

where

$$f(\xi, \zeta, \mu) = \frac{[(\xi^2 + \zeta^2) \sin \mu + 2\zeta]}{[(\xi^2 + \zeta^2)\{4 \cos^2 \mu - 4\zeta \sin \mu - (\xi^2 + \zeta^2)\} - 4\zeta^2]^{\frac{1}{2}}}$$

Substituting for  $2\alpha_i$  in terms of  $2\alpha_n$  in the three cases we have,

$$\Delta\varphi = m f(\xi, \zeta, \mu) \quad (10)$$

where  $m = 2\alpha_n$ ,  $2\alpha_n \sec \mu$  and  $2\alpha_n[1 + k \sec \mu]/[1 + k]$  for cases I, II and III respectively. Since  $\Delta\Omega = \Delta\varphi \cdot C_2$  ( $C_2$  being the constant of the Weissenberg goniometer), it can be easily verified that  $\Delta\Omega/\Omega$  is same in the three cases. This explains why Lonsdale's expression for  $(\Omega \pm \Delta\Omega)/\Omega$  in the case of

*Acta Cryst.* (1966). **21**, 449

**Molecular interactions involving double bonds and aromatic rings.** By C.K. PROUT, *Chemical Crystallography Laboratory, University of Oxford, England* and S.C. WALLWORK, *Department of Chemistry, University of Nottingham, England*

(Received 22 March 1966)

In a previous review of organic charge-transfer complexes (Wallwork, 1961) it was concluded that only in the case of complexes between powerful electron acceptors and electron donors were the relative orientations and modes of stacking of the two component molecules those expected for maximum overlap of their  $\pi$  orbitals. In complexes of trinitrobenzene, for example, the relative dispositions were consistent rather with maximum van der Waals interaction though, for two complexes of this type, Hanson (1964) has found indications of a specific interaction between the nitrogen atom of an indole ring in the donor molecules and a non-substituted carbon atom of trinitrobenzene.

Quinhydrone seems to form an intermediate case in that the relative orientation of the phenol and quinone components are the same, as might be expected for maximum interaction, but their molecular centres are displaced sideways so that one C=O group of the quinone lies approximately over the centre of the aromatic ring of the phenol. Further examples of this have since been found in the crystal structures of 1:1 and 2:1 complexes of *p*-halogenophenols with *p*-benzoquinone (Shipley & Wallwork, 1966) and in a second form of quinhydrone itself (Sakurai, 1965). A suggested interpretation was that this arrangement represents a compromise between the requirements of charge transfer and hydrogen bonding. However, the retention of this arrangement in charge-transfer complexes of quinones where no hydrogen bonding is possible, as in the perylene-fluoranol complex (Hanson, 1963) suggests that there might be a specific interaction between C=O groups and aromatic rings. This view is supported by the molecular arrangements in other complexes, e.g. that between bis-8-hydroxyquinolinatopalladium(II) and chloranil (Kamenar, Prout & Wright, 1966), and in some crystals containing only one type of molecule, e.g. 1,4-naphthoquinone (Gaultier & Hauw, 1965), 5,8-dihydroxy-1,4-naphthoquinone (Pascard-Billy, 1962), and bis-8-hydroxyquinolinatopalladium(II) (Prout & Wheeler, 1966).

Two types of molecular interaction involving C=O groups have previously been recognized by their influence on crystal structures. In the first type, exemplified by the structures of chloranil (Chu, Jeffrey & Sakurai, 1962) and allroxan (Bolton, 1964), one C=O group points towards

the equi-inclination method is the same as that obtained by Phillips, though their expressions for  $\Omega$  and  $\Delta\Omega$  are different.

Thanks are due to Prof. S. Ramaseshan for encouragement and help and to Dr S. Swaminathan for some helpful discussions.

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the carbon atom of a second C=O group inclined at a large angle to the first, with a separation O...C of about 2.8 Å.

In the second type, found for example in violuric acid (Craven & Mascarenhas, 1964), dilituric acid (Craven, Martinez-Carrera & Jeffrey, 1964) and tetrahydroxy-*p*-benzoquinone (Klug, 1965), C=O groups in adjacent molecular layers overlap in an antiparallel manner with separations of about 3.15 Å. These interactions seem to be polar in character and the interaction now reported between C=O groups and aromatic rings may be an extension of this type, involving dipole-induced dipole forces. An example of an end-on interaction between a P=O group and an aromatic ring perpendicular to it, recently found in the structure of a complex between triethyl phosphate and benzotrifuroxan (Cameron & Prout, 1966), lends further plausibility to this view.

There is evidence that carbon-carbon double bonds that are polarized by their environment can also interact with aromatic rings in adjacent molecules. This effect is found in the complexes formed by 7,7,8,8-tetracyanoquinodimethane with *NNN'*-tetramethyl-*p*-phenylenediamine (Hanson, 1965) and by tetracyanoethylene with naphthalene (Williams & Wallwork, 1966). In both these structures, a C=C group of the acceptor molecule lies parallel to an aromatic ring of an adjacent donor molecule in the molecular stack, in such a way that there are close intermolecular contacts to the 1 and 4 positions in the ring. The bond distances in the components are consistent with their being at least partially in the ionic form, by the transfer of charge from donor to acceptor, and the close approaches are presumably due to a combination of polar and charge-transfer interactions. Such complexes as these are probably formed as intermediates in Diels-Alder reactions and, in fact, this type of reaction does take place at room temperature between tetracyanoethylene and anthracene, with the transitory formation of a coloured intermediate.

Where specific interactions involving C=O or C=C groups do occur in charge-transfer complexes they will compete with the tendency towards maximum overlap of the molecular  $\pi$  orbitals of the two components, often resulting in the staggered type of molecular stacking.

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*Acta Cryst.* (1966). **21**, 450

**A computer program to investigate reticular pseudomerohedry.** By G. M. WOLTEN, *Materials Sciences Laboratory, Aerospace Corporation, El Segundo, Calif., U.S.A.*

(Received 11 March 1966)

The theory of twinning (Friedel, 1926) states that twinning on (*hkl*) by pseudomerohedry or reticular pseudomerohedry is likely to occur if the twin obliquity is less than 6° and the twin index does not exceed 5.

The twin obliquity is defined as the small angle between the normal to the net plane (*hkl*) and that row line [*uvw*] that is nearly normal ('quasi-normal') to (*hkl*).

The rotation that carries the lattice from its original orientation to the twinned orientation carries a certain fraction of the lattice points onto or near other lattice points. The reciprocal of the fraction of lattice points thus restored by twinning is the twin index. If it is unity one speaks of pseudomerohedry, otherwise of reticular pseudomerohedry. The twin index can be calculated as a simple function of the indices of the net plane and the row line (Donnay & Donnay, 1959).

Once the twin law of a given crystal has been ascertained, it is relatively easy to find the quasi-normal and compute the twin obliquity and the twin index, thus 'explaining' the twinning in terms of the theory. On the other hand, if one wishes to predict likely twin planes or twin axes from the theory, or indeed, to examine how well such predictions are borne out, then one needs to have a complete list of all those net-row combinations that are quasi-normal to one another and have low values of the twin index.

A computer program has been written to furnish such a complete list, since it is not easily obtained by graphical

means or hand computation. The input data are the lattice parameters, the crystal system, the type of centering if any, and the maximum obliquity to be considered. The latter will usually be 6° or less, but any value may be used at the option of the user. The maximum twin index is fixed at 6, since a value greater than 5 need rarely be considered. The range of Miller indices is wide enough to insure completeness of the list, but an option exists to consider a smaller range at a great saving in execution time.

The printed output consists of six lists, one for each value of the twin index from 1 to 6. Each list gives pairs of net planes and row lines that are quasi-normal to one-another, the numerical value of the obliquity for each pair, and the direction angles for both plane and row.

The program is written in 7094 Fortran IV. All operating instructions are contained on comment cards at the head of the program listing. Interested parties in the U.S. and Canada may obtain a source deck by writing to the author. Requestors residing elsewhere will receive a listing of the program.

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*Acta Cryst.* (1966). **21**, 450

**Erratum: nuclear magnetic resonance in BaCl<sub>2</sub>·2H<sub>2</sub>O.** By Z. M. EL SAFFAR, *Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.*

(Received 13 May 1966)

In Table 1 (El Saffar, 1966) the neutron diffraction *r* values given in columns 2 and 3 should be interchanged. These *r* values are shown for purposes of comparison with the

nuclear magnetic resonance results and have no bearing on the conclusions drawn.

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