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Choice of the starting set of reflexions in direct methods: some simple criteria.

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The origin-defining reflexions should be approximately orthogonal to one another and, in appropriate cases, should also define the mean plane and orientation of a major fragment of the molecule.

The determination of the crystal structures of all-light-atom compounds by direct methods has become almost routine thanks to the well known programs for centrosymmetric crystals (Long, 1965) and for non-centrosymmetric crystals (Main, Woolfson & Germain, 1971). Both programs can be run automatically or with the intervention of the user at the stage where the origin-defining and variable phases are chosen.

For compounds of very high molecular symmetry, particularly those containing fused six-membered rings, the intensity distribution is abnormal and often leads to problems in the direct determination of phases. Groups of reflexions with large E's and having closely related sets of indices often belong to only a limited fraction of the parity groups. This problem was encountered in the solution of the structure of 1,3,5-triacetylbenzene (O'Connor, 1973). In the automatic mode, the programs will typically choose the origin-defining reflexions so that each (i) has a large E, (ii) is involved in a large number of sigma-2 triples, (iii) belongs to the correct parity group.

Consider Fig. 1(*a*): the three planes $\mathbf{h},\mathbf{h}',\mathbf{h}''$ can conceivably obey the criteria (i), (ii) and (iii) yet are close to parallel in real space. For example, reflexions 214 (*eoe*), 225 (*eeo*) and 315 (*ooo*) could legitimately have been chosen as origin definers had this particular phenanthrene-like molecule been in space group $P2_1/c$. However, were these reflexions to be used as the origin definers in *SAYRE* (Long, 1965) or *MULTAN* (Main *et al.*, 1971) they would never yield a correct solution. In a naive sense they do not define the position of the molecule in three dimensions – it can 'slide' parallel to the planes.

A simple solution to the problem is to choose the origin-defining reflexions not only to satisfy the usual criteria but also to have two of them parallel to two sides of the six-membered rings while the third should be in the approximate plane of the molecule. Planes $\mathbf{h},\mathbf{h}'$ and $\mathbf{h}''$ in Fig. 1(*b*) satisfy all these criteria. The interplanar spacings of $\mathbf{h}$ and $\mathbf{h}'$ would be about 1·2 Å and that of $\mathbf{h}''$ would be about 3·5 Å. This set of reflexions has effectively fixed the molecule in three dimensions.

The choice of suitable reflexions can be made by direct examination of the appropriate Weissenberg or precession photographs – equivalent to examining the Fourier transform or weighted reciprocal lattice (Taylor & Lipson, 1964). A possibly better procedure is first to calculate a Patterson map (E^2 or F^2), then to examine the distribution of peaks near the origin for information about the orientation of the larger fragments. A search within the body of the map may yield the position of the approximate centre of gravity of the molecule and this information will be of use later for evaluating the E maps.

In addition to the origin-defining reflexions, the reflexions whose phases will be varied (usually four) should be chosen so that, as well as being involved in a large number of sigma-2 triples, (i) they each come from a parity group different from those of the origin definers, (ii) the planes are approximately perpendicular rather than parallel to those of the origin definers, (iii) they correspond to d spacings that are intermolecular [because two of the origin definers already are related to intramolecular separations, Fig. 1(*b*).]

These simple criteria have been used successfully to solve two structures which would not yield to the direct-method programs operated in the automatic mode. The first (Laing & Sommerville, 1974) was centrosymmetric, Fig. 2(*a*); the second (Candy, Laing, Weeks & Kruger, 1975) was non-centrosymmetric, Fig. 2(*b*). In both cases the set of phases with the most favourable figures of merit proved to be correct and the E map calculated from this set of phases showed all the atoms of the molecule; 23 in 2(*a*), 44 in 2(*b*).

In space group $P\bar{1}$ the problem is exacerbated (Lai & Marsh, 1974) but can be overcome by using the criteria

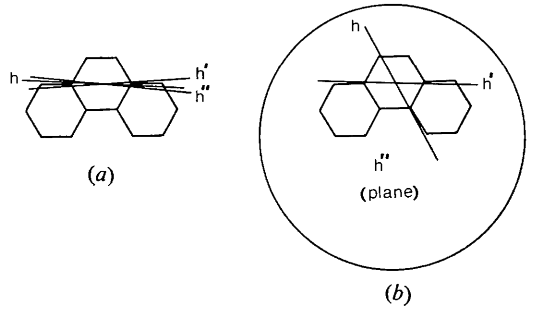

Fig. 1. A typical fused six-atom ring system. In (*a*) the planes **h**, **h**′ and **h**″ are approximately parallel to one another and so are unsuitable for origin definition. The planes **h**, **h**′ and **h**″ in (*b*) would be good origin definers. The d spacings of **h** and **h**′ are about 1·2 Å, while that of **h**″, which is normal to **h** and **h**′, is about 3·5 Å.

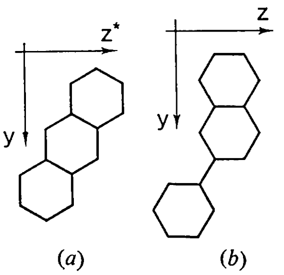

Fig. 2. These represent schematically the frameworks of the major portions of the molecules whose structures were solved. In (*a*) the structure is centrosymmetric; in (*b*) the structure is non-centrosymmetric. In both cases, one pair of sides of the six-membered ring system is nearly parallel to a crystallographic axis.

described above and five, rather than four, reflexions whose signs will be varied. The *h*, *k* and *l* indices of these five reflexions should also include all possible combinations of + and − signs. Structures in space group $P2_12_12_1$ are routinely solved by using as origin definers reflexions *h*0*l*, 0*kl* and *hk*0; the need for orthogonality is automatically satisfied for this case. The problems involved in correct phasing of reflexions in structures containing fused six-membered rings have previously been discussed in detail and different approaches to their solution have been suggested (Thiessen & Busing, 1974; Hazell & Hazell, 1975).

The suggestions outlined above seem to offer a simpler and more direct approach because the maximum amount of structural and chemical information is used before the phase refinement is even begun. Most of these suggestions can be programmed into the automatic modes of the programs by requiring that the origin-defining reflexions should correspond to the appropriate *d* spacings and, as far as possible, be orthogonal; and that the reflexions whose phases will be varied should have *d* spacings between 3 and 4 Å.

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The Debye–Waller factor of KBr by powder elastic neutron diffraction.

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The Debye–Waller parameter *B* of KBr has been determined by triple-axis neutron diffraction with a powder sample. Calculations have also been made to find the contributions of TDS to the diffraction peaks obtained by this technique and they were found to be negligible as expected. The *B* value thus found is $2{\cdot}33 \pm 0{\cdot}09$ Å^2.

Introduction

The temperature factors of alkali halide crystals have been the subject of several X-ray and neutron investigations (Table 1). The Debye–Waller parameter *B* for KBr has been determined by Meisalo & Inkinen (1967) using X-ray powder diffraction and by Pryor (1966) and Atoji (1972) using the double-axis powder neutron-diffraction technique. The *B* value has also been determined by Bacon, Titterton & Walker (1973) using the single-crystal neutron-diffraction method. Pryor (1966) has calculated the *B* value from the phonon dispersion relations measured by Woods, Cochran & Brockhouse (1960) at 400 K. Reid & Smith (1970) have theoretically calculated the *B* values using the shell model. In two-axis diffraction the corrections due to thermal diffuse scattering (TDS) are quite large and are often corrected by the method of Chipman & Paskin (1959).

In the present work, *B* has been determined from a powder sample by observing the diffraction pattern in the triple-axis mode of a neutron spectrometer. By this method the TDS correction is essentially eliminated (Caglioti, 1964; Beg, Aslam, Butt, Khan & Rolandson, 1974). Further, the diffraction peaks can be well focused in this geometry.

Experimental procedure and data analysis

KBr powder was ground, dried at 100°C and sealed in a 2 cm diameter and 10 cm high cylindrical vanadium container. The triple-axis neutron spectrometer TKSN-400 installed at the PINSTECH 5 MW research reactor was used to measure the triple-axis powder diffraction pattern. Cu(220) single crystals were used as monochromator and analyser at a neutron wavelength of 1·07 Å. The horizontal collimations used before and after the sample were 30′ and 40′ respectively. Three odd-order and eight even-order reflexions up to the index 620 were measured. The structure factors were evaluated from the diffraction data in the usual manner (Bacon, 1975). The scattering lengths given by Bacon (1975) were used.

Calculations were performed to evaluate the percentage thermal diffuse scattering under the Bragg peaks according to Beg (1976). For the TDS calculations an isotropic value of the sound velocity on the model of Nilsson (1957) was used, employing the elastic constants given by Federov (1968). The TDS varied from 0·45% for the 111 peak to 4·8% for the 620 peak. The correction to the *B* value due to TDS was found to be small and was within the experimental errors.

Results and discussion

The Debye–Waller parameter *B* for KBr was evaluated from the data of 11 peaks by a least-squares fit. Sufficient data could not be obtained on the odd peaks due to the intensity and angular constraints; therefore separate values for B_{K} and B_{Br} could not be determined accurately and only the average value B_{KBr} was obtained. This was found to be $(2{\cdot}33 \pm 0{\cdot}09)$ Å^2 which corresponds to a Debye temperature