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**The variation of reflexion-spot size in upper-level Weissenberg photographs.** By A. K. SINGH\*, *Department of Physics, Indian Institute of Technology, Madras 36, India*

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It was pointed out by Buerger (1942) that the variation in the lengths of the reflexion-spots in upper-level Weissenberg photographs is due to the divergence of the X-ray beam emerging from the collimator. The expressions for the spot-size variation were deduced by Phillips (1954) for the normal-beam and equi-inclination methods and by Lonsdale (1964) for the general case. Some of Lonsdale's formulae differed from those of Phillips by a factor  $\sec \mu$  or  $\sec \nu^\dagger$ . A re-examination of the matter reported in this note indicates that the formulae deduced by Phillips and Lonsdale are under two different experimental conditions regarding the position and the length of the crystal in the beam. It has been shown, by using the concepts of total and effective divergences, that the length of the reflexion spot,  $\Omega$ , on a stationary camera and the change,  $\Delta\Omega$ , due to camera translation, depend on the manner in which the crystal is bathed in the beam but the ratio  $\Delta\Omega/\Omega$  is independent of it.

• **Total and effective divergences**

Although the beam emerging from the collimator has a definite divergence, the divergence which is effective in the diffraction experiments is determined by the length of the crystal in the beam. Referring to Fig. 1, the angle  $2\alpha$  between the extreme rays,  $SX$  and  $SY$ , is the total divergence

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† The notation used in this paper is the same as that used by Lonsdale (1964).

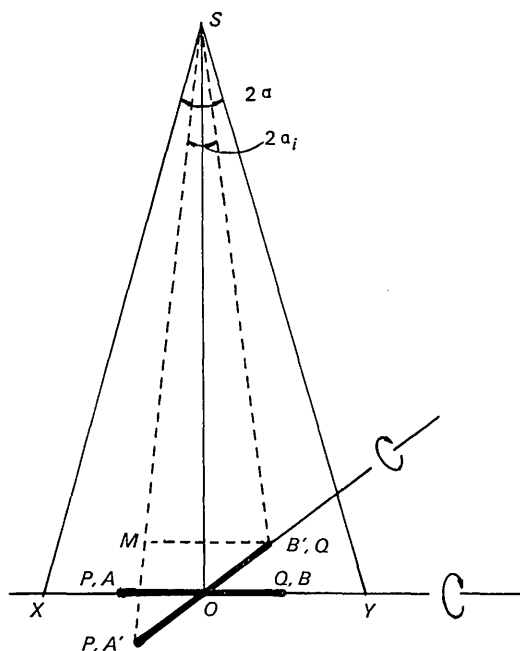


Fig. 1. Case I.  $L < 2\alpha r_0$ . The positions of the crystal are marked by heavy lines.

of the beam. If  $AB$  is the portion of the crystal in the beam  $\angle ASB = 2\alpha_i$  is the effective divergence. The length of the crystal,  $PQ$ , is denoted by  $L$  and the length of the crystal in the beam by  $l_i$  or  $l_n$ . The subscripts  $i$  and  $n$  denote inclined-beam and normal-beam cases respectively.

Let us study the variation of  $2\alpha_i$  and  $l_i$  with  $\mu$  in the following distinct cases.

Case I

$L < 2\alpha r_0$  and  $AO = OB$  (Fig. 1).  $r_0$  is the source-to-crystal distance,  $SO$ .

Since the crystal remains in the beam for all values of  $\mu$ ,

$$l_i = l_n = L. \quad (1)$$

From triangles  $ASB$  and  $A'MB'$  we have

$$L = 2\alpha_n r_0 \quad (1a)$$

and

$$MB' = L \cos \mu = 2\alpha_i r_0. \quad (1b)$$

Equations (1a) and (1b) give

$$2\alpha_i = 2\alpha_n \cos \mu. \quad (2)$$

Case II

$L > 2\alpha r_0$  and  $AO = OB$  (Fig. 2).

If  $A'N$  and  $B'N'$  are perpendiculars drawn from  $A'$  and  $B'$  on  $PQ$ ,

$$A'B' = l_i = (NO + ON') \sec \mu \\ = NN' \sec \mu.$$

Since  $\alpha$  is small,  $AN = N'B$ , and therefore  $NN' = AB = l_n$ . Thus

$$l_i = l_n \sec \mu. \quad (3)$$

Obviously,

$$2\alpha_i = 2\alpha_n = 2\alpha. \quad (4)$$

Equations (3) and (4) hold good for  $\mu < \cos^{-1}(2\alpha r_0/L)$ . For  $\mu > \cos^{-1}(2\alpha r_0/L)$ , the crystal is completely in the beam and case II degenerates into case I.

Case III

The crystal is situated in the beam as shown in Fig. 3.

The two portions  $OA$  and  $OB$  can be treated separately. It is easily seen that  $AO$  remains in the beam for all values of  $\mu$ , and therefore corresponds to case I, while  $OB$  (if  $OB > \alpha r_0$ ) corresponds to case II. Let

$$OA = l_n^I, \quad OB = l_n^{II}, \quad AB = l_n^I + l_n^{II} = l_n \\ OA' = l_i^I, \quad OB' = l_i^{II}, \quad A'B' = l_i^I + l_i^{II} = l_i \\ \angle ASO = \alpha_n^I, \quad \angle OSB = \alpha_n^{II} = \alpha, \\ \angle A'SO = \alpha_i^I \text{ and } \angle OSB' = \alpha_i^{II} = \alpha.$$

Now

$$l_i = l_i^I + l_i^{II} \\ = l_n^I + l_n^{II} \sec \mu \\ = l_n [1 + k \sec \mu] / [1 + k], \quad (5)$$

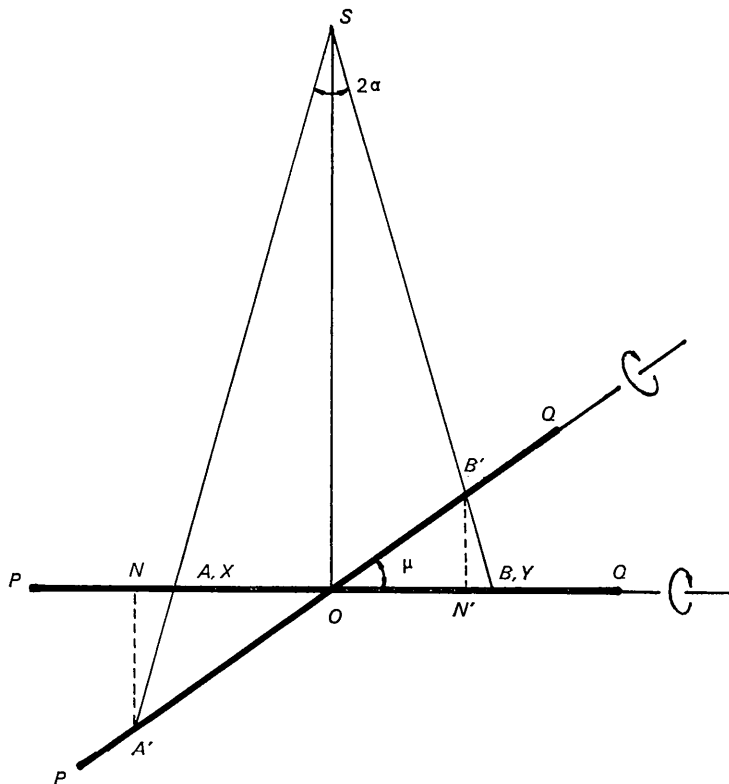


Fig.2. Case II.  $L > 2\alpha r_0$ . The positions of the crystal are marked by heavy lines.

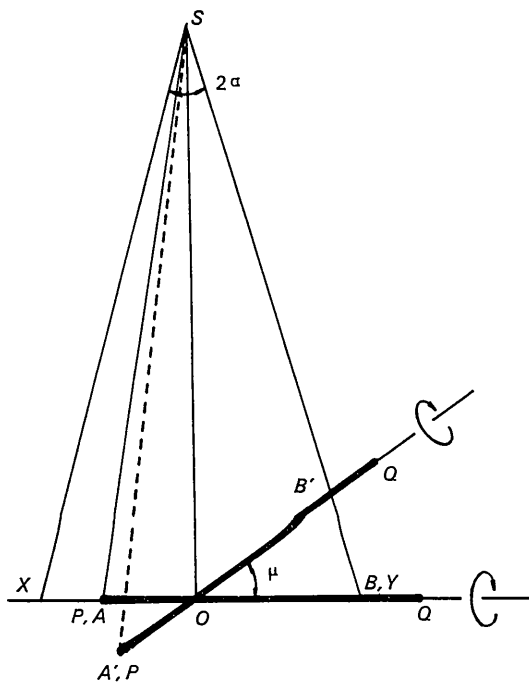


Fig.3. Case III.  $OQ > \alpha r_0$ . The positions of the crystal are marked by heavy lines.

$$2\alpha_i = 2\alpha_n [k + \cos \mu] / [1 + k] . \quad (6)$$

Thus the variations of  $l_i$  and  $2\alpha_i$  with  $\mu$  are given by equations (5) and (6) for  $\mu < \cos^{-1}(\alpha r_0 / OQ)$ .

Any other possible position of the crystal can always be described in terms of these three cases.

#### Reflexion-spot length on a stationary camera of radius $r_1$

For the derivation of the expressions for  $\mathcal{L}$ , see Phillips (1954) and Lonsdale (1964). Replacing  $l$  by  $l_i$  and  $\alpha$  by  $\alpha_i$  in Lonsdale's equation (1), we have

$$\mathcal{L} = 2\alpha_i r_1 \cos \mu / \cos^3 \nu + l_i . \quad (7)$$

Substituting the values of  $2\alpha_i$  and  $l_i$  in terms of  $2\alpha_n$  and  $l_n$  in equation (7) and noting that  $l_n = 2\alpha_n r_0$ , we have

$$\mathcal{L} = m [r_1 \cos^2 \mu / \cos^3 \nu + r_0] \quad (8)$$

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. Equation (8) for case II is same as Lonsdale's equation (3). Thus the derivations of Lonsdale correspond to case II. Equation (8) for case I reduces to Phillips's equation (26). Phillips's equations correspond to case I. It must be noted that equation (8) reduces to the same form in all the three cases for the normal-beam method.

#### The angular range of reflexion, $\Delta\phi$

Replacing  $\alpha$  by  $\alpha_i$  in Lonsdale's equation (5), we have

$$\Delta\phi = 2\alpha_i f(\xi, \zeta, \mu) \sec \mu \quad (9)$$

where  $k = l_n^I / l_n^II$ . In the above derivation equations (1) and (3) have been used.

Since  $\alpha / \alpha_n^I = l_n^II / l_n^I = k$ , it can be shown similarly that

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

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**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*

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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.

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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 benzotrihydroxan (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.