Acta Cryst. (1953). **6**, 745

The direct use of three-dimensional X-ray data in crystal-structure determination.

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(*Received* 17 *April* 1953)

Introduction

In the early stages of the determination of a crystal structure a two-dimensional $|F|^2$ synthesis (Patterson, 1935) may give valuable information. The same information can often be obtained, however, in a simpler, more rapid and less laborious manner by direct interpretation of a weighted reciprocal-lattice section, in terms of Fourier-transform principles (Taylor, 1952; Hanson, Lipson & Taylor, 1953). Extension of the $|F|^2$-synthesis technique to three dimensions increases its usefulness very considerably (Shoemaker, Donohue, Schomaker & Corey, 1950; Robertson & Beevers, 1951), and it therefore seems likely that direct interpretation of the weighted reciprocal lattice in three dimensions will be correspondingly more informative than in two. In order to explore this possibility, a representation of the full, three-dimensional weighted reciprocal lattice of naphthalene has been prepared from the data of Abrahams, Robertson & White (1949).

Preparation of the model

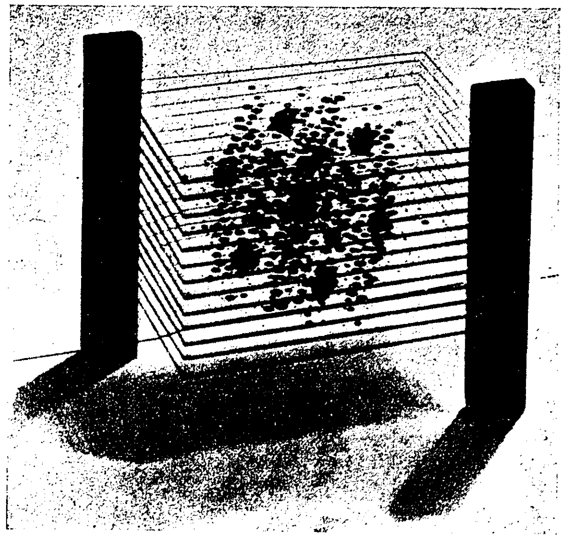

Fig. 1. Photograph of the model taken in a direction along one set of cylinders, that is, normal to the plane of one molecule.

The model (Fig. 1) consists of thirteen glass plates, each representing a section of the reciprocal lattice of constant k value (k ranges from $\bar{6}$ to 6). Photographic plates which had been fixed and washed were used and spots representing unitary F-values were drawn in indian ink on the clear emulsion. As recommended for two-dimensional sections (Hanson *et al.*, 1953), a scale of 5 cm. ≡ 1 Å^{-1} was used and the F's are represented by spots of only five different sizes. The plates are mounted in a frame which holds them parallel to each other with a perpendicular separation corresponding to b^*.

Disturbing multiple reflexions occur from the glass plates, and to eliminate these it has been found convenient to view and photograph the model through a suitably oriented polaroid filter.

Interpretation

The weighted reciprocal lattice may be regarded as a set of samples, at the reciprocal-lattice points, of the three-dimensional transform of the contents of one complete unit cell of the structure. The space group for the naphthalene structure is $P2_1/a$, and there are two molecules in the unit cell; the total transform will thus be the vector sum of the transforms of the two molecules. The molecules are planar and, if we consider them to be composed of point atoms, there will be no variation in the transform along a direction perpendicular to the plane; the three-dimensional transform of one molecule is thus the figure swept out when the plane transform is translated in the direction of its normal. The plane transform of an idealized naphthalene molecule (Knott, 1940) is shown in Fig. 2, and it can be seen from this that the principal feature of the three-dimensional transform is a set of six cylinders, of roughly elliptical cross-section, arranged hexagonally around a similar cylinder passing through the origin. In the transform of the complete unit cell, therefore, two sets of cylinders should exist with their axes equally and oppositely inclined to b^*.

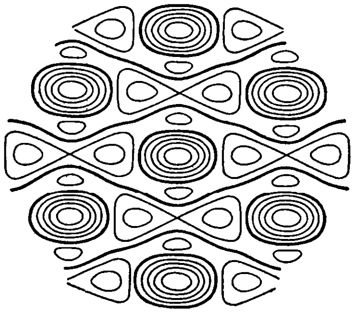

Fig. 2. Plane transform of idealized naphthalene molecule (after Knott, 1940).

The density of the reciprocal-lattice points is sufficiently high for the form of the cylinders to be seen in the actual model. In Fig. 1, which is a photograph taken along the direction of one set of cylinders, the dense packing of spots along them can clearly be seen; the angles χ_N and ψ_N which this direction makes with the axes a and b can be determined with a consistency of about 2°. The results obtained, together with those of Abrahams *et al.* (1949), are:

	χ_N (°)	ψ_N (°)
Abrahams *et al.*	32·8	116·3
From model	31	116

Conclusions

It has already been found in two dimensions that, for structures with large unit cells, difficulties arising from the increased complexity of the molecule are to some extent offset by the increase in the number of points at which the transform is sampled, and it seems probable that the same consideration will apply in three dimensions. The ease with which the two separate sets of columns can be identified in the present model suggests the possibility of detecting the existence of planar portions of more complicated molecules, and of specifying their orientation. Similarly, it may be possible to detect the presence of long chains and to determine their directions, as they give rise to flat discs in reciprocal space.

Since only approximate intensity data are required and the labour of preparing a model of the type described is not very great, the technique might prove to be a useful preliminary to a full three-dimensional structure determination.

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Acta Cryst. (1953). **6**, 746

Bonding in benzene iododichloride and related molecules.

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(*Received* 18 *May* 1953)

In the recent investigation of the structure of benzene iododichloride, $C_6H_5ICl_2$, (Archer & van Schalkwyk, 1953) the authors reported what they considered to be a rather long I–Cl bond distance. If one draws the analogy between this substance, the diarylselenium dihalides, and related compounds pointed out by the present author (McCullough, 1942), the long I–Cl distance, the molecular structure and the chemical properties (dissociation into iodobenzene and chlorine) are all to be expected. It is reasonable to expect that compounds of the general type R_3(P,As,Sb,Bi)X_2, R_2(S,Se,Te)X_2 and RIX_2 should have the structure of a trigonal bipyramid with the halogen atoms at the apices and the three equatorial positions occupied by the R groups and unshared electron pairs. The X–M–X bond angle should be nearly linear and the M–X distance longer than the sum of the normal single covalent bond radii. The nature of the bonding in the *p*-tolylselenium dihalides and related molecules has been discussed by McCullough & Marsh (1950). Data on compounds of this general type which have been studied by X-ray diffraction methods are given in Table 1.

Semi-quantitative predictions based on the data in the table are probably of little value since selenium is in the row above that occupied by antimony and iodine. Data on compounds of the type R_2TeX_2 now under investigation in this laboratory should be of more use in this connection and the trends in the M–X distances in trigonal bipyramidal structures both horizontally and vertically in the periodic chart should be of interest.

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Table 1. *M–X distances in some organometallic dihalide molecules having the trigonal bipyramid structure*

Compound	Reference	Observed M–X distance (Å)	Sum of single covalent bond radii (Å)	Difference (Å)
$(CH_3)_3SbCl_2$	Wells (1938)	2·49	2·40	0·09
$(CH_3)_3SbBr_2$	Wells (1938)	2·63	2·55	0·08
$(C_6H_5)_2SeCl_2$	McCullough & Hamburger (1942)	2·30*	2·16	0·14*
$(C_6H_5)_2SeBr_2$	McCullough & Hamburger (1941)	2·52	2·31	0·21
(*p*-Tolyl)$_2SeCl_2$	McCullough & Marsh (1950)	2·38	2·16	0·22
(*p*-Tolyl)$_2SeBr_2$	McCullough & Marsh (1950)	2·55	2·31	0·24
$C_6H_5ICl_2$	Archer & van Schalkwyk (1953)	2·45	2·32	0·13

* Subject to greater error than that in the *p*-tolyl compound owing to there being 8 molecules per unit cell as compared to 2 in *p*-tolylselenium dichloride.