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On the determination of molecular location.

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A number of techniques have been described recently for determining the positions $\mathbf{r}_j$ of a known group of atoms in a molecular crystal with respect to an arbitrarily chosen origin. Once the positions $\mathbf{r}_j$ are known, it remains to determine the position $\mathbf{r}_0$ of their arbitrary origin with respect to the origin of the chosen unit cell. Methods for determining $\mathbf{r}_0$ have been described by Nordmann & Nakatsu (1963), Vand & Pepinsky (1952), and Tollin & Cochran (1964) (the last will be called TC hereafter). All of these methods require the computation of a three-dimensional function of the three coordinates of $\mathbf{r}_0$.

The slightly modified derivation of the function $Q(\mathbf{r}_0)$ (TC) given here shows that a separate function $Q(\mathbf{r}_0)$ is not required for each space group. It is now apparent that separate one- and two-dimensional functions can be obtained which determine the position of the arbitrary origin relative to individual symmetry elements. These simpler Q-functions are fewer in number, faster to compute and easier to interpret than the three-dimensional $Q(\mathbf{r}_0)$ of TC. A similar separation into one- and two-dimensional functions has been observed by Hoppe in the application of the convolution molecule method (Hoppe, 1957).

The new Q-functions are obtained by considering each symmetry element of the space group separately.

If there are n atoms in the known group the sum function (Buerger, 1959) obtained by setting down the origin of the Patterson function at the ends of the n vectors $\mathbf{r}_j$ is

$$S_n(\mathbf{r}) = \sum_{\mathbf{h}} |F(\mathbf{h})|^2 \sum_{j=1}^{n} \cos 2\pi\mathbf{h}\,.\,(\mathbf{r}_j - \mathbf{r})\,. \qquad (1)$$

Concentrating on one particular symmetry operation, T, in the space group and defining $\mathbf{R}_0$ as the position of the arbitrary origin with respect to the symmetry operation under consideration, the sum function should have peaks at the positions $\mathbf{r} = T(\mathbf{r}_j + \mathbf{R}_0) - \mathbf{R}_0$. Substituting for $\mathbf{r}$ in (1) and summing over all the sites gives a new Q-function,

$$Q(\mathbf{R}_0) = \sum_{\mathbf{h}} |F(\mathbf{h})|^2 \sum_{j,j'=1}^{n} \cos 2\pi\mathbf{h}\,.\,[\mathbf{r}_j + \mathbf{R}_0 - T(\mathbf{r}_{j'} + \mathbf{R}_0)]\,. \qquad (2)$$

The explicit forms of the Q-functions required for twofold axes and planes of symmetry are given as an example.

If T represents a twofold axis parallel to $\mathbf{b}$,

$$T(xyz) = -x,\ y + \delta y,\ -z$$

where $\delta y = 0$ if the axis is a rotation axis and $\delta y = \frac{1}{2}$ if it is a screw axis. This can be substituted in (2). If we define

$$C = \sum_{j=1}^{n} \cos 2\pi(hx_j + ky_j + lz_j)$$

$$C' = \sum_{j=1}^{n} \cos 2\pi(hx_j - ky_j + lz_j)$$

and S and S' the corresponding sine functions, then equation (2) can be rearranged in the most convenient form for computation as

$$Q(X_0Z_0) = \sum_{hl} U(hl) \cos 4\pi(hX_0 + lZ_0) - V(hl) \sin 4\pi(hX_0 + lZ_0)$$

where

$$U(hl) = \sum_{k} (-1)^q |F(hkl)|^2 (CC' - SS')$$

and

$$V(hl) = \sum_{k} (-1)^q |F(hkl)|^2 (CS' + SC')$$

where

$$q = 2k\delta y\,.$$

Similarly if T represents a plane of symmetry it will be of the form

$$T(xyz) = x + \delta x,\ -y,\ z + \delta z$$

and substitution in (2) gives

$$Q(Y_0) = \sum_{k} U(k) \cos 4\pi k Y_0 - V(k) \sin 4\pi k Y_0$$

where

$$U(k) = \sum_{hl} (-1)^q |F(hkl)|^2 (CC' + SS')$$

and

$$V(k) = \sum_{hl} (-1)^q |F(hkl)|^2 (SC' - CS')$$

where

$$q = 2(h\delta x + l\delta z)\,.$$

Once the U's and V's have been calculated, the Q-functions can be calculated with the use of standard Fourier programs.

Examination of equation (2) shows that a large peak will occur in the Q-function whenever there are two atoms in the known group having relative coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ such that the relationship

$$T(\mathbf{r}_1 + \mathbf{R}_0) - (\mathbf{r}_2 + \mathbf{R}_0) = 0 \qquad (3)$$

holds for some value of $\mathbf{R}_0$. At this value of $\mathbf{R}_0$ the magnitude of $Q(\mathbf{R}_0)$ is of the order of $\sum_{\mathbf{h}} |F(\mathbf{h})|^2$. It can be shown that the relationship (3) will be satisfied whenever there is a pair of atoms in the known group which would give rise to a non-Harker peak in the appropriate Harker section (Lipson & Cochran, 1953, p.159). For example, in a structure containing a 2_1 axis and having two atoms with relative fractional coordinates (x_1, y_1, z_1) and $(x_2, \frac{1}{2} + y_1, z_2)$ a 'false' peak will occur in the Q-function at

$$X_0 = -\tfrac{1}{2}(x_1 + x_2) \quad Z_0 = -\tfrac{1}{2}(z_1 + z_2)\,.$$

The false peaks will have the same order of magnitude as the peak which defined the true position of the known group. The false peaks can be removed from the Q-function by modifying the $|F|^2$ values to remove the origin peak from the Patterson function (Lipson & Cochran 1953, p.174). However, this is not necessary since their positions can be accurately predicted before the Q-function is calculated. Since, in the final summation, the trigonometric functions have arguments of the form $4\pi(\mathbf{h}\,.\,\mathbf{r})$ the peaks in the Q-functions are very sharp. It follows therefore that the false peaks cannot cause confusion by overlapping the origin-locating peaks. Because of the sharpness of the peaks in the Q-functions it is important to evaluate them over sufficiently closely spaced intervals.

In all the examples which follow, 'sharpened' $|F|^2$ values were used in the calculation of the Q-functions. $Q(X_0Z_0)$ was calculated using the relative coordinates of the eleven atoms in the plane of the purine residue in deoxyadenosine. The relative coordinates were those obtained from the determination of the molecular orientation (Watson, Sutor & Tollin, 1965). The space group is $P2_1$. The map obtained is shown in Fig. 1(*a*). The expected positions of peaks due to atoms separated by $b/2$ are marked in the map. The largest remaining peak is that which determines the position of the origin. The map of $Q(X_0Z_0)$ obtained using the relative coordinates for the atoms of the sugar residue in deoxyadenosine is shown in Fig. 1(*b*). In this case only eight out of a total of twenty heavy atoms in the molecules were used. The coordinates used were the final coordinates from the refined structure with an arbitrary change of origin to $x=0{\cdot}2$, $z=0{\cdot}3$. In this case there are no atoms separated by half in their fractional y coordinates.

The function $Q(Y_0)$ was calculated from relative coordinates for pyrimidine obtained by taking the final published coordinates (Wheatley, 1960) and giving them an arbitrary shift of origin to $x=-0{\cdot}15$, $y=-0{\cdot}3$. The space group is $Pna2_1$. $Q(Y_0)$ was used to define the position of the molecule relative to the a-glide plane. Only the fifty largest 'sharpened' $|F|^2$ values were used. The resulting map is shown in Fig. 2 with the origin shifted to $y=-\frac{1}{4}$ to allow for the fact that the a-glide occurs at $y=\frac{1}{4}$. The dotted vertical line represented the correct answer of $y=-0{\cdot}3$. The results show that even with this small amount of data the origin position is well defined. It can also be seen that the determination of the y coordinate is independent of the fact that at this stage the x coordinate of the arbitrary origin is not known. In all these examples the error in determining the origin position was less than 0·05 Å.

These Q-functions have also been used to determine the structure of 4-acetyl-2′-fluorobiphenyl (Tollin, Young & Sutherland, 1965).

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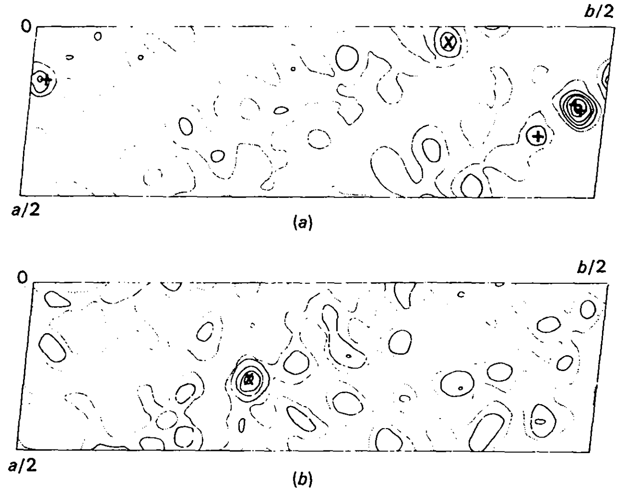

Fig. 1. $Q(X_0Z_0)$ for deoxyadenosine (*a*) using purine relative coordinates (*b*) using sugar relative coordinates. + indicates false peaks. × indicates expected positions.

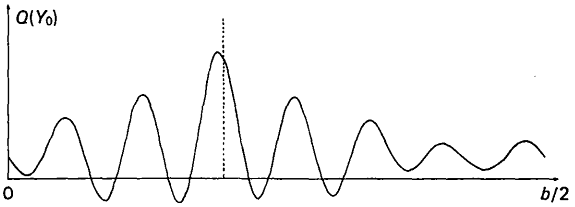

Fig. 2. $Q(Y_0)$ for pyrimidine. Dotted line indicates expected peak position.

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The crystal structure of bis(*N*-2-hydroxyethylsalicylaldiminato)copper (II).

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There is considerable current interest in the crystal structures of *N*-substituted salicylaldiminato complexes of transition metals (see Table 5, Frasson, Panattoni & Sacconi, 1964; Fox, Lingafelter, Orioli & Sacconi, 1963; Wei, Stogsdill & Lingafelter, 1964; Cheeseman, Hall & Waters, 1965). Attention has been mainly focused on the dimensions and stereochemistry of the molecule, as in all but the simplest such molecules there appears to be little molecular interaction. The substituents in compounds studied to date have been alkyl or phenyl groups, and it is of interest to consider the influence on such structures of groups with hydrogen-bonding potential. In this connection studies of the crystal structure of bis(*N*-2-hydroxyethylsalicylaldiminato)copper(II) were begun both at Providence and Auckland, the results from one of these being announced at the Rome Congress (Boyko, 1963). It transpired that the two investigations were similar in scope and achievement, and a joint publication has been decided upon.