The Use of Transforms with Three-dimensional Data

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Any planar group in real space will give rise to a spike through the origin of reciprocal space, which points in a direction at right angles to the planar grouping. Similar spikes will occur on the remaining Fourier transform peaks. By studying upper layers of the weighted reciprocal lattice the orientation of a planar group can be quickly established and a more accurate fit obtained than by merely fitting the calculated transform on a central section of the weighted reciprocal lattice. Different planar groups may be more readily resolved and their vector separation obtained from the overlapping transform peaks. Transform fits on upper layers may be used to determine phases for generalized projections in order to locate the remainder of the molecule.

Introduction

The Fourier transform of a set of atoms, (x_n, y_n, z_n) may be represented by $G = \Sigma f_n \exp (hx_n + ky_n + lz_n)2\pi i$, where h, k, and l may have any integral values. G is invariant to the choice of axes x, y, z. If x and y are chosen in the plane containing a group of atoms, the transform of that group will, except for the fall-off in the scattering factor, f_n, be independent of z. The matching of such a 'two-dimensional' transform with central sections of the weighted reciprocal lattice has provided a simple and elegant method for the solution of crystal structures containing a single planar molecule in the unit cell, or half-cell (*e.g.* Stadler, 1953; Lipson & Taylor, 1958).

This essentially two-dimensional approach, however, ignores readily available information, which can extend the scope of the Fourier transform method considerably and lead to a three-dimensional fit. A brief account of methods utilizing such extra information was given at the International Congress at Cambridge (Stadler, 1960). Related methods were also developed by Iball & MacKay (1962).

Orientation of planar groups

The orientation of a plane in space is completely described by the direction of its normal, or, as was done by MacKay (1962) by giving its 'axis of tilt' in a given reference plane by an angle, ψ, and the 'angle of tilt' out of this plane, φ (Fig. 1). The position of a group of atoms in this plane can then be further characterized by specifying the coordinates of its origin and the angle ω between any vector through its origin and the axis of tilt.

Kenyon & Taylor (1953) have shown that the two-dimensional transform of naphthalene can be recog-
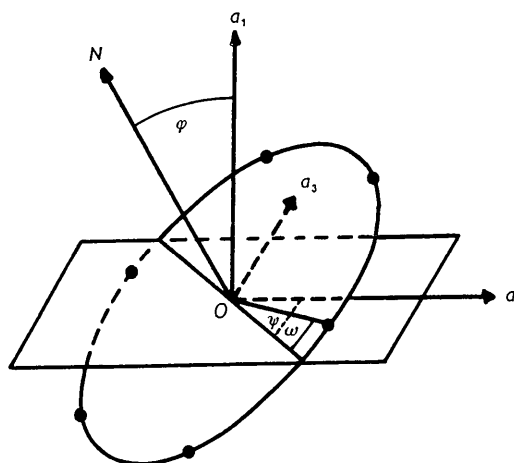
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Fig. 1. Orientation of a planar group in space. The coordinate axes are given as $a_1a_2a_3$ and ON is the normal to the planar group.

nized by viewing its three-dimensional weighted reciprocal lattice at the appropriate angle, and this can give a good estimate of the inclination of the molecule. To obtain this information it is, however, generally sufficient to examine only the 'origin peak' of the transform, to which all the atoms in the unit cell contribute. For any coplanar atoms this peak will have a spike in reciprocal space — in the direction of the normal to this plane — which can be traced through its intersections with the upper layer lines of the reciprocal lattice (Fig. 2). For a tilt φ, and a layerline separation ζ, these intersections will be displaced $\zeta \tan \varphi$ for successive layers at right angles to the line of tilt.

If there are several planar groupings or molecules, there will be several associated spikes on the origin peak each of which may be thought of as growing out normal to the plane of atoms giving rise to it. Where these spikes are resolved they give a direct indication of the orientation of the associated plane of atoms. They therefore fix both the angles ψ and φ.
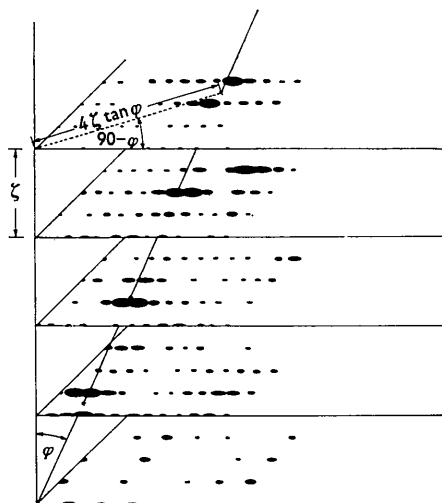
Fig. 2. Intersections of the 'origin peak' with upper layers of the weighted reciprocal lattice of flavanthrone. The orientation of the molecular plane is given by the angle ψ and the displacement $4\zeta \tan \varphi$ indicated on the fourth layer of the reciprocal lattice.

For the case of aromatic molecules (MacKay,1962) the benzene peaks must lie on an ellipse which is fully determined by these two angles. It will be invariant for all parallel layers of the reciprocal lattice, as will be the rotation angle ω which determines the fit; this can therefore be obtained most accurately by considering all the layers.

Vector separation of planar groups

In some cases, particularly at low angles, spikes due to different planes of atoms overlap. They are then modified with a fringe function, $\exp 2\pi i \mathbf{r} . \mathbf{S}$, according to their vector-separation $\mathbf{r}$ in real space, such that $G(\mathbf{S}) = G_1(\mathbf{S}) + G_2(\mathbf{S}) \exp 2\pi i \mathbf{r} . \mathbf{S}$. Fig. 3 shows an actual example where two space-group unrelated molecules of pyranthrone (Maitland & Stadler, 1964) gave rise to overlapping peaks. In this case, the molecular transform was real, and the planar molecules were known — from space-group considerations — to be on centres of symmetry. Inspection of the intensities in the overlap region made it clear that the fringe function governing the addition of the transforms must be $\cos 2\pi(k+l)/2$, and hence, that the vector separation of the molecular centres must be $\frac{1}{2}(\mathbf{b}+\mathbf{c})$. This information, together with the projection along the b axis and the approximate molecular orientations derived from the spike directions, which were resolved at higher layer-lines, gave a trial structure which refined by least-squares methods. A similar extension from two to three dimensions was possible by observing the direction and fringe function for the spikes for the two unrelated molecules in the isoviolanthrone structure (Bolton, 1964) as shown in Fig. 4.

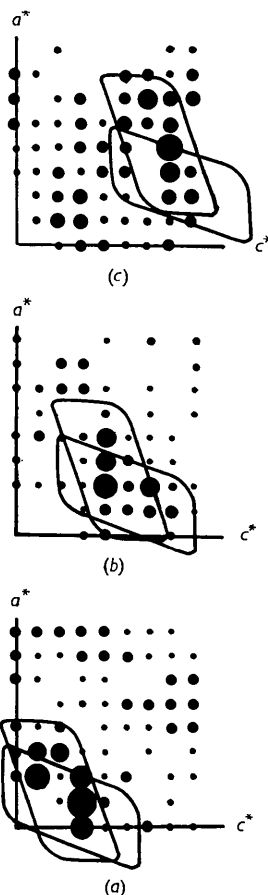Origin peaks also occur where both the transform

Fig. 3. Intersections of the 'origin peaks' of two independent molecules of pyranthrone on (a) the $(h1l)$, (b) the $(h2l)$, and (c) the $(h3l)$ layer of the reciprocal lattice. It is evident that the two peaks are out of phase for $l=2$ and 4 on $k=1$; $l=3$ and 5 for $k=2$; $l=6$ and 8 for $k=3$. The two molecules tilting in the directions indicated by the traces of the origin peaks must therefore be separated by $\frac{1}{2}(\mathbf{b}+\mathbf{c})$.

and fringe function are complex, as in the case of violanthrone (Bolton & Stadler, 1964a), but in that case the complex fringe function governing the superposition of the molecular transforms would be more difficult to interpret. Fig. 5, however, shows how the intersection of the spikes with the second layer determined the relative tilts of the two unrelated molecules in that structure. (There are four molecules in the unit cell, forming two unrelated pairs.)

In the examples cited above, the planar groupings are always complete aromatic molecules, in which spikes, similar to that on the origin peak, could be observed on all the 'benzene peaks' (Lipson & Cochran, 1953). It should be stressed, however, that the spike on the origin peak will be present for any planar, or nearly planar configuration, however irregular; moreover, it is usually stronger than any other transform peak in which all the atoms in a plane scatter in phase because the atomic scattering factor is higher near the origin. It will also be generally recognizable
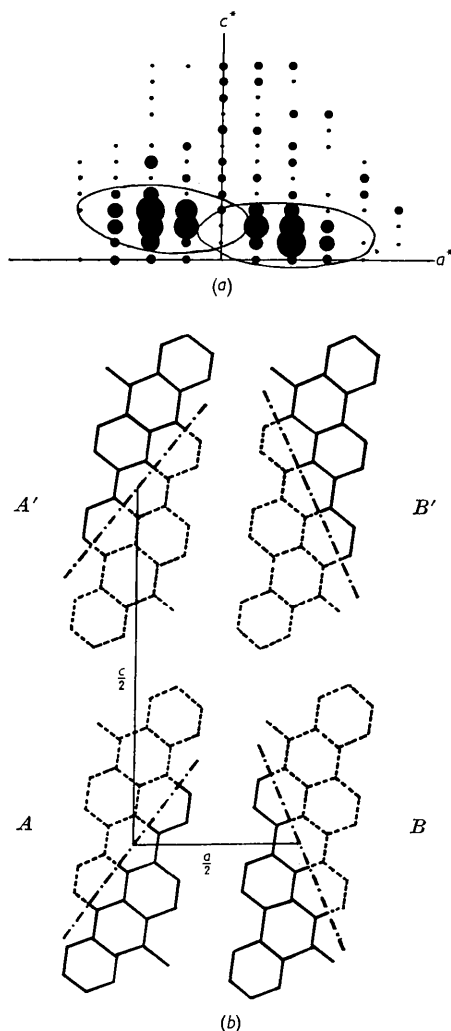
(a)

(b)

Fig. 4. (a) 'Origin peaks' in the $(h1l)$ weighted reciprocal lattice of isoviolanthrone. The weak $01l$ intensities in the overlap region indicate a fringe function $\cos 2\pi(h+k)/2$ and a separation of $(a+b)/2$. (The off-peak contributions of the molecules may be neglected). (b) The resulting arrangement of molecules. Taking molecule A on one centre of symmetry at 000, molecule B must be at $\frac{1}{2}\frac{1}{2}0$ with the tilt indicated by the broken lines. Molecules A' and B' are related by $P2_1/c$ symmetry to A and B.

in structures in which only a part of the molecule is planar.

Sign determination from transforms

Since the Fourier transform of the unit cell contains not only the structure amplitudes but also the phases, the transform fit can be used to assign phases to the individual reflexions. It was pointed out by MacKay (1962) that the signs of the principal (P) and secondary (S) peaks of aromatic systems can be found by inspection, although he gives the wrong criterion for the signs of the S peaks. It is difficult, however, to estimate how far the peaks extend, and in some distri-
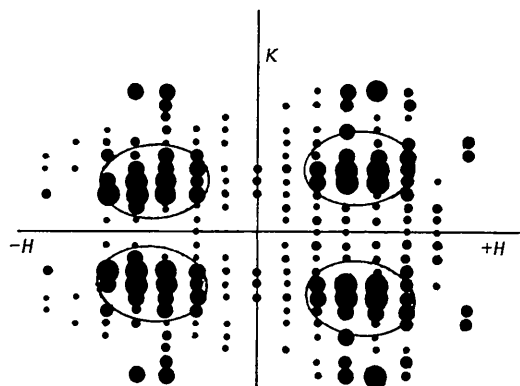

Fig. 5. 'Origin peaks' in the $(hk2)$ weighted reciprocal lattice of violanthrone — space group $P2_1$. The two pairs of spikes clearly indicate the directions of the normals to the planar molecules.

butions (e.g. Stadler, 1953) where the peaks are traversed by fringes, such signs are only applicable to the central portion of the peaks. It is, in any case, so simple to calculate the transforms of molecules with a hexagonal framework that it would be false economy not to do so. For other planar groupings the calculations may be more laborious, but structure factor programs can usually be adapted for the purpose.

Where only a part of the molecule is planar, its transform can be used in a kind of 'heavy atom method' to find the rest of the structure, as was done, for instance, by Crowder, Morley & Taylor (1959) using optical transforms and two-dimensional Fourier maps. Here again, an extension into three dimensions can be most valuable, particularly since the origin peak of the transform can be included in the upper layers, whereas this falls into the unobservable region for any central sections of the reciprocal lattice. In this way, the flat part of the molecule can be used as sign determining for generalized projections or three-dimensional Fourier syntheses. This method was tried in the determination of structure of the pyranthrone-sulphuric acid compound (Bolton & Stadler, 1964b). The generalized projections, obtained with the signs in all the 'benzene peak' regions, confirmed the positions of the planar parts of the structure (the pyranthrone molecules) and gave an indication of the positions of the sulphur atoms in the SO_4 groups.

Conclusions

The transform of any planar portion of a molecule can be regarded as a series of spikes or irregular columns parallel to its normal. These spikes will intersect the upper layer lines of the reciprocal lattice. Their traces, particularly that of the origin spike, which is present in all planar configurations, will give a good indication of the orientation of the plane in space, which is characterized by the angles ψ and φ. The rotation

angle ω can then be found by fitting the two-dimensional transform — allowing for its elongation by a factor sec φ in a direction at right angles to its axis of tilt — on each of the layers of the reciprocal lattice, with the transform fits identical except for the lateral displacement by $\zeta \tan \varphi$. A knowledge of the direction of the normal may considerably facilitate the fitting of the transform where the tilt, φ, and therefore the elongation of the transform is large (e.g. Bolton, 1963a,b, where the tilts are of the order of 60°).

Where the spikes on the origin peak overlap, the fringe function governing their addition in reciprocal space may suggest the vector separation of their associated centres in real space. In other cases, the method of Taylor & Morley (1959) of plotting $\Sigma||G|-|F_0||$ for selected reflexions may be used to determine the positions in the unit cell of the centres chosen for the calculation of each planar transform. Once the orientation and separation of the planar parts of the molecule are known, the intersection of their transforms with upper layers may be used to determine signs of structure factors, which can then be used either for generalized projections or with direct methods, to find the rest of the cell contents. Phases obtained in this manner from transforms are preferable to those obtained from the direct calculation of structure factors, since doubtful signs are more readily recognized. For the method to be successful, a reasonable proportion of scattering matter must lie in the planar parts of the molecule.

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The Rate of refinement of Coordinates in the Minimum Residual Method

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An investigation is made of the rate at which the residual is reduced as the positional parameters are refined. Good agreement is obtained between theoretical and observed values at the later stages of refinement where the errors are small. Where the errors are large there may be no agreement in spite of the success of the refinement process.

Introduction

The method considered is that proposed by Bhuiya & Stanley (1963) in which each parameter, u_j, is varied individually from $u_j - n\Delta u_j$ to $u_j + n\Delta u_j$ in $2n$ increments of Δu_j. The lowest value of the residual, $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ within the range is noted and the corresponding value of u_j is taken as the best value within the permitted range of variation. This method has worked very well with a variety of

structures even where other methods have failed. It is interesting to investigate the theoretical rates of refinement by this method and to compare them with those obtained in practice.

The nature of the refinement process

Luzzati (1952), using an elegant statistical method, has obtained details of the variation of the residual, R, as a function of $|s|$ and of the average error in