method is a true member of the set of direct methods. It is interesting to note that the conditions under which Sayre's equation is most valid, that is when p is nearly constant except at atomic positions, are also the conditions under which the bound given in (2) is tight.

The bound used in this paper can be improved by going to a higher-order expansion of $\ln p$. This would correspond to the use of higher-order invariants. However, a word of caution is needed, since the next uniform bound occurs with a cubic expansion of $\ln p$ (it is important that a uniform, i.e. a single-function, bound be used, because it is not trivial to perform the Fourier substitution with a non-uniform bound). This would correspond to the use of at least a quintet expansion.

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Are (TSeT)$_2$I crystals homochiral or microtwinned?

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Abstract

A simple experimental test is described for deciding whether a crystal with a chiral space group is built from homochiral or heterochiral domains; this test is applied to (TSeT)$_2$I {TSeT = tetraselenotetracene (naphthaceno[5,6-cd, 11,12-c'd']bis[1,2]diselenole)}.

Introduction

Crystals in chiral space groups are sometimes obtained under achiral conditions by spontaneous resolution. It may then be important to know whether a given crystal specimen is homochiral or built from domains of opposite chirality [e.g. hexahelicene. Green & Knossow (1981)]. In principle, chiroptical measurements may provide an answer but they may not always be feasible, especially for very small or highly absorbent crystals. We describe here a simple non-destructive test which may provide an answer.

Example

Although the tetraselenotetracene (TSeT) molecule (Fig. 1) has potential D_{2h} symmetry, (TSeT)$_2$I, prepared by co-sublimation of TSeT and iodine, crystallizes in the chiral space group $P2_12_12$, $a = 18 \cdot 336$, $b = 17 \cdot 450$, $c = 5 \cdot 077$ Å (Hilti, Mayer & Rihs, 1978). In connection with our interest in chiral conductors (Wallis, Karrer & Dunitz, 1986), we wanted to know whether the crystals were actually
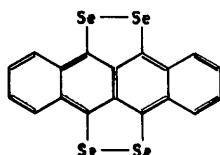

Fig. 1. Structural formula of tetraselenotetracene (TSeT).

homochiral or multiple twins consisting of left- and right-handed domains.

Method

The intensity ratio $\alpha = I(hkl)/I(\bar{h}\bar{k}\bar{l})$ of a Bijvoet pair of reflections is measured on a diffractometer with as fine a collimator as possible. The primary-beam cross section must be considerably smaller than the crystal under investigation. The measurement is repeated over the whole length of the (preferably needle-shaped) crystal.

Several results are conceivable:

$\alpha \simeq 1$. Crystal is microtwinned (consists of heterochiral domains that are smaller than the primary-beam cross section), or else anomalous dispersion is too weak to be detectable.

α changes to $1/\alpha$. Crystal is macrotwinned (consists of heterochiral fragments comparable in size with the primary beam).

α does not change. Crystal is homochiral.

Note that refinement of the absolute-structure (twin) parameter, as proposed by Flack (1983) and Bernardinelli & Flack (1985), would not distinguish between the first two cases if only one intensity measurement per reflection were available.

Experimental

Weissenberg photographs of five sample crystals showed that all were macroscopically twinned across the (110) planes, so that the hhl reflections of both reciprocal lattices coincided. Most of the other reflections were easily resolvable. The ratio between the two macrotwins varied widely from crystal to crystal. The crystal structure of (TSeT)$_2$I had been established without considering anomalous scattering (Hilti, Mayer & Rihs, 1978). The cell dimensions and

Table 1. *Bijvoet ratio,* $\alpha = [I(hkl) + I(\bar{h}\bar{k}l)]/[I(\bar{h}kl) + I(h\bar{k}l)]$, *with e.s.d.'s in parentheses, as a function of crystal displacement for reflections* 281 *and* 12,5,1 *for both macrotwins in a typical crystal specimen*

Crystal size *ca* $2.3 \times 0.24 \times 0.20$ mm; the major twin was about three times larger than the minor one.

Displacement (mm)	Major twin 281	Major twin 12,5,1	Minor twin 281	Minor twin 12,5,1
0·2	2·10 (4)	0·53 (2)	0·68 (3)	2·02 (9)
0·5	2·03 (4)	0·54 (2)	0·59 (3)	2·06 (11)
0·8	2·13 (4)	0·50 (2)	0·58 (3)	2·03 (13)
1·1	2·11 (5)	0·49 (3)	0·52 (4)	2·01 (13)
1·4	2·04 (5)	0·48 (3)	0·49 (4)	2·0 (2)
1·7	2·23 (5)	0·52 (4)	0·52 (6)	1·6 (2)
2·0	2·20 (6)	0·60 (4)	0·50 (8)	1·8 (4)
Calc.	2·07	0·51	0·48	1·95

space group were confirmed by our measurements. From calculations based on the known atomic parameters and including anomalous scattering for Se and I, we could pick out Bijvoet pairs expected to differ appreciably in intensity. We chose the reflections 281 and 12,5,1 with calculated α values of 2·07 and 0·51 for Cu $K\alpha$ radiation. The needle-like crystals (2–3 mm in length) were mounted on a Stoe Stadi-2 two-circle Weissenberg diffractometer with [001] parallel to the ω axis. The intensities of the Bijvoet pairs $(hk1, \bar{h}\bar{k}1)$ and $(\bar{h}k1, h\bar{k}1)$ were measured for both macrotwins, using a 0·3 mm collimator and the ω-scan technique. The crystal was then displaced by *ca* 0·3 mm along the ω axis (this is very easily done on a Weissenberg-type diffractometer) and the same reflections remeasured. Results for one typical crystal are summarized in Table 1.

Results

In all five crystal specimens studied, the macrotwins were of opposite chirality. Also, the measured α values were approximately constant over the length of the crystal and sometimes even larger than the calculated values. This is not unexpected, since it is known that in non-centrosymmetric space groups with polar axes neglect of anomalous dispersion in the structure refinement (Hilti, Mayer & Rihs, 1978) will yield atomic parameters that tend to eliminate the difference between Bijvoet pairs (Cruickshank & McDonald, 1967). In fact, it seems obvious that generally the resulting errors in atomic parameters will be approximately half of those produced by a refinement including anomalous dispersion but with the wrong chirality sense. We deduce that each macrotwin was indeed homochiral.

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Non-tensorial arrays for physical properties and the direct-inspection method.

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Abstract

It is shown that the invariance relations between the elements of a non-tensorial array for a physical property are identical to the invariance relations between the corresponding tensorial components when one is only dealing with symmetry elements of order 1, 2 or 4 and with the trigonal axis $3_{[111]}$ of the cubic groups.

It is an unfortunate common practice in crystal physics to use non-tensorial arrays to represent physical properties of crystals. A well known example is given by the non-tensorial elastic compliance constants $S_{ij} = S_{ji}[i, j = 1(\equiv xx), 2(\equiv yy), 3(\equiv zz), 4(\equiv yz), 5(\equiv zx), 6(\equiv xy)]$, related to the corresponding tensorial elastic compliance constants $S_{mnpq} = S_{nmpq} = S_{mnqp} = S_{pqmn}[m, n, p, q = 1(\equiv x), 2(\equiv y), 3(\equiv z)]$ by

the following equations [see *e.g.* Nye (1985), p. 134]:

$$S_{ij} = S_{mnpq} \quad \text{when } i \text{ and } j \text{ are } 1, 2 \text{ or } 3,$$

$$S_{ij} = 2S_{mnpq} \quad \text{when } i \text{ or } j \text{ are } 4, 5 \text{ or } 6,$$

$$S_{ij} = 4S_{mnpq} \quad \text{when } i \text{ and } j \text{ are } 4, 5 \text{ or } 6.$$

It is also commonly stated in crystal physics [see *e.g.* Nye (1985), p. 135] that to impose rotational invariance on the elements of non-tensorial arrays it is best to go through the corresponding tensorial components. An alternative procedure which has been used is to apply the cumbersome method by Love of imposing invariance on a scalar, such as the elastic energy, expressed in terms of non-tensorial arrays [*e.g.* Hearmon (1953)].

Here we should like to point out that whenever the direct-inspection method is applicable as such (Fumi,