<j} P(\mathbf{u}_j-\mathbf{u}_k)\,. \quad (3)$$

These functions differ from the product functions defined by Buerger (1951) in that factors are included which are the values of the Patterson function at the ends of the displacement vectors, $\mathbf{u}_j-\mathbf{u}_k$. It is clear that Q_n is large whenever $\mathbf{u}_1 = \mathbf{r}_j-\mathbf{r}_k$, $\mathbf{u}_2 = \mathbf{r}_l-\mathbf{r}_k$, etc., or when $\mathbf{u}_1 = \mathbf{r}_k-\mathbf{r}_j$, $\mathbf{u}_2 = \mathbf{r}_k-\mathbf{r}_l$, etc., $\mathbf{r}_j$, $\mathbf{r}_k$, $\mathbf{r}_l$, etc. being atomic-position vectors. The similarity between D_n and Q_n is therefore obvious. We will consider the possibility of comparing the Fourier coefficients of the functions D_2 and Q_2. Now Q_2 always has a center of symmetry whereas D_2 has a center of symmetry only if $\varrho(\mathbf{r})$ is centrosymmetric. We will consider both cases but we will not take explicit account of any other symmetry elements.

Centrosymmetric structures

A Fourier coefficient of $D_2(\mathbf{u}_1, \mathbf{u}_2)$ is $F_{\mathbf{H}_1}F_{\mathbf{H}_2}F_{\mathbf{H}_1+\mathbf{H}_2}$, and the corresponding coefficient of $Q_2(\mathbf{u}_1, \mathbf{u}_2)$ is $\sum_{\mathbf{K}} F^2_{\mathbf{H}_1+\mathbf{K}}F^2_{\mathbf{H}_2-\mathbf{K}}F^2_{\mathbf{K}}$. It is clear that one cannot gain information by comparing these quantities since the latter is always positive. The situation can be improved by considering the two particularly large differences between D_2 and Q_2. (i) The peak at the origin of Q_2 is too large, and (ii) the special peaks on Q_2 for which $u_1 = 0$, $u_2 = 0$, or $u_1 = u_2$ are too large relative to the general peaks. Both of these discrepancies can be eliminated on the average by adjustment of the origin peak of $P(\mathbf{u})$ and by removing the peaks at the origins of both D_2 and Q_2. In accordance with these ideas, we will consider the possibility of making the following approximate equality:

$$E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2} - \sum_{j=1}^{N} g_j^3$$
$$\approx A\overline{(E^2_{\mathbf{H}_1+\mathbf{K}}-1+B)(E^2_{\mathbf{H}_2-\mathbf{K}}-1+B)(E^2_{\mathbf{K}}-1+B)}^{\mathbf{K}} - AB^3 . \tag{4}$$

In this expression, the left side corresponds to a Fourier coefficient of D_2 and the right side corresponds to the same Fourier coefficient of Q_2 to which the changes indicated above have been made. The constant B is essentially an adjustment to the origin peak of $P(\mathbf{u})$, A is a normalizing constant, and $\sum_j^N g_j^3$ and AB^3 are terms which remove the origin peaks of the corresponding functions (or, in other words, they make the average values of the left and right sides of the above expression equal to zero). Also, the sum in the Fourier coefficient of Q_2 has been replaced by an average and the result has been expressed in terms of the normalized structure factors $E_{\mathbf{H}}$ defined by

$$E_{\mathbf{H}} = \sum_{j=1}^{N} g_j \exp\,[2\pi i\mathbf{H}.\mathbf{r}_j] ,$$

with

$$g_j = f_j \Big/ \Big(\sum_{j=1}^{N} f_j^2\Big)^{\frac{1}{2}} ,$$

and

N = number of atoms per unit cell.

We have now to consider the best values for the constants A and B. Since equation (4) is presumably to be used to determine the sign of $E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}$, A and B should be chosen such that the right side of this expression has the same sign as the left for the largest part of the region of the atomic configuration space for which $E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}$ has a given fixed magnitude. Since solving this problem does not seem to be practicable, we will seek the values of A and B which minimize the square of the difference between the right and left sides of equation (4) integrated over the entire configuration space of the atoms. In other words, we treat this as a regression problem. The quantity which is to be minimized can be written

$$\sigma^2 = \overline{(L_{\mathbf{H}_1,\mathbf{H}_2} - AM_{\mathbf{H}_1,\mathbf{H}_2} - ABN_{\mathbf{H}_1,\mathbf{H}_2} - AB^2P_{\mathbf{H}_1,\mathbf{H}_2})^2} , \tag{5}$$

in which the bar indicates integration over the space coordinates of all $\mathbf{r}_j$. In the above equation,

$$L_{\mathbf{H}_1,\mathbf{H}_2} = E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2} - \sum_{j=1}^{N} g_j^3 , \tag{6}$$

$$M_{\mathbf{H}_1,\mathbf{H}_2} = \overline{(E^2_{\mathbf{H}_1+\mathbf{K}}-1)(E^2_{\mathbf{H}_2-\mathbf{K}}-1)(E^2_{\mathbf{K}}-1)}^{\mathbf{K}} , \tag{7}$$

$$N_{\mathbf{H}_1,\mathbf{H}_2} = \overline{(E^2_{\mathbf{H}_1+\mathbf{K}}-1)(E^2_{\mathbf{K}}-1) + (E^2_{\mathbf{H}_2-\mathbf{K}}-1)(E^2_{\mathbf{K}}-1)}$$
$$+ \overline{(E^2_{\mathbf{H}_1+\mathbf{K}}-1)(E^2_{\mathbf{H}_2-\mathbf{K}}-1)}^{\mathbf{K}} , \tag{8}$$

$$P_{\mathbf{H}_1,\mathbf{H}_2} = \overline{(E^2_{\mathbf{H}_1+\mathbf{K}}-1) + (E^2_{\mathbf{H}_2-\mathbf{K}}-1) + (E^2_{\mathbf{K}}-1)}^{\mathbf{K}} . \tag{9}$$

In finding the values of A and B which minimize σ^2, the term $AB^2P_{\mathbf{H}_1,\mathbf{H}_2}$ on the right side of equation (5) will be neglected. It will be shown later that this is a reasonable approximation in cases for which the derived expression can be expected to give useful results. Minimizing σ^2 gives

$$A = \overline{L_{\mathbf{H}_1,\mathbf{H}_2}M_{\mathbf{H}_1,\mathbf{H}_2}} \Big/ \overline{M^2_{\mathbf{H}_1,\mathbf{H}_2}} , \tag{10}$$

and

$$B = \overline{L_{\mathbf{H}_1,\mathbf{H}_2}N_{\mathbf{H}_1,\mathbf{H}_2}} \Big/ \overline{N^2_{\mathbf{H}_1,\mathbf{H}_2}} , \tag{11}$$

since

$$\overline{M_{\mathbf{H}_1,\mathbf{H}_2}N_{\mathbf{H}_1,\mathbf{H}_2}} = 0 .$$

In these expressions the bars over the symbols indicate that the corresponding functions are averaged over all atomic coordinates. Evaluation of these averages gives

$$\overline{L_{\mathbf{H}_1,\mathbf{H}_2}M_{\mathbf{H}_1,\mathbf{H}_2}} = 8S_3^3 - 36S_6S_3 + 40S_9 , \tag{12}$$

$$\overline{M^2_{\mathbf{H}_1,\mathbf{H}_2}} = \frac{n_K-1}{n_K}(64S_4^3 - 336S_8S_4 + 416S_{12})$$
$$+ \frac{1}{n_K}(8 - 36S_4 + 54S_4^2 - 27S_4^3) , \tag{13}$$

$$\overline{L_{\mathbf{H}_1,\mathbf{H}_2}N_{\mathbf{H}_1,\mathbf{H}_2}} = 12S_4S_3 - 21S_7 , \tag{14}$$

$$\overline{N^2_{\mathbf{H}_1,\mathbf{H}_2}} = \frac{n_K-1}{n_K}(24S_4^2 - 45S_8)$$
$$+ \frac{1}{n_K}(12 - 36S_4 + 27S_4^2) , \tag{15}$$

in which $n_{\mathbf{K}}$ is the number of terms used to compute the averages over $\mathbf{K}$ in equations (6)–(9), and

$$S_n = \sum_{j=1}^{N} g_j^n .$$

In the case of equal atoms, $S_n = N^{-n/2+1}$.

In deriving these expressions it has been assumed that the space group is $P\bar{1}$ and that all atoms are in general positions. Similar expressions can be derived for other space groups. In general these will be considerably more complicated, mostly because the average values of the products of structure factors will be different for various classes of reflections.

An idea as to the magnitudes of A and B and their approximate dependance on the number of atoms in the unit cell can be gained by evaluating these quantities under the conditions that (i) all atoms are equal,

(ii) n_K is infinite, and (iii) only terms of lowest order in $1/N$ are kept. Then, $A = \frac{1}{8}N^{3/2}$, and $B = 4/N$. These expressions are approximately valid for moderate N and $8n_K \gg N^3$.

It is clear that if the signs of enough $E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}$ could be determined from equation (4) one could proceed to the solution of a structure problem. The signs of even structure factors are obtained directly (by putting $\mathbf{H}_1 = \mathbf{H}_2$) and the signs of three structure factors of different origin classes can be chosen arbitrarily. Since the various $E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}$ are not independent, the signs of these quantities give an overabundance of data. Furthermore, Σ_2 of Hauptman & Karle (1953) can be used when enough signs are known.

The non-centrosymmetric case

In this case, $P(\mathbf{u}_1)P(\mathbf{u}_2)P(\mathbf{u}_2-\mathbf{u}_1)$ has a center of symmetry whereas $D_2(\mathbf{u}_1, \mathbf{u}_2)$ does not. Hence the former function is to be compared with $D_2(\mathbf{u}_1, \mathbf{u}_2)+D_2^*(\mathbf{u}_1, \mathbf{u}_2)$,† which has Fourier coefficients $F_{\mathbf{H}_1}F_{\mathbf{H}_2}F_{-\mathbf{H}_1-\mathbf{H}_2}+F_{-\mathbf{H}_1}F_{-\mathbf{H}_2}F_{\mathbf{H}_1+\mathbf{H}_2}$. If we proceed in the manner similar to that described for the centrosymmetric case we obtain

$$\begin{aligned} &E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{-\mathbf{H}_1-\mathbf{H}_2}+E_{-\mathbf{H}_1}E_{-\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}-2\sum_{j=1}^{N} g_j^3 \\ &\quad\approx \overline{A(|E_{\mathbf{H}_1+\mathbf{K}}|^2-1+B)(|E_{\mathbf{H}_2-\mathbf{K}}|^2-1+B)} \\ &\qquad\qquad \overline{(|E_{\mathbf{K}}|^2-1+B)}^{\mathbf{K}}-AB^3\,. \end{aligned} \tag{16}$$

Again, (neglecting the term containing AB^2) the values of A and B which minimize σ^2, the mean square deviation between the left and right sides of this expression, are given by equations (10) and (11). However, in this case we have

$$\overline{L_{\mathbf{H}_1,\mathbf{H}_2}M_{\mathbf{H}_1,\mathbf{H}_2}} = 2S_3^3-6S_6S_3+4S_9\,, \tag{17}$$

$$\overline{M^2_{\mathbf{H}_1,\mathbf{H}_2}} = \frac{n_K-1}{n_K}(2S_4^3-6S_8S_4+4S_{12})+\frac{1}{n_K}(1-S_4)^3\,, \tag{18}$$

$$\overline{L_{\mathbf{H}_1,\mathbf{H}_2}N_{\mathbf{H}_1,\mathbf{H}_2}} = 6S_3S_4-6S_7\,, \tag{19}$$

$$\overline{N^2_{\mathbf{H}_1,\mathbf{H}_2}} = \frac{n_K-1}{n_K}(3S_4^2-3S_8)+\frac{3}{n_K}(1-S_4)^2\,. \tag{20}$$

These equations are strictly correct only for space group $P1$. If all atoms are equal, $n_K \gg N^3$, and we keep only the term of lowest order in $1/N$, we obtain $A = N^{3/2}$ and $B = 2/N$.

It will now be demonstrated that, if the values of $E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{-\mathbf{H}_1-\mathbf{H}_2}+E_{-\mathbf{H}_1}E_{-\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}$ determined by the above equation are sufficiently precise, the phase angles of the structure factors can be determined. We first note that

$$\begin{aligned} \cos\varphi_{\mathbf{H}_1,\mathbf{H}_2} &= \cos(\varphi_{\mathbf{H}_1}+\varphi_{\mathbf{H}_2}-\varphi_{\mathbf{H}_1+\mathbf{H}_2}) \\ &= \frac{\frac{1}{2}(E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{-\mathbf{H}_1-\mathbf{H}_2}+E_{-\mathbf{H}_1}E_{-\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2})}{|E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{-\mathbf{H}_1-\mathbf{H}_2}|}\,, \end{aligned} \tag{21}$$

in which φ is a phase angle. This gives us $|\varphi_{\mathbf{H}_1,\mathbf{H}_2}|$, in which we take $-\pi < \varphi_{\mathbf{H}_1,\mathbf{H}_2} \leq \pi$. Now the sign of one $\varphi_{\mathbf{H}_1,\mathbf{H}_2}$ can be arbitrarily assigned; this makes the choice between D_2 and D_2^*, which is also the choice between ϱ and ϱ^*. Furthermore, the phase angles of three structure factors belonging to different origin classes may be arbitrarily assigned (Hauptman & Karle, 1956). We also note that the various $\varphi_{\mathbf{H}_1,\mathbf{H}_2}$ are not independent; for example

$$\varphi_{\mathbf{H}_1,\mathbf{H}_1}+\varphi_{2\mathbf{H}_1,\mathbf{H}_2}+\varphi_{2\mathbf{H}_1+\mathbf{H}_2,-\mathbf{H}_1}+\varphi_{-\mathbf{H}_1,\mathbf{H}_1+\mathbf{H}_2} = 0\,, \tag{22}$$

and

$$\varphi_{\mathbf{H}_1,\mathbf{H}_2}+\varphi_{\mathbf{H}_1+\mathbf{H}_2,\mathbf{H}_1-\mathbf{H}_2}+\varphi_{-\mathbf{H}_1,\mathbf{H}_2-\mathbf{H}_1}+\varphi_{-2\mathbf{H}_1+\mathbf{H}_2,-\mathbf{H}_2} = 0\,. \tag{23}$$

These relations involve the phase angles of just seven structure factors, two of which may be assigned arbitrarily. It is clear that we may, in favorable cases, find the phase angles which give the best agreement for the $\varphi_{\mathbf{H}_1,\mathbf{H}_2}$ involved and which also best satisfy (22) and (23).

Estimation of errors

Equations (4) and (16) are probable relations. Some idea of their reliability can be obtained from the mean square deviation given by equation (5). If this expression is expanded we obtain

$$\begin{aligned} \sigma^2 = {} & \overline{L^2_{\mathbf{H}_1,\mathbf{H}_2}}+A^2\overline{M^2_{\mathbf{H}_1,\mathbf{H}_2}}+A^2B^2\overline{N^2_{\mathbf{H}_1,\mathbf{H}_2}} \\ & -2A\overline{L_{\mathbf{H}_1,\mathbf{H}_2}M_{\mathbf{H}_1,\mathbf{H}_2}} \\ & -2AB\overline{L_{\mathbf{H}_1,\mathbf{H}_2}N_{\mathbf{H}_1,\mathbf{H}_2}}+3A^2B^4\overline{\left(\overline{E^2_{\mathbf{K}}-1}^{\mathbf{K}}\right)^2}\,. \end{aligned} \tag{24}$$

With A and AB given by equations (10) and (11) this becomes

$$\begin{aligned} \sigma^2_{\text{min.}} = {} & \overline{L^2_{\mathbf{H}_1,\mathbf{H}_2}}-\frac{\overline{L_{\mathbf{H}_1,\mathbf{H}_2}M_{\mathbf{H}_1,\mathbf{H}_2}}}{\overline{M^2_{\mathbf{H}_1,\mathbf{H}_2}}}-\frac{\overline{L_{\mathbf{H}_1,\mathbf{H}_2}N_{\mathbf{H}_1,\mathbf{H}_2}}}{\overline{N^2_{\mathbf{H}_1,\mathbf{H}_2}}} \\ & +3A^2B^4\overline{\left(\overline{E^2_{\mathbf{K}}-1}^{\mathbf{K}}\right)^2}\,, \end{aligned} \tag{25}$$

in which we evaluate

$$\overline{L^2_{\mathbf{H}_1,\mathbf{H}_2}} = 1+3S_3^2-7S_6\,, \tag{26}$$

$$\overline{\left(\overline{E^2_{\mathbf{K}}-1}^{\mathbf{K}}\right)^2} = \frac{2-3S_4}{n_K} \tag{27}$$

for the centrosymmetric case; and

$$\overline{L^2_{\mathbf{H}_1,\mathbf{H}_2}} = 2+6S_4-8S_6\,, \tag{28}$$

$$\overline{\left(\overline{|E_{\mathbf{K}}|^2-1}^{\mathbf{K}}\right)^2} = \frac{1-S_4}{n_K} \tag{29}$$

for the non-centrosymmetric case. The other quantities

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† The symbol * in this case refers to the inverted structure.

appearing in equation (25) are given by equations (12), (13), (14), (15), (17), (18), (19), and (20). Insight into the above expression for $\sigma^2_{\text{min.}}$ can be obtained by considering the case of equal atoms and by keeping only the terms of lowest order in $1/N$ in the expressions for $\overline{L^2_{\mathbf{H}_1,\mathbf{H}_2}}$, $\overline{L_{\mathbf{H}_1,\mathbf{H}_2}M_{\mathbf{H}_1,\mathbf{H}_2}}$, etc. We then have the approximation, valid for large N and n_K,

$$\sigma^2_{\text{min.}} \sim 1-\frac{1}{1+N^3/8n_K}-\frac{6}{N(1+N^2/2n_K)}+\frac{24(1+N^3/8n_K)^2}{n_K N(1+N^2/2n_K)^4} \qquad (30)$$

for the centrosymmetric case. It is obvious that if we are to have $\sigma^2_{\text{min.}}$ significantly less than unity (or $\overline{L^2_{\mathbf{H}_1,\mathbf{H}_2}}$) we must not have the condition $N^3 \gg 8n_K$. On the other hand, for large n_K (~ 100) and moderate N (~ 10), the last term in this expression is certainly small compared to unity. This justifies the neglect of this term in determining A and B which minimize σ^2, since conditions which cause this term to become significant are just those conditions under which the whole procedure would fail.

The conditions are similar in the non-centrosymmetric case. The expression corresponding to equation (30) is

$$\sigma^2_{\text{min.}} \sim 2-\frac{2}{1+N^3/2n_K}-\frac{12}{N(1+N^2/n_K)}+\frac{48(1+N^3/2n_K)^2}{n_K N(1+N^2/n_K)^4}. \qquad (31)$$

The condition for failure in this case is $N^3 \gg 2n_K$.

An important consideration is the behavior of $\sigma^2_{\text{min.}}$ as $n_k \to \infty$. For equal atoms, and on expanding (25) in a power series in $1/N$, the asymptotic value of $\sigma^2_{\text{min.}}$ becomes

$$\lim_{n_K\to\infty} \sigma^2_{\text{min.}} = \frac{0{\cdot}75}{N}-\frac{1{\cdot}313}{N^2}-\frac{0{\cdot}794}{N^3}+0\left(\frac{1}{N^4}\right) \qquad (32)$$

for the centrosymmetric case, and

$$\lim_{n_K\to\infty} \sigma^2_{\text{min.}} = 0 \qquad (33)$$

for the non-centrosymmetric case. If the atoms are not equal, the limiting values of $\sigma^2_{\text{min.}}$ will be larger than these.

If we let G be the numerical value of the function used to estimate $E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}$ (centrosymmetric case), then the probability that these quantities have the same sign as given by

$$P_+ = \tfrac{1}{2}+\tfrac{1}{2}\tanh\left(\frac{|G||E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}|}{\sigma^2}\right), \qquad (34)$$

provided that $E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}$ is normally distributed about G with variance σ^2. Since the distribution of these quantities is unknown, this equation can serve as only a rather crude indication of the reliability of a sign determination.

Numerical test

The validity of the procedure described above was tested by applying it to a two-dimensional non-centrosymmetric structure which consists of four equal atoms placed in positions:

$$x_1 = 0,\ y_1 = 0; \qquad x_2 = \tfrac{3}{15},\ y_2 = \tfrac{2}{15};$$
$$x_3 = \tfrac{5}{15},\ y_3 = \tfrac{11}{15};\ \ x_4 = \tfrac{9}{15},\ y_4 = \tfrac{10}{15}.$$

Equation (16) was used with $A = 8$ and $B = \frac{1}{2}$. In this case we have

$$2|E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{\mathbf{H}_1+\mathbf{H}_2}|\cos\varphi_{\mathbf{H}_1,\mathbf{H}_2} \approx 8\,\overline{(|E_{\mathbf{H}_1+\mathbf{K}}|^2-\tfrac{1}{2})(|E_{\mathbf{H}_2-\mathbf{K}}|^2-\tfrac{1}{2})(|E_{\mathbf{K}}|^2-\tfrac{1}{2})}^{\mathbf{K}}. \qquad (35)$$

These values of A and B minimize σ^2 for infinite n_K. In the calculation the maximum values of $|h|$ and $|k|$ were 7; all possible terms subject to this restriction were used. This equation was applied to sixteen different combinations $\mathbf{H}_1, \mathbf{H}_2$; the results are summarized in Table 1. The values of σ^2 given in the last column of Table 1 are computed from equation (24), which, in this case, reduced to $\sigma^2 = 60/n_K$. The root mean value of σ^2 is 0·70 whereas the root-mean-square deviation between the numbers in the second and third columns of Table 1 is 0·50.

Table 1. $2|E_{\mathbf{H}_1}E_{\mathbf{H}_2}E_{-\mathbf{H}_1-\mathbf{H}_2}|\cos\varphi_{\mathbf{H}_1,\mathbf{H}_2}$

$(hk)_1$	$(hk)_2$	True value	Equation (35)	n_K	σ^2
$1\bar{1}$	11	1·95	2·09	169	0·35
$1\bar{1}$	$3\bar{4}$	4·44	4·02	110	0·55
$1\bar{1}$	$2\bar{3}$	3·55	2·99	132	0·45
$1\bar{1}$	$4\bar{5}$	2·06	2·18	90	0·67
$1\bar{1}$	$1\bar{2}$	1·12	0·88	156	0·38
$2\bar{2}$	$3\bar{4}$	7·90	9·43	90	0·67
$2\bar{2}$	$1\bar{2}$	6·70	6·56	132	0·45
$2\bar{2}$	$2\bar{3}$	1·53	1·36	110	0·55
$1\bar{1}$	41	5·16	5·13	140	0·43
$1\bar{1}$	32	2·65	2·42	143	0·42
$1\bar{1}$	50	2·30	2·25	126	0·48
$1\bar{1}$	23	1·30	1·18	144	0·42
$1\bar{1}$	15	4·85	4·99	129	0·47
$1\bar{1}$	06	2·99	3·51	126	0·48
$1\bar{1}$	24	1·69	1·81	132	0·45
06	17	1·66	2·47	112	0·54

The first eight numbers in the fourth column of Table 1 were used to compute phase angles of individual structure factors. The phase angles of $1\bar{1}$ and $3\bar{4}$ were put equal to values which placed the origin at atom 1 and the remaining five phase angles were computed by a least-squares procedure from the eight equations. The result are summarized in Table 2. The mean absolute deviation between the true and computed phase angles (excluding assumed phase angles) is 15·4°.

It is to be noted that this procedure will give un-

Table 2. *Comparison of true and computed phase angles*

(hk)	True phase angle (°)	Computed phase angle (°)
$1\bar{1}$	−16·2	−16·2
$3\bar{4}$	24·5	24·5
$4\bar{5}$	7·7	29·6
$5\bar{6}$	41·5	46·1
$2\bar{2}$	20·6	16·9
$2\bar{3}$	41·3	72·3
$1\bar{2}$	3·6	19·5

satisfactory results in many circumstances. It is always necessary to determine the signs of the φ_{H_1,H_2} by making use of the redundancy of equations. An error made at this step could introduce serious errors in the individual phase angles. In more complex structures, with correspondingly larger values of σ, this danger becomes greater. On the other hand, one would expect that the use of a larger group of related structure factors would improve matters because of the increased redundancy.

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The Crystal and Molecular Structure of 2:5-Diamino-4-Mercapto-6-Methyl-Pyrimidine

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The crystal and molecular structure of 2:5-diamino-4-mercapto-6-methyl-pyrimidine has been determined from projections about the a and c axes of the crystal. The space group is $P2_1/n$, and the unit cell dimensions are $a = 17{\cdot}036$, $b = 10{\cdot}045$, $c = 4{\cdot}339$ Å, $\beta = 90°\ 56'$. The $hk0$ projection has been solved by locating the heavy atom in a modified Patterson synthesis, and refined by calculation of successive difference syntheses. The z coordinates have been determined from the modified $0kl$ Patterson, using steepest-descents methods for the refinement of the atomic coordinates.

1. Introduction

Following the investigation of the 4:5- and 4:6-diamino-pyrimidines (Clews & Cochran, 1949; White & Clews, 1956), a study was made of the structure of 2:5-diamino-4-mercapto-6-methyl-pyrimidine to obtain information on the type of hydrogen bonding in the amino groups in this class of diamino pyrimidine, and on the positions of the other hydrogen atoms in the molecule. The results indicated the existence of a mixed structure among these atoms.

The calculated structure gave a markedly non-planar pyrimidine ring, but this is shown to have resulted from the inability of the method of structure determination to cope adequately with the anisotropy and asymmetry of the thermal motions in the molecule.

2. Experimental

The crystals of 2:5-diamino-4-mercapto-6-methyl-pyrimidine were kindly provided by Dr F. L. Rose of I.C.I. Limited, Manchester, England, who obtained satisfactory crystals, in the form of fine needles, by recrystallization from cellosolves.

These crystals were shown by Weissenberg photographs to be monoclinic, space group $P2_1/n$. Using the θ-method of Weisz, Cochran & Cole (1948), the 100 and 010 spacings were measured with Cu $K\alpha$ radiation, and the 015 spacing with Cu $K\alpha_1$. The β angle was obtained from the distance between two sets of $00l$ reflexions on Weissenberg photographs of a crystal twinned about the $h00$ plane. From these measurements the lattice parameters were calculated to be

$$a = 17{\cdot}036 \pm 0{\cdot}006,\quad b = 10{\cdot}045 \pm 0{\cdot}004,\\ c = 4{\cdot}339 \pm 0{\cdot}002\ \text{Å}\,,\\ \beta = 90°\ 56' \pm 6'\,.$$

$$(\lambda(\text{Cu } K\alpha,\ \text{mean value}) = 1{\cdot}5418\ \text{Å},\\ \lambda(\text{Cu } K\alpha_1) = 1{\cdot}5405\ \text{Å}.)$$