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Determination of the Positions of Molecules in a Unit Cell

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Taylor's method for determining the relative positions of molecules in projections with plane group *pgg* has been extended so that the choice of useful reflexions is less restricted and the final result is more precise.

Introduction

In investigating crystal structures by X-ray diffraction methods it is often possible to determine the shape and orientation of molecules by Fourier-transform methods or by interpreting the intramolecular vectors in Patterson projections. With this information available, the relative positions of the molecules in a projection with plane group *p*2 may be derived by a method described by Taylor (1954), which involves setting up equations for a particular reflexion *hk* which limit the choice of the true origin to points which lie on a family of straight lines of slope $-h/k$. If the equations are set up for a second plane, a second family of straight lines is produced and the origin must lie at an intersection of the two sets of lines. By adding lines for further reflexions all but one of the intersections may be eliminated.

In theory all the reflexions can be used in applying the method, but practical considerations indicate that great care is necessary in selecting the reflexions to be used, and some general rules are given, the most important for the present discussion being:

(1) Since the scale factor is generally not accurately known in the initial stages of the analysis, it is important to use reflexions which are unobserved or have small observed values, and which lie on high parts of the transform of a single molecule.

Taylor then extends the method, with slight modifications, to plane group *pgg* with four molecules in the unit cell. An important additional condition is introduced:

(2) Reflexions must be chosen for which the contribution of one molecule of the pair of molecules related by a centre of symmetry at (0, 0) is large, and the contribution of one molecule of the pair at $(\frac{1}{2}, \frac{1}{2})$ is zero.

This extra condition restricts the choice of useful reflexions so much that 'in order to obtain enough usable reflexions it is necessary to relax the condition and make allowance for the margin of error introduced'. The loci of possible positions for the origin are then no longer families of lines but families of bands of width depending on the deviation from zero of the contribution of the second molecule.

Recently Taylor & Morley (1959) have shown that in certain cases condition (2) cannot be satisfied, and they describe a modified method which overcomes this difficulty. While investigating the crystal structure of nitromesitylene (Trotter, 1959) we found it advantageous to apply a similar type of modification, and the method is presented here since it shows clearly how these modified methods are related to Taylor's original procedure.

Theory for plane group *pgg*

If (x_j, y_j) are the coordinates of the atoms in a molecule with respect to some fixed point within the molecule (the centre of an aromatic ring for example) and (X, Y) are the coordinates of this molecular centre with respect to the crystallographic origin, then the structure factor expressions for plane group *pgg* are

$$F = 4\Sigma \cos 2\pi h(x_j+X)\,.\cos 2\pi k(y_j+Y) \quad \text{when } h+k = 2n$$

$$F = -4\Sigma \sin 2\pi h(x_j+X)\,.\sin 2\pi k(y_j+Y) \quad \text{when } h+k = 2n+1\,.$$

The expression for $(h+k)$ even can be readily expanded to

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$$\begin{aligned} F &= A\,.\cos 2\pi hX\,.\cos 2\pi kY \\ &\quad + B\,.\sin 2\pi hX\,.\sin 2\pi kY \\ &\quad + C\,.\cos 2\pi hX\,.\sin 2\pi kY \\ &\quad + D\,.\sin 2\pi hX\,.\cos 2\pi kY \end{aligned}$$

where

$$\begin{aligned} A &= 4\Sigma \cos 2\pi hx_j\,.\cos 2\pi ky_j \\ B &= 4\Sigma \sin 2\pi hx_j\,.\sin 2\pi ky_j \\ C &= -4\Sigma \cos 2\pi hx_j\,.\sin 2\pi ky_j \\ D &= -4\Sigma \sin 2\pi hx_j\,.\cos 2\pi ky_j \end{aligned}$$

with a similar type of expression for planes with $(h+k)$ odd.

The variation of the function F over the unit cell may then be computed for any plane (using Beevers–Lipson strips) and a family of *curves* drawn corresponding to the observed value of the structure factor. These curves are then the loci of possible positions of the molecular centre, corresponding to the straight lines for plane group $p2$ and the bands for pgg obtained by Taylor's method. The bands have thus been replaced by curves, the amplitude of the curves corresponding to the half-width of the bands. In theory all the reflexions can be used, but as with Taylor's method best results are obtained if not all of A, B, C, D are small, so that the function F has reasonably large fluctuations (corresponding to the reflexion being on a high part of the transform of a single molecule), and if the reflexions are unobserved or have small structure factors, so that the method is independent of scale factor. If the scale factor is known even approximately however (from a Wilson plot for example), then for reflexions with structure factors which are relatively small but not negligible, narrow bands can be drawn with boundaries corresponding to the estimated possible maximum and minimum values of the structure factors, and this extends the range of useful reflexions still further.

The important point about the method is that condition (2) above is no longer necessary, so that the number of reflexions which may be used is very much increased, and in addition the curves give greater precision than the bands.

Application to nitromesitylene

Crystals of nitromesitylene (Fig. 1) are orthorhombic

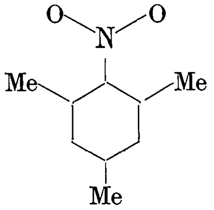

Fig. 1. Nitromesitylene.

with four molecules in a unit cell of dimensions $a = 15{\cdot}14$, $b = 8{\cdot}41$, $c = 7{\cdot}26$ Å, space group $Pna2_1$ (Trotter, 1959). The c-axis projection has plane group pgg. The orientations of the benzene rings were readily obtained from the $hk0$ weighted reciprocal lattice, the planes of the rings being exactly perpendicular to the c-axis. Steric considerations suggested that the nitro groups are tilted at least 60° out of the aromatic planes, and utilizing this information there were three possible non-equivalent orientations for the molecule, and all three had to be considered separately in applying the method for determining the molecular positions. The planes 220 and 530 have small observed structure factors, and the functions $F = 0$ for these planes for the correct molecular orientation (taking the centre of the benzene ring as the molecular centre) are shown in Fig. 2(a) and 2(b), Figs. 2(c) and 2(d) showing the correspond-

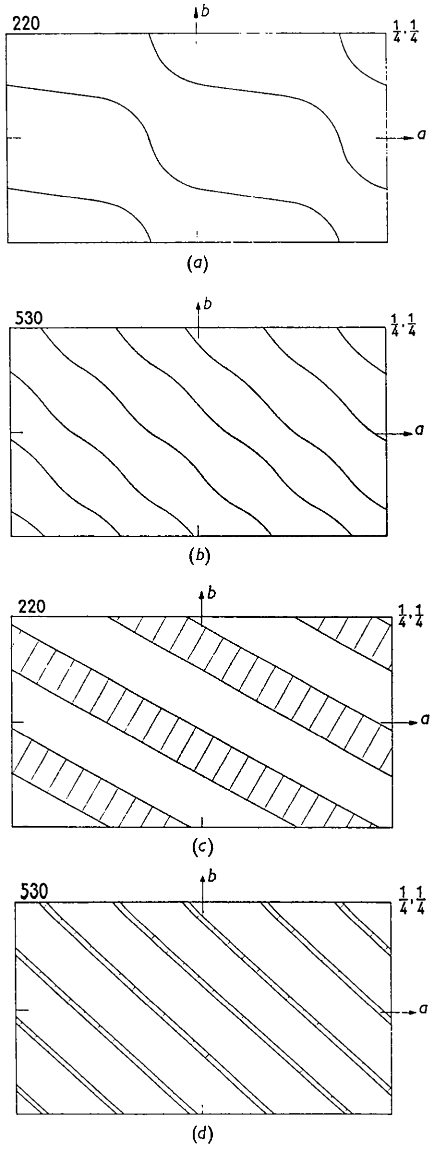

Fig. 2. (a), (b) Curves for the 200 and 530 reflexions of nitromesitylene. (c), (d) Taylor's bands for 220 and 530 reflexions.

ing bands obtained by Taylor's method. These diagrams indicate that for the reflexion 530, condition (2) above is approximately obeyed and a narrow band is obtained, but for 220 the band is wide and not very useful in restricting the possible position of the molecular centre. The curves of Figs. 2(*a*) and 2(*b*) however are much more useful in limiting the possible positions since the molecular centre must lie at one of the intersections of the sets of curves for 220 and 530, and by adding further reflexions all but one were eliminated. This procedure was simplified considerably in this case by using the reflexions 400 and 020 which have small observed structure factors, give only a few *straight lines*, and so restrict the possible positions very greatly.

When the position of the molecular centre had been determined approximately, allowance was made for the small observed values of the structure factors, and narrow bands were drawn with boundaries corresponding to the reasonable maximum and minimum values of the structure factors (for both positive and negative signs), allowing quite a large variation in possible scale factor. For example:

	F_{relative}	$F_{\text{max.}}$	$F_{\text{min.}}$	Final $F_{\text{obs.}}$
220	1·71	2	5	3·5
530	1·07	1	3	2·2
400	2·54	3	7	5·3
020	1·96	2	6	4·1

The position giving best agreement for the planes was obtained, giving for the coordinates of the molecular centre $X = -1{\cdot}602$ Å, $Y = +0{\cdot}599$ Å. Structure factors were calculated for all the *hk*0 reflexions and the value of *R*, the usual discrepancy factor, was 27%. After refinement the mean centre of the benzene ring was at $X = -1{\cdot}600$ Å, $Y = +0{\cdot}601$ Å, so that the value determined initially was quite accurate.

Further extensions

The method is not of course confined to plane group *pgg*, but can be applied to any plane group, centrosymmetric or non-centrosymmetric, by writing the structure factor expression for a given plane with the coordinates of the *j*th atom as (x_j+X, y_j+Y), expanding as a trigonometric function of *X* and *Y*, and evaluating the function over the unit cell. The curves of $F = F_{\text{obs.}}$ are then the loci of possible positions of the molecular centre. The method could also be used in three dimensions, but three-dimensional methods are generally used for molecules which are too complex for the shape and orientation to be easily determined. Since the shape and orientation must be deduced initially, the method is of course limited to relatively simple molecules.

The procedure described by Taylor & Morley (1959) is a further extension of the method given here, and it presents the data for all the reflexions very conveniently on one contour map.

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Interpretation of Some γ-MnO_2 Diffraction Patterns

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The analysis of three line-rich γ-MnO_2 patterns leads to the conclusion that the position of the sharper lines is in perfect accordance with a ramsdellite-type lattice. Certain broad lines, however, are shifted away from the positions consistent with the sharper lines in the same pattern.

Both the anomalous broadening and the shift are satisfactorily accounted for by a structure model consisting of randomly alternating layers of two kinds, derived from the known structures of ramsdellite and pyrolusite, respectively. It appears that each pattern can be characterized by one parameter *p*, the 'pyrolusite concentration', in addition to the apparent unit-cell and crystallite dimensions as derived from the sharper lines. However, the simplified theoretical treatment used here holds for small *p* only, corresponding to line-rich patterns. It is suggested that an exact treatment might be able to explain poor types of γ-MnO_2 patterns as well.

1. Introduction

Gamma-MnO_2 is at present used (Brenet (1956)) as a collective name for a series of phases, characterized mainly by their diffraction pattern. The poorest patterns consist of a strong diffuse background with some lines (Fig. 1*C*), the greater part of which happen