

Purpurogallin : by Optical Diffraction Methods

THE unit-cell dimensions found for purpurogallin, $C_{11}H_8O_5$, indicate that the molecules, which are assumed to be planar, lie almost parallel to the (001) planes and that they do not overlap in the c -axis projection. The present communication is concerned only with this projection, and the structure is described in terms of the plane-group pgg , with four molecules in general positions in a cell which has $a = 9.78$ and $b = 24.6$ Å. There are certain complications in the full three-dimensional structure which need not concern us here.

The weighted reciprocal-lattice section containing the $hk0$ reflexions is given in Fig. 1 and the form assumed for the molecule is indicated in Fig. 2. It will be observed that the molecule contains one six-membered ring and that a number of the atoms adjacent to this ring form portions of regular hexagons approximately parallel to it. The transform of any regular hexagonal arrangement of atoms contains six peaks which, if the molecule lies in the plane of projection, lie at equal intervals around a circle with its centre at the origin and of radius 0.83 \AA^{-1} . (We have called this the 'benzene circle' since the peaks appear in the transform of any molecule containing a benzene ring.) If the molecule is tilted out of the plane, some or all of the peaks will move away from the circle. In purpurogallin there are four molecules of different orientation; but since they are related by two-fold axes (equivalent to centres of symmetry in projection) there are only two different orientations of the hexagon to consider, and we should therefore expect to find twelve peaks in the transform of a complete unit cell. Since the molecules lie close to the plane of projection, these peaks should appear close to the benzene circle. An inspection of Fig. 1 (on which the benzene circle has been indicated) shows at once that there are twelve strong reflexions in about the expected positions. Closer inspection shows that there are, in fact, twelve groups of reflexions (indicated by broken lines on one half of the diagram), which give a clear indication of the positions of the peaks in the underlying transform. The orientation of the hexagonal portions of the molecules with respect to the three crystallographic axes follows immediately.

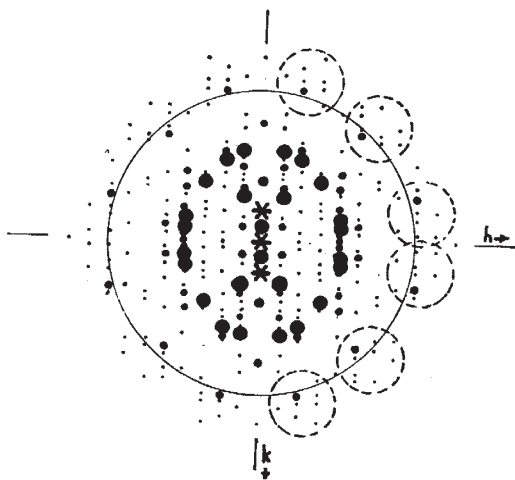


Fig. 1. Weighted reciprocal-lattice section containing the $hk0$ reflexions for purpurogallin. The 'benzene circle' is also shown

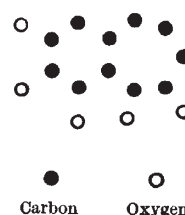


Fig. 2. Assumed form of the molecule of purpurogallin

On the basis of this deduction, together with some simple packing considerations, and the fact that the 040 reflexion is particularly strong, a set of atomic positions was postulated. These were then checked and modified slightly by the optical method^{1,2}. When reasonable agreement seemed to have been obtained, the signs of the structure factors were determined optically² and a calculated Fourier synthesis with these signs showed all the atoms unequivocally.

Two points are emphasized by this result :

(1) A considerable amount of information can be derived directly from the weighted reciprocal-lattice section without explicit use of optical transforms.

(2) Subsequent calculation showed that the factor of agreement of the first proposed structure was about 0.6, but a large proportion of the signs derived optically proved to be right. The factor of agreement fell to less than half this figure for the atomic positions derived from the first Fourier synthesis. This underlines the fact that although optical methods may not always lead directly to a structure with a small factor of agreement, they do lead to structures which can be rapidly refined, that is, which have a high proportion of correct signs. This arises naturally from the method employed. Fourier transforms of centrosymmetrical projections consist of peaks within which the phase is constant, separated by zero lines across which the phase changes³. Optical methods aim at placing the majority of the reciprocal-lattice points on the correct peaks of the transform; subsequent refinement corresponds to finding the correct position within a given peak. Obviously there is much more latitude in finding the right peak than in finding the correct position for each reflexion, which is effectively the aim of methods based on quantitative agreement.

I am indebted to Mrs. D. Hodgkin for suggesting the problem and allowing me to make use of the X-ray data. These data had been available for some time; but work had not been carried beyond the earliest stages because of the large amount of computational work involved. The optical methods proved to be quite rapid, the work described, although interspersed with teaching and other duties, being completed in about five weeks.

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¹ Taylor, C. A., and Lipson, H., *Nature*, **167**, 809 (1951).

² Lipson, H., and Taylor, C. A., *Acta Cryst.*, **4**, 458 (1951).

³ Taylor, C. A., *Acta Cryst.*, **5**, 141 (1952).

Purpurogallin : by X-Ray Fourier Synthesis

ALTHOUGH the oxidation product of pyrogallol, purpurogallin, has been known to chemists for more than eighty years, its structure remained unsolved until Barltrop and Nicholson¹, and almost simultaneously Haworth, Moore and Pauson², formulated it as the benzo-tropolone derivative (I). This