

## A Direct Application of Electronically-Presented Optical Transforms

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The orientation of a plane molecule in a crystal structure can be found relatively quickly by the optical-transform method. An appreciable amount of time, however, is taken up by the production of the transform on a suitable scale and by the subsequent steps necessary to deduce the orientation. Both these stages can be eliminated by the direct presentation on a television monitor; it then becomes possible to orient the mask in the optical diffractometer so that the diffraction pattern matches the weighted reciprocal-lattice section. The two parameters giving the orientation of the molecule can then be read directly on circular scales.

Two examples of the procedure are described, one for a known structure and one for an unknown structure. Each result was obtained in about 45 min.

### 1. Introduction and description of the method

Several applications of optical methods to the determination of crystal structures have been described in the last few years (e.g. Hanson, Lipson & Taylor, 1953) but these methods all involve considerable photographic work. This work is necessary in order to produce transforms large enough for reasonably accurate study; direct optical enlargement is not practicable because the intensity is too small.

The apparatus described by Hanson & Menarry (1956) provides a method of presenting a transform of the size required on a television monitor in less than 30 sec. Such a rapid means of producing a transform of the required scale introduces the possibility of new experimental methods and the present paper describes the first application of the apparatus.

It was decided to choose a simple problem—the determination of the orientation of a plane molecule fixed on a centre of symmetry. Two variables are introduced: the tilt,  $\varphi$ , of the plane of the molecule and the direction,  $\psi$ , of the axis of tilt. The angle  $\varphi$  can be measured with respect to a crystallographic plane and the angle  $\psi$  with respect to a reference line in the molecule.

### 2. The apparatus and method of procedure

The weighted reciprocal-lattice section was drawn on transparent material and supported as closely as possible to the screen of the television monitor. The scale of reproduction of the transform presented on the monitor was adjusted to correspond to that of the weighted reciprocal lattice by the use of a square mesh as a test object. A mask representing the molecule was then mounted in the diffractometer with the two necessary degrees of freedom by means of the device shown in Fig. 1; this device is similar to that described by Liquori (1956) for use with calculated transforms. The angles  $\varphi$  and  $\psi$  are read directly from scales

*A* and *B* (Fig. 1) respectively. Optical principles should indicate how the mask should be tilted to give an approximate correspondence between transform and

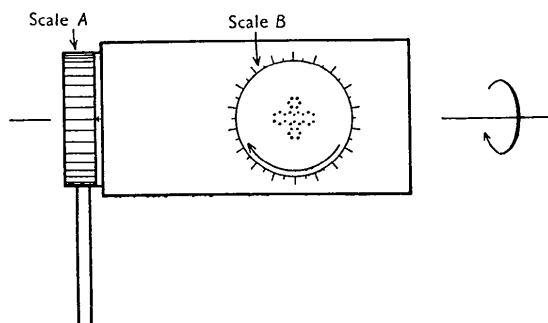


Fig. 1. Device for tilting mask.

weighted reciprocal lattice. Various positions of the mask can be tried and the best solution arrived at by a process of trial and error. However, as the tilt of the mask increases, less light is transmitted and the pattern becomes fainter; as a final check, therefore, a new mask representing the chosen orientation may be punched to examine some of the finer detail of the transform.

### 3. Application to diphenylene naphthacene

It must first be decided which features of the weighted reciprocal lattice correspond with particular features of the transform. This is, of course, the basic problem in crystal-structure determination. For diphenylene naphthacene the solution is fairly obvious; the four strong peaks along the lines indicated by the arrows in Fig. 2(a) should be made to correspond with the four sets of strong reflexions similarly indicated in Fig. 2(b). In about 45 min. a solution was reached that, within the limits of the apparatus, could not be appreciably improved. The result is illustrated in

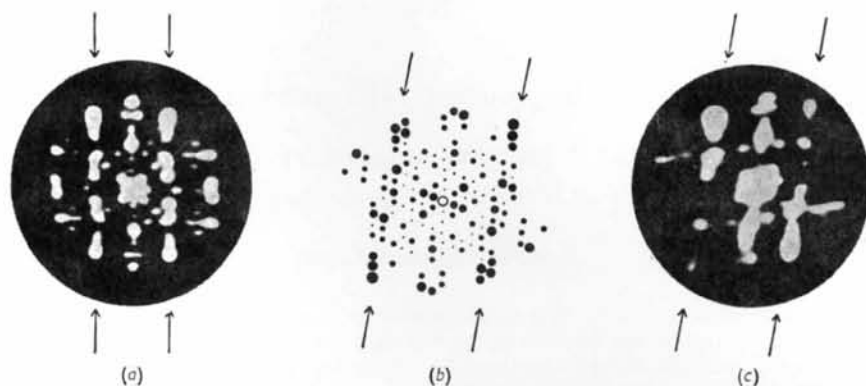


Fig. 2. (a) Optical transform of diphenylene naphthacene as presented on the television screen. (b) Weighted reciprocal-lattice section ( $h0l$ ) of diphenylene naphthacene. (c) Optical transform of tilted diphenylene naphthacene molecule as presented on the television screen.

Fig. 2(c), which shows the transform of the tilted mask. This may be compared with the weighted reciprocal lattice shown in Fig. 2(b).

To gain some idea of the accuracy obtained, the process was repeated several times and the results are summarized in Table 1.  $\psi$  is the angle, measured in the

Table 1

	Independent measurements						Mean	Bennett & Hanson
$\varphi$ ( $^\circ$ )	46	46	46	48	48	44	$46 \pm 2$	49
$\psi$ ( $^\circ$ )	64	63	65	70	69	66	$66 \pm 4$	62

plane of the molecule, between the reference line, shown in Fig. 3(a), and the axis of tilt. In the last

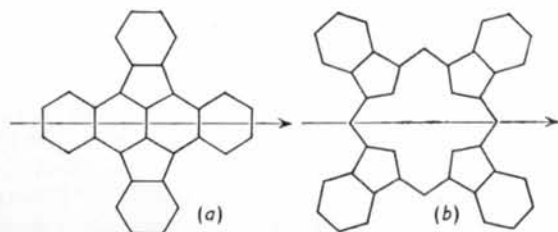


Fig. 3. Idealized molecules of (a) diphenylene naphthacene, (b) tetrabenzmonazaporphin, showing reference lines adopted.

column of Table 1 the values of  $\varphi$  and  $\psi$  derived from the results of Bennett & Hanson (1953) are also shown for comparison. It will be seen therefore that the method is capable of arriving quickly at an approximate result.

#### 4. Application to tetrabenzmonazaporphin

Similar methods were used for tetrabenzmonazaporphin, which has a molecule (Fig. 3(b)) similar to that of phthalocyanine except that one of the carbon atoms is replaced by nitrogen (Woodward, 1940). The

space group is  $P2_1/a$  (No. 14) and the unit cell, whose dimensions are  $a = 17.6$ ,  $b = 6.61$ ,  $c = 12.5$  Å,  $\beta = 122.7^\circ$ , contains two molecules. Thus the molecules lie on centres of symmetry in spite of the asymmetry produced by the nitrogen atom.

The weighted reciprocal lattice was derived from a Weissenberg photograph kindly supplied by Dr Woodward. No accurate measurements of intensity were made because the Bragg angles of the spots extended only to about  $27^\circ$  and a complete structure determination would therefore not be accurate enough to be worth while. An unambiguous solution for the orientation was found, however, and several independent measurements are shown in Table 2.

Table 2

	Independent measurements					Mean
$\varphi$ ( $^\circ$ )	58	57	58	57	58	$58 \pm 1$
$\psi$ ( $^\circ$ )	33	34	30	32	30	$32 \pm 2$

These results confirm the statement by Woodward (1940), that the angle of tilt is about  $60^\circ$ ; this deduction was made on the basis of cell dimensions, but the complete orientation of the molecule could have been found only if a full crystal-structure determination had been undertaken.

#### 5. Limitations of the method

It can be seen that approximate results can be obtained quickly with the apparatus described. There are several reasons why the accuracy is not better than that indicated by Table 1.

First, the molecule of diphenylene naphthacene is not truly planar; according to Bennett & Hanson (1953) the phenylene rings are inclined at about  $10^\circ$  to the plane of the naphthacene group. The masks in both the examples given are representations of an ideal molecule, and any distortions are not taken into account. It is suggested by Woodward (1940) that the

molecule of tetrabenzmonazaporphin may be distorted by the presence of the nitrogen atom.

Secondly, some detail in the transforms is lost by reproduction and some geometrical distortion is introduced by non-linearities in the electronic equipment. The transforms in Figs. 2(a) and 2(c) are not as detailed as those shown by Hanson, Lipson & Taylor (1953). The lack of clarity is, however, partly caused by the difficulty of photographing the television screen; the exposure for Figs. 2(a) and 2(c) is of the order of 30 sec. and the pattern is not completely steady over this period.

Finally, the weighted reciprocal lattice is not in the same plane as the television screen and some parallax errors may result.

Work is in progress to reduce as far as possible those difficulties caused by the apparatus itself, but obviously the problem of non-planarity of the molecule is one that sets a limiting factor to the methods de-

scribed. Nevertheless, the results should serve as a sound basis for refinement by standard methods.

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## On the Crystal Structure of Silver Thiocyanate

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The crystal structure of AgSCN has been determined from three-dimensional X-ray data. There is still some question about the exact positions of the light atoms, but the general picture of the structure is well established. The structural unit is an endless chain with the composition AgSCN, formed by covalent bonds from a silver atom to the end sulphur of one thiocyanate group and the end nitrogen of another thiocyanate group. The chain has a zigzag shape and is bent at S ( $104^\circ$ ) as well as at Ag ( $165^\circ$ ). There is silver-sulphur interaction between the chains as they are packed together.

A thorough reinvestigation of the structure has been started.

### 1. Introduction

This investigation forms part of a study of the crystal chemistry of silver salts. Its aim is to elucidate the stereochemistry of the monovalent silver ion in solid compounds. The results are incomplete and a thorough reinvestigation has been started by Mr Strandberg in this Institute along lines indicated in this paper. It has, however, been thought worth while to publish the paper in the present state because of the theoretical interest of the structure.

### 2. Crystals

AgSCN was first precipitated as a powder in two different ways: with a slight excess of  $\text{SCN}^-$  and with a large excess of  $\text{Ag}^+$ . The two precipitates gave identical powder photographs, thus showing no sign of the dimorphism existing in the case of AgI (Block &

Müller, 1931). The powder was dissolved in an aqueous ammonia solution and single crystals of AgSCN were formed by free evaporation from this solution. The identity of the crystals with the powder was confirmed by powder photographs.

A roughly prismatic needle with the dimensions  $0.2 \times 0.1 \times 0.04$  mm.<sup>3</sup> was used for the X-ray work. Rotation and Weissenberg photographs were taken around the needle axis (*c* axis) with Cu *K* radiation. Seven layer lines (0-6) were obtained.

The crystal symmetry was found to be monoclinic and the cell dimensions are

$$a = 8.74, b = 7.96, c = 12.32 \text{ \AA}, \beta = 138.6^\circ,$$

as determined from powder photographs taken with Cu *K* $\alpha$  radiation in a Guinier camera. The density of AgSCN has been determined as  $3.746 \text{ g.cm.}^{-3}$  (Huttner & Knappe, 1930). This corresponds to 7.7 formula units