

Deductions from the Molecular Transform of 9:10-Anthrahydroquinone Dibenzoate

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9:10-Anthrahydroquinone dibenzoate has a centrosymmetric molecule, and crystallizes with one molecule per unit cell. As a result, its transform can be distinguished directly in its reciprocal lattice, without complication from fringe functions or complex phase considerations. From a study of this transform has been developed a simple graphical method of deriving accurately the orientation, within the crystal, of any aromatic molecule, and, with favourable centrosymmetric molecules, of estimating the signs of the principal structure factors.

1. Introduction

The importance of the molecular-transform concept in the solution of crystal structures has been understood for some time, particularly since the development of the optical diffractometer. Indeed several recent publications, acknowledging the stimulus provided by optical experiments, have emphasized the central role which the mathematics of the Fourier transform should play in crystallographic teaching (Lipson & Taylor, 1956 & 1958). It is unfortunate that those molecules which appear to possess the most easily demonstrable transforms are complicated in practice by unhelpful space groups.

The accompanying figures illustrate some of the basic features of transform theory. They have been obtained during structure investigations on the dibenzoate of anthrahydroquinone, not in itself a simple compound, but one which crystallizes conveniently with one centrosymmetric molecule to the unit cell. It therefore displays its transform directly in the intensity variations from point to point in its reciprocal lattice. The interpretation of this transform led naturally and rapidly to the approximate structure, the refinement of which is described elsewhere (Iball & Mackay, 1962).

Once more, a debt is acknowledged to the optical diffractometer for providing the initial understanding of the diffraction phenomena. It should be emphasized however, that had the basic transform theory been familiar to start with, much if not all of the experimental work with the optical diffractometer would have been unnecessary. This is not intended to belittle the use of the instrument, which did in fact provide instantaneous and reliable guidance throughout the investigation.

2. Recognition of transforms

The molecule of 9:10-anthrahydroquinone dibenzoate

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contains an anthracene nucleus to which are attached, centrally, two benzoate groups. Because of the centre of symmetry, the benzoate groups must occupy parallel planes, and from steric considerations, these planes should lie at right angles to the anthracene plane.

In attempting to identify the molecular transform within the three-dimensional reciprocal lattice, it was necessary to consider the form which it might be expected to take. Remembering that the transform of a compound molecule is the algebraic sum of the transforms of its component parts, it was in this case possible to estimate that the individually planar, but mutually perpendicular, portions of the molecule would give rise, each in its appropriate direction, to columnar transforms showing basically the same hexagonal arrangement of intensity as the benzene transform. The main difference between the two transforms would be expected to lie in the shapes of the principal maxima of each; i.e. these peaks would appear contracted in the direction of the greatest dimension of the originating portion of the molecule. The forms of these transforms were determined optically and are shown on the right of Fig. 1.

On inspecting a reconstruction of the major portion of the three-dimensional reciprocal lattice, the expected transforms were confirmed, and allocated to their respective components by comparison with the optical transforms, the photographs on the left of Fig. 1 being deliberately defocussed to bring out the overall similarities. Unfortunately the fine fringes visible in the optical transform of the benzoate groups were not distinguishable in the reciprocal lattice.

3. Measurements on transforms

From the reciprocal lattice it was possible to measure the angles of tilt in the projection studied, but this alone was not sufficient to establish the molecular orientation. Without more elaborate equipment, it proved inconvenient to perform quantitative measurements on the three-dimensional lattice as a whole and examination was confined to the intersection of each

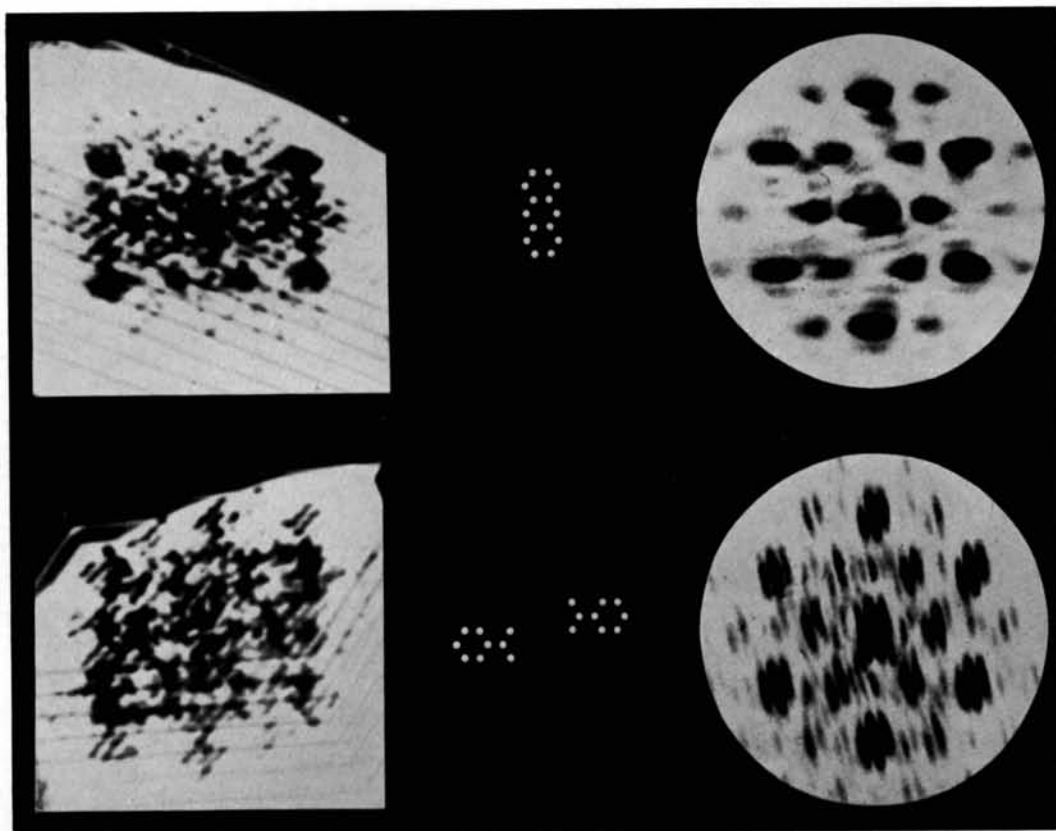


Fig. 1. Identification of transforms of anthracene (above) and benzoic acid (below) in three dimensional reciprocal lattice. Reference optical patterns on right. (Lattice shown out of focus to aid recognition).

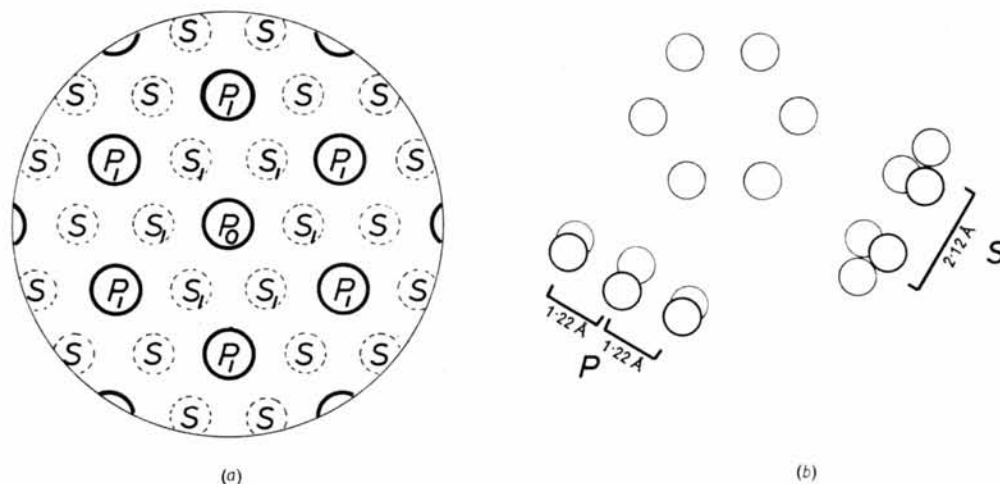


Fig. 2. (a) The basic pattern of transforms of condensed benzene ring structures. (b) The benzene ring spacings which give rise to *P*- and *S*-peaks in transform.

'part-transform', in turn, with successive planes of the reciprocal lattice, the location of the principal maxima of the transforms being indicated by particular groups of intense reflections.

The essential features of the transforms of all aromatic molecules are:

- (a) the hexagonal arrangement of principal maxima, P_1 , around the central peak, P_0 , and
- (b) the accompanying secondary maxima, *S*, which lie at the centroids of the triangles formed by three adjacent principal maxima (Fig. 2(a)).

From one compound to another, other details change, including the shapes, amplitudes and signs of these maxima, but the basic framework—which we may call the *P-S-S-P* net—is common to all.

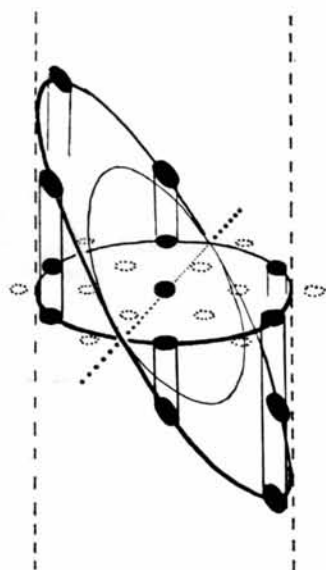


Fig. 3. Orthogonal and oblique sections of *P-S-S-P* net.

In reciprocal space, the distance from P_0 to P_1 is $\lambda/1.22$ r.l.u., representing in real space the prominent spacings of 1.22 \AA across the benzene ring when it is viewed from a direction parallel to one of the sides (Fig. 2(b)). In the same way, the spacing of $\lambda/2.12$ r.l.u. between P_0 and S_1 is related to the less well-defined real spacing of 2.12 \AA , in evidence when the benzene ring is viewed perpendicular to one of its sides.

The P_1 peaks occur at a radius of $\lambda/1.22$ r.l.u., but this can be measured only when a reciprocal plane cuts the transform orthogonally. In general, the plane of section is oblique, and the P_1 -regions lie on an ellipse, the length of its major axis being a measure of the obliquity of the section. The minor axis remains at $\lambda/1.22$ r.l.u. (Fig. 3).

To facilitate measurements, therefore, on the transform of the present compound, the *P-S-S-P* net for

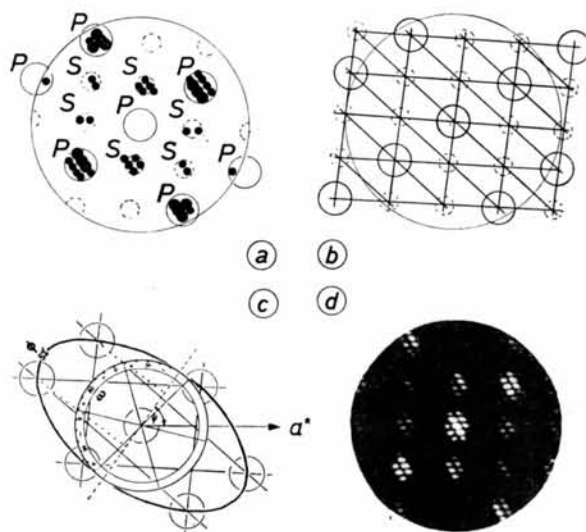


Fig. 4. Recognition (a), construction (b), measurement (c) and verification (d) of oblique section of *P-S-S-P* net.

the $hk0$ reciprocal plane was drawn, using three sets of parallel equidistant lines and ensuring that the intersections of the net lay satisfactorily on the corresponding intense regions on the plane (Fig. 4). Instead of attempting to construct the ellipse through the P -regions, a transparent chart consisting of a family of ellipses having the same minor axis ($\lambda/1.22$ r.l.u.) and representing various oblique sections was adjusted to give the optimum fit (Fig. 5). Hence the apparent obliquity ϕ , and the angle ψ , between the axis of tilt and a principal direction in the reciprocal plane, were both obtained. By a simple extension of the geometrical argument, it was also possible to establish the angle ω between the axis of tilt and a symmetry axis of the benzene ring. All three measurements were further checked by repeating the observations on the S_1 peaks.

From the knowledge of these three angles—later shown to have been less than 2° in error—the co-

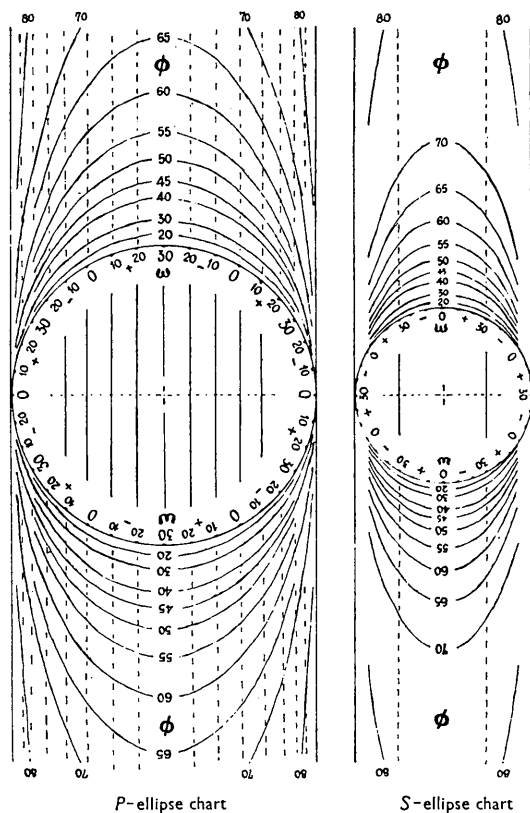


Fig. 5. Charts for determining benzene ring orientation from P - S - S - P net.

Table 1. Co-ordinates of vertices of regular hexagon, of side R , referred to centre, as function of rotation angle ω and tilt angle ϕ

	x	y	z
A	$R \sin \omega$	$R \cos \omega \cos \phi$	$\mp R \cos \omega \sin \phi$
B	$R \cos (30^\circ - \omega)$	$R \sin (30^\circ - \omega) \cos \phi$	$\mp R \sin (30^\circ - \omega) \sin \phi$
C	$R \cos (30^\circ + \omega)$	$-R \sin (30^\circ + \omega) \cos \phi$	$\pm R \sin (30^\circ + \omega) \sin \phi$

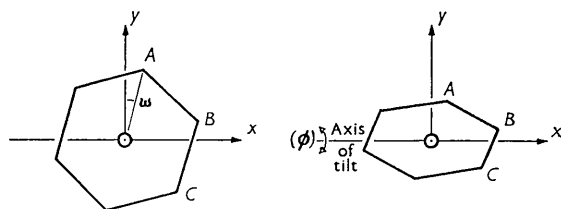


Fig. 6. Derivation of projection of regular hexagon, from knowledge of ω and ϕ .

ordinates of the atoms composing the 'basic-benzene-ring' for each component were obtained using the relations of Table 1. These benzene rings were then employed as structural units and the co-ordinates of all the atoms in the molecule were easily established.

4. Sign estimation

Having compared the optical diffraction pattern of the proposed structure with the weighted reciprocal lattice, and observed the overall similarity, it was a simple matter—also by optical means—to obtain the signs of the stronger reflections (Pinnock & Taylor, 1955).

If the optical diffractometer had not been available, the signs of the more intense reflections could have been derived from comparison with the calculated transform. Even this labour, however, may be avoided if only the signs within P and S regions are required, and a mental procedure, similar in principle to the optical method of sign determination, may be reliably employed.

The P -spacing is prominent when the aromatic molecule is viewed parallel to the sides of the benzene

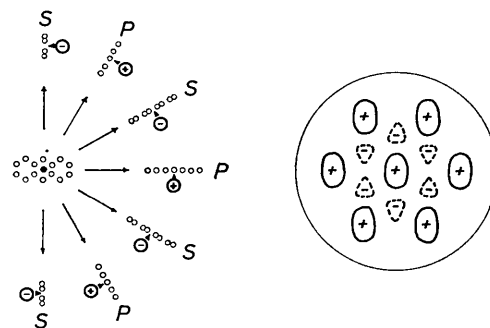


Fig. 7. Deduction of signs in anthracene transform. When additional 'central atom' does not affect existing spacing, sign of corresponding peak is positive. When addition halves spacing, sign is negative.

ring, and the S -spacing when viewed at right angles to a side. If an additional atom, placed at the centre of the molecule, is found not to disturb an existing spacing, the sign of the corresponding transform peak is positive. If the added atom bisects an existing spacing, the sign of the transform peak is negative.

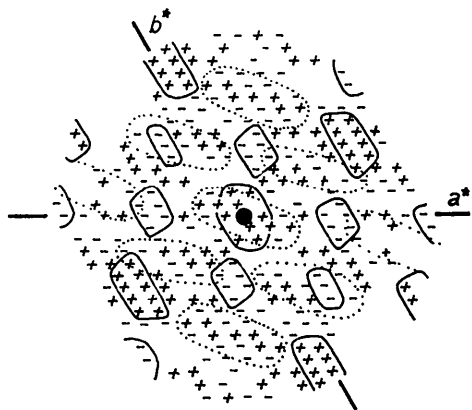


Fig. 8. The signs of structure factors in the $hk0$ zone. Solid lines outline anthracene contribution. (P regions are entirely positive, S regions negative). Dotted lines outline benzoate contribution. (Bands of alternating sign indicate position of fringes).

The derivation of the signs of the P and S peaks in the anthracene transform is demonstrated in Fig. 7, which may be compared with Fig. 8 giving the signs obtained from the final structure. This diagram displays the contributions of the two components of the molecule to the $hk0$ layer of the reciprocal lattice. Provided the transforms are truly columnar, the sign distribution in each will be preserved throughout the reciprocal lattice.

Some comment should be made about the sign distribution in the benzoate transform. As would be expected from transform theory, this is seen in Fig. 8 to consist of a benzene-type pattern crossed by fringes of alternate sign which are to the first order parallel, and whose spacing corresponds to the separation between the centres of gravity of the benzoate groups. Estimation of sign, by the quasi-optical method discussed above, gives the correct signs for reflections occurring in the central fringe of each maximum, but because the fringe-width is inversely dependent on the

extension of the molecule, the fringes are, in this case, considerably finer than the individual benzene-peak. Consequently the benzoate groups do not form a favourable subject for mental calculations.

However—and this also is applicable to any centrosymmetric aromatic molecule—reliable and general sign distributions are obtainable by performing, for instance with the aid of Beavers–Lipson strips, rapid (5–10 minute) one-dimensional Fourier summations parallel to the six principal (benzene) interatomic vectors. From these line sections, too, it is relatively straightforward to construct a complete plane section of the molecular transform. Where more than one such molecule occur in the unit cell, the combination of transforms follows recognized rules (see e.g. Lipson & Taylor (1958)) and leads to the transform of the unit-cell contents.

5. Conclusion

The results of this investigation demonstrate in a convincing manner the usefulness of the Fourier-transform approach in the calculation of molecular structure. The ease of interpretation is due principally to the fact that the compound crystallizes with one molecule to the unit cell, and also to the planarity of the component portions of the molecule, the hexagonal pattern of the transforms being readily detected.

It is clear that many of the ideas discussed may be transferred to calculations on more complex crystalline compounds, where the application of space group phase relations and the theory of fringe functions will be required.

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References

- IBALL, J. & MACKAY, K. J. H. (1962). *Acta Cryst.* **15**, 152.
- LIPSON, H. & TAYLOR, C. A. (1956). *The Teaching of Crystallography*, p. 19. (I.U.C., Madrid. P. Dep. Crist. Min. 7 (1960)).
- LIPSON, H. & TAYLOR, C. A. (1958). *Fourier Transforms and X-ray Diffraction*. London: Bell.
- PINNOCK, P. R. & TAYLOR, C. A. (1955). *Acta Cryst.* **8**, 687.