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Enantiomorphism of the Oxalate Ion in Ammonium Oxalate Monohydrate

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There must be enantiomorphic forms of ammonium oxalate monohydrate because, in this structure, where the oxalate ion is twisted about its central bond, there is neither *m* nor $\bar{1}$ symmetry. It is intrinsically possible that these may exhibit enantiomorphous morphology. In fact, this can readily be observed and has been reported several times in the literature of classical crystallography.

The twisted oxalate ion is optically active and it is predicted that the crystal of ammonium oxalate monohydrate will rotate the plane of polarized light passing along its optic axes.

The ion $^{-}$OOC.COO^{-} is one that is so simple and so symmetrical that superficially one would not suspect it of even the possibility of enantiomorphism. It contains only two kinds of atom and only two different bond lengths. It has no asymmetric carbon atom. Its carbon atoms are not tetrahedral and there are no bulky substituents to hinder grossly the rotation about the central bond. In crystalline oxalates, it is almost invariably planar, with *mmm* symmetry. In solution, when the flexibility of the molecule gives it in effect its highest possible symmetry, no enantiomorphism is possible. In the solid state, however, where the molecule has a fixed configuration, it requires only a simple twist of the central bond to render the molecule enantiomorphic. This is exactly the case in ammonium oxalate monohydrate, where the oxalate ion is twisted by about 27°.

To be enantiomorphic, it is necessary only that a molecule or structure be not superposable on its mirror image. The absence of mirror planes and of symmetry centres is essential. The presence of rotation axes is irrelevant. Ammonium oxalate monohydrate is orthorhombic and in the class 222; the space group is $P2_12_12$ and contains no centre of symmetry. The structure is well known; a refinement of it is reported in the preceding article (Robertson, 1965). The oxalate ion itself is situated at a special position with the twofold axis of the crystal bisecting the central bond. Crystallographically, the point group symmetry of this position is 2; in fact the molecule is more symmetrical, for its C–O bonds and C–C–O angles are all equal within the limits of error, so that it has actually the point group symmetry 222. Nevertheless, in the twisted configuration it lacks both mirror planes and a symmetry centre. Each oxalate ion in the unit cell has the same enantiomorphism, reproduced unaltered by the screw axes parallel to *a* and *b*. Thus the entire crystal is enantiomorphic.

If the crystal structure itself is not superposable on its mirror image, the possibility exists that enantiomorphic development of the crystal faces may occur, thereby providing macroscopically visible evidence of the enantiomorphism of the oxalate ion. Careful observation of the crystals, which are very easy to grow from aqueous solution by cooling or by evaporation, confirms that this is the case. The solid crystallizes as stout needles or prisms elongated along *c*, formed by the faces $\{110\}$. The ends of these prisms have well developed faces with the typical appearance illustrated in Fig. 1. The face (001) is present with $\{011\}$ and $\{021\}$ and faces of the type, $\{111\}$. The latter appears on some crystals only as (111), with its equivalents, $(\bar{1}\bar{1}1)$, $(1\bar{1}\bar{1})$ and $(\bar{1}1\bar{1})$ according to 222 symmetry, while on other crystals it is present only as $(1\bar{1}1)$ with the corresponding equivalents. It is easy to recognize and separate out right handed and left handed crystals.

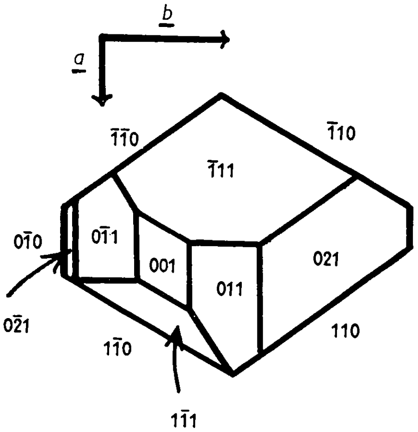

Fig. 1. Typical faces shown by ammonium oxalate monohydrate, seen looking down the needle axis (*c*). The enantiomorph shown corresponds to the 'linker Krystall' of Anschütz & Hintze.

Consultation of the literature reveals that this morphological peculiarity of ammonium oxalate was noticed well over a century ago. The early English crystallographer, H. J. Brooke, co-editor with Miller of the 1852 edition of *Phillips' Mineralogy*, first identified the faces and noted 'an irregularity of figure', *viz.* the occurrence on some crystals of only one set of bisphenoidal faces and on others, the mirror-related form (Brooke, 1823). De la Provostaye (1842) observed, apparently, only one bisphenoid. The crystal was further investigated by Rammelsberg (1854), by Grailich & v. Lang (1857) and by Brio (1867). Definitive results were obtained by Hintze who examined crystal specimens prepared by Anschütz (Anschütz & Hinze, 1885); Hintze showed that either only the right or only the left bisphenoid occurred, and pronounced the crystal rhombic hemihedral. (Later, Groth (1917) corrected the terminology and the axial ratios.) This was verified by Rewutzky (1902) who used etch figures to establish the bisphenoidal symmetry. Rewutzky found that the forms $\{111\}$ and $\{1\bar{1}1\}$ occurred together on only five crystals out of 150.

Observations on ammonium oxalate crystals thus have an antiquity similar to that associated with the sodium and ammonium tartrates, whose hemihedral character was recognized by Pasteur in 1848. Pasteur at once correlated the asymmetry of the crystal morphology with the sign of the optical rotation of the dissolved material. Brooke's observations on ammonium oxalate, however, were prior to the discovery of optical rotation by solutions by Biot in 1835. All this took place well before the advent, in 1874, of the tetrahedral carbon atom of Le Bel and Van't Hoff. Hintze (1887), following Pasteur some 40 years afterwards, tried to observe rotation of the plane of polarized light by solutions of enantiomorphous ammonium oxalate crystals, but without success. It is interesting to speculate what Pasteur might have concluded had he experimented with oxalates as well as with tartrates.

There are of course numerous examples of enantiomorphism of crystal structures built up of symmetrical components — quartz, $NaClO_3$, $MgSO_4.7H_2O$, barium formate, to cite only a few. In all these, enantiomorphism of morphology arises as the consequence of lack of symmetry in the crystallographic arrangement of the component ions or groups. In ammonium oxalate it is again the crystallographic arrangement that lacks *m* or $\bar{1}$ symmetry and this is due in part at least to the special character of the ammonium ion, *i.e.* its tetrahedrally directed hydrogen bonding ability. Here, however, the enantiomorphic environment is such as to twist the oxalate ion itself, otherwise very highly symmetrical, into an enantiomorphous configuration. The D- and L-forms of the oxalate ion so produced can be stable only in the solid state.

It may confidently be predicted that the crystal of ammonium oxalate, viewed along its optic axes, will rotate the plane of polarized light. The effect should be comparatively large in view of the polarizability of the carboxyl groups. In practice, an attempt to observe this rotation by the method of Wooster (1957), using a small crystal section cut, and polished, to within about 2° of the optic axial orientation, has been unsuccessful, presumably because this method requires a very accurately cut plate of crystal. Observations on the eye of a magnified interference figure, however, given by the same crystal specimen, were consistent with a *positive* rotation (clockwise as seen by the observer looking towards the light source) of about 9° ± 5° per mm, for the crystal having the morphology of Fig. 1. It is hoped to confirm this result and to measure the magnitude of the rotation reliably in due course.

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The Crystal Structure of *p*-Iodobenzonitrile

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p-Iodobenzonitrile forms monoclinic crystals in the space group $C2/c$ (C_{2h}^6) with four molecules in a unit cell of dimensions, $a = 10{\cdot}36$, $b = 10{\cdot}63$, $c = 9{\cdot}10$ Å and $\beta = 133{\cdot}1°$. The molecules lie on two-fold axes of the crystal and have C_{2v} symmetry. The cyanide group in one molecule is involved in a weak external bond to the iodine atom in the adjacent molecule. The external bond is similar to, but weaker than, that found in iodine cyanide.

Introduction

Recognizable solid state intermolecular interactions between cyanide groups and heavy non-metal atoms are known in a number of cases. The first known and most studied of these is in iodine cyanide (Ketelaar & Zwartsenberg, 1939; Townes & Dailey, 1952) where the external nitrogen-iodine distance is 0·8–0·9 Å less than the sum of the van der Waals radii. Similarly short distances are found in bromine cyanide (Geller & Schawlow, 1955), chlorine cyanide (Heiart & Carpenter, 1956), selenium selenocyanate (Aksnes & Foss, 1954), dimethyl arsenic cyanide (Camerman & Trotter, 1963), and arsenic tricyanide (Emerson & Britton, 1963). As a part of an examination of the condition necessary for the formation of such bonds we have determined the crystal structure of *p*-iodobenzonitrile, with the expectation that a similar sort of bond could occur here.

Experimental

p-Iodobenzonitrile was prepared by the dehydration of *p*-iodobenzamide, which had been prepared from *p*-iodobenzoic acid. The sample melted at the accepted value of 124–125·5 °C. The melting point of a sample prepared by the substitution of $-CN$ for $-NH_2$ in *p*-iodoaniline was identical. Crystals suitable for the X-ray work, short needles, were grown by sublimation.

From density and unit-cell measurements we have determined the molecular volumes of *p*-chloro- and *p*-bromo-benzonitrile to be 100·1 and 102·9 Å^3, respectively. The assumption of four molecules per unit cell yields a molecular volume of 110·1 Å^3 for *p*-iodobenzonitrile. The calculated density is 2·08 g.cm^{-3}.

Weissenberg and precession photographs (Cu $K\alpha = 1{\cdot}5418$, Mo $K\alpha = 0{\cdot}7107$ Å) showed this to be the *c* axis of a monoclinic cell with dimensions:

$$a = 9{\cdot}10 \pm 0{\cdot}05,\ b = 10{\cdot}63 \pm 0{\cdot}05,\ c = 7{\cdot}83 \pm 0{\cdot}05 \text{ Å};\ \beta = 105{\cdot}0 \pm 0{\cdot}2°.$$

The systematic extinctions for hkl data ($h+k+l = 2n+1$) and for $h0l$ data ($h = 2n+1$, $l = 2n+1$) indicate the space group to be Ic or $I2/c$. A roughly cylindrical needle 0·3 mm in diameter was chosen for intensity measurements, and multiple film Weissenberg photographs using Mo $K\alpha$ radiation were collected for the zero through 8th layers for rotation around the *c* axis. Intensity photographs were taken of the $h0l$ and $0kl$ zones on a precession camera to provide data to