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Optical Properties of *p*-Dichlorobenzene

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The optical properties of two polymorphic forms of *p*-dichlorobenzene have been determined, and a correlation between those properties and the known crystal structures established. From the values of the principal polarizabilities for the *p*-dichlorobenzene molecule, and taking into account the orientation of the molecule in the crystal cell, the refractive indices α, β, γ, have been calculated for both crystal forms, and their values compared with those measured experimentally. An interpretation of the magnitude and sign of the birefringence is offered. The calculated values of the extinction angles and the orientation of the indicatrix agree with the experimental results.

To study the optical properties of *p*-dichlorobenzene, suitable crystals were obtained from technical grade British Drug Houses material by slow sublimation on glass surfaces kept at 24 °C. Under these conditions two polymorphic forms were obtained: a monoclinic phase as thin (100) plates, and a triclinic phase as prismatic crystals elongated along **c**. Both crystal forms have been studied by several authors (Frasson, Garbuglio & Bezzi, 1959; Hendricks, 1933; Jeffrey & McVeagh, 1955; Kitaigorodskii, Mnyukh & Asadov, 1963; McCrone, 1957) and their crystal structures are well known.

The monoclinic plates have rectangular outline and show parallel extinction. The triclinic crystals are four-sided prisms showing oblique extinction; according to which face the prism is lying on, the extinction angle observed, referred to the *c* axis, is 14° or 26°.

For X-ray diffraction study, Weissenberg and precession patterns were taken. The crystals had to be sealed in glass capillaries filled with glycerol to avoid evaporation during exposure.

The optical constants were determined in a Leitz–Wetzlar petrographic microscope, fitted with a four-axis universal stage; a sodium lamp was used as light source ($\lambda = 5{\cdot}890$ Å). Refractive indices were measured by the Becke line method.

When dissolution of the crystal in the immersion medium was observed, care was taken to saturate the liquid with *p*-dichlorobenzene beforehand. The refractive indices of the immersion media were measured in an Abbe refractometer. The liquids employed were:

	μ
Sodium iodide + glycerol	1·532
Methylene iodide	1·740
Methylene iodide saturated with *p*-dichlorobenzene	1·674
Methylene iodide saturated with sulphur	1·778
Methylene iodide saturated with sulphur and *p*-dichlorobenzene	1·72

For better accuracy in the measurements on the universal stage, the segments with index $\mu = 1{\cdot}516$ were employed. Their index being very similar to the indices of the other glass surfaces (glass slides $\mu = 1{\cdot}514$, cover glass $\mu = 1{\cdot}52$), refraction in the central area of the mounting was avoided (Munro, 1963).

Monoclinic crystals

Weissenberg and precession patterns showed that the plates belonged to the known monoclinic form of *p*-dichlorobenzene.

The cell dimensions obtained agree with those given by Croatto, Bezzi & Bua (1952). The best developed faces of the plates are {100} faces. Measurements obtained with some thicker plates in an optical goniometer showed that the other faces belonging to the [001] zone are {110} faces. (Fig. 1).

Optical data:

$\beta \| \mathbf{b}$

$\alpha = 1{\cdot}52 \pm 0{\cdot}01$, $\beta = 1{\cdot}69 \pm 0{\cdot}01$, $\gamma(\text{calc}) = 1{\cdot}75$

$2V = 54°$ (corrected)

$\alpha \wedge \mathbf{c} = 19{\cdot}5°$ (corrected).

Optical sign: negative (determined with the quartz wedge).

One optic axis and γ were located on the universal stage by the conoscopic method. In the determination of refractive indices, the orthoscopic method was applied to locate α and β.

The $2V$ angle could not be measured directly. On account of the crystal habit, not changed after crystallization from alcohol or benzene, it was possible to observe the emergence of only one optic axis. On the other hand, it was not possible to obtain fragments with the desired orientation by grinding and rolling, because the material is very plastic and twins easily under pressure.

To determine the values of $2V$, the value of angle $2V_\gamma$ was considered the most accurate, the orientation of γ having been determined from interference figures.

Correction of the universal stage readings

For crystals with a refractive index very different from that of the segments, a correction has to be applied to the readings on the arcs or drum of the universal stage. It is usual to consider β as the mean refractive index in the calculation of these corrections. When, as in the case of p-dichlorobenzene, the crystal has a high birefringence, this approximation is not valid; depending on the orientation of the section, the refractive index for the vibration parallel to that of the polarizer may depart considerably from β, and reach α or γ.

For sections having an optic axis parallel to the microscope axis the refractive index is obviously β. In negative crystals sections giving obtuse bisectrix interference figures have γ parallel to the microscope axis; the refractive index for the vibration direction parallel to that of the polarizer may vary from α to β. As interference figures are observed at 45° from extinction, a value $\mu = \frac{1}{2}(\alpha + \beta)$ was adopted to calculate the corrections for those sections.

Triclinic crystals

Weissenberg and precession patterns showed that the prismatic crystals belong to the known triclinic polymorph of p-dichlorobenzene. The cell dimensions obtained agree with those given by Housty & Clastre (1957).

From goniometer measurements the observed faces, referred to the X-ray cell are: {100}, extinction angle 26°; {010}, extinction angle 14°; and {001} (Fig. 2). In some crystals the {$\bar{1}\bar{1}$1} faces develop.

Optical data

$\alpha = 1{\cdot}45 \pm 0{\cdot}01$

$\beta = 1{\cdot}64 \pm 0{\cdot}02$

$\gamma(\text{calc}) = 1{\cdot}9$

$2V \simeq 90°$

From the interference figure the emergence of only one optic axis was located.

The optical sign could not be determined with certainty, $2V$ being very near 90°. The orientation of α, β and γ was found from extinction observations. The universal stage readings were corrected as explained for the monoclinic form, taking into account the high birefringence of the crystals.

Owing to the errors involved in the orthoscopic method by which α, β and γ were located, only an approximate value can be given for $2V$.

Relation between the optical properties and the crystal structure of p-dichlorobenzene

The refractive index of a medium is closely related to, and increases with, the polarizability of its atoms. The optical anisotropy of molecular crystals depends both on the polarizability of the constituent molecules and on the symmetry of the crystal structure.

The polarizability has the properties of a tensor, which, when diagonalized, presents three directions normal to each other for which the polarizability takes the principal values b_i ($i = 1,2,3$).

For plate-like molecules (*i.e.* those having one dimension much smaller than the other two) the polarizability for the direction normal to the plane of the molecule is much smaller than for the other two principal directions, contained in the plane of the molecule. That means that the molecule is most easily polarized by light vibrating in the plane of the molecule.

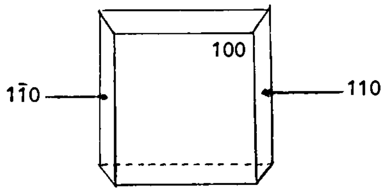

Fig. 1. Crystal of the monoclinic form of p-dichlorobenzene grown by sublimation.

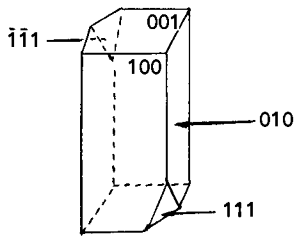

Fig. 2. Crystal of the triclinic form of p-dichlorobenzene grown by sublimation.

For rod-shaped molecules (*i.e.* those having one dimension much larger than the other two) the polarizability is much greater in the direction parallel to the length of the molecule.

In Table 1, column (*a*), the principal polarizabilities for the molecule of *p*-dichlorobenzene, taken from Landolt–Börnstein (1951) are given.

Table 1. *Principal polarizabilities of the p-dichlorobenzene molecule*

i	$b_i \times 10^{25}$ (cm^3)*	
	(*a*)†	(*b*)‡
1	(124·8)	151·2
2	(88·3)	93·6
3	212·9	180·2

* $b_1 \perp$ to $b_2 b_3$; $b_2 \perp$ to the benzene ring plane; b_3 parallel to the Cl–Cl direction.

† Values taken from Landolt–Börnstein.

‡ Calculated from the tensor sum of the ellipsoids of the polarizabilities for the molecular bonds.

The principal polarizabilities b_i can be calculated from the tensor sum of the ellipsoids of the polarizabilities for the molecular bonds.

We have

$$b_{xy} = \sum_{n=1}^{N} \sum_{m=1}^{3} b_{nm} (\cos nm, y)(\cos nm, x)$$

where

b_{nm} = principal polarizability for the n bond,

$m = 1,2,3$, $m = 1$ in the direction parallel to the bond

$m = 2,3$ in the direction normal to the bond

xyz orthogonal Cartesian axes.

These axes have been chosen as follows:

x parallel to the Cl–Cl direction

z normal to the plane of the molecule

y normal to x and z.

Values of b_i for *p*-dichlorobenzene, calculated by means of the above formula, are given in column (*b*) of Table 1. The polarizabilities of bonds were taken from Landolt–Börnstein.

In these calculations the benzene ring has been considered a regular hexagon, the Cl atoms being placed along one diagonal.

As shown by our results the relationship among the principal polarizabilities corresponds neither to a plate-like molecule nor to a linear molecule elongated along b_3.

To correlate the structure with the optical properties of *p*-dichlorobenzene, we have regarded the mutual effect of neighbouring molecules as negligible. This is equivalent to accepting that, to a first approximation, the values of b_i given in Table 1 are valid for *p*-dichlorobenzene in the solid state.

Triclinic crystals

Orientation of the indicatrix

In the triclinic form, the molecules lie approximately parallel to the $(45\bar{7})$ plane (Housty & Clastre, 1957). We have calculated the acute angles which the mean planes of the molecules make with the three basal crystallographic planes:

$$\left.\begin{array}{l} (45\bar{7}) \wedge (001) = 31^\circ 54' \\ (45\bar{7}) \wedge (010) = 66 \\ (45\bar{7}) \wedge (001) = 86 \;\; 11 \end{array}\right\} \qquad (1)$$

The molecules being arranged parallel to one another, the principal refractive indices for the crystal must coincide with the directions of the principal molecular polarizabilities. In particular the smallest index α must be parallel to b_2, that is, normal to the plane $(45\bar{7})$.

The poles of the crystal faces, and the indicatrix obtained from measurements on the universal stage, were located on a stereographic projection. The three angles formed by α with the poles of the basal faces, as read on the stereogram are:

$$\begin{array}{l} \alpha \wedge (001) = 32^\circ \\ \alpha \wedge (010) = 64 \\ \alpha \wedge (100) = 88 \end{array}$$

As shown, they agree with the calculated values given in (1).

The extinction angles obtained from the stereogram according to the Biot–Fresnel law also agree with the experimental values.

Values of α, β, γ, calculated from the molecular polarizabilities

The values of the principal refractive indices were calculated by applying the Lorentz–Lorenz formula:

$$R_i = \frac{n_i^2 - 1}{n_i^2 + 2} \cdot \frac{M}{\varrho}$$

and the relation

$$b_i = \frac{3R_i}{4\pi N_0}$$

where: M = molecular weight

R_i = molecular refractivity

ϱ = specific weight

N_0 = Avogadro's number.

The results appear in Table 2; column (*a*) gives the values of n_i obtained with the b_i taken from Landolt–Börnstein, column (*b*) those obtained with the calculated values of b_i appearing in column (*b*) of Table 1; the experimental values appear in column (*c*). As can be seen, there is a better agreement between the n_i measured and those calculated with our b_i.

Table 2. *Calculated and measured refractive indices for the triclinic crystals of p-dichlorobenzene*

	(*a*)*	(*b*)†	(*c*)
b_i	n_i calc.	n_i calc.	n_i measured
b_2	$\alpha = 1{\cdot}36$	$\alpha = 1{\cdot}40$	$\alpha = 1{\cdot}45$
b_1	$\beta = 1{\cdot}54$	$\beta = 1{\cdot}70$	$\beta = 1{\cdot}64$
b_3	$\gamma = 2{\cdot}09$	$\gamma = 1{\cdot}89$	$\gamma_{\text{calc}} = 1{\cdot}9$

* Calculated from b_i Table 1 (*a*).

† Calculated from b_i Table 1 (*b*).

For these calculations the anisotropic character of the C–Cl bond has not been taken into account; the benzene ring has been considered a regular hexagon although this is not strictly valid for the triclinic phase.

Optical sign

A high birefringence is to be expected in crystals constituted by non-equant molecules arranged parallel to each other; the optical sign will be negative when the molecules are planar, positive if they are rod-shaped.

The molecular polarizabilities of *p*-dichlorobenzene being characteristic of neither a plate-like nor a rod-shaped molecule, a value of $2V$ near 90° is to be expected. The observed value is actually very near 90°.

Monoclinic crystals

In the monoclinic crystals, the molecules lie with the plane of the benzene ring nearly parallel to the (001) plane.

There are two molecules per unit cell, related by a 2_1 axis; *i.e.* one results from the other by a 180° rotation and a $b/2$ translation.

We obtained the orientations and magnitude of the principal polarizabilities B_i for the monoclinic crystal, (Table 3) by obtaining the tensor sum of the ellipsoids of the molecular polarizabilities (Appendix).

Table 3. *Principal polarizabilities B_i for the monoclinic crystals*

i	$B_i \times 10^{25}$ (cm^3) (*a*)*	$B_i \times 10^{25}$ (cm^3) (*b*)†
1	99·39	108·08
2	151·35	151·33
3	176·09	166·40

* Calculated from b_i, Table 1, column (*a*).
† Calculated from b_i, Table 1, column (*b*).

The principal refractive indices must correspond to directions parallel to the B_i obtained. Accordingly it is possible to calculate α,β,γ, from the B_i obtained, by applying the Lorentz–Lorenz relation. The results thus obtained are shown in Table 4, columns (*a*) and (*b*); in column (*c*) the measured refractive indices are given.

The differences between calculated and measured n_i may be in part explained by the errors involved in the calculations of the B_i; in particular the angles formed by the b_i with the Cartesian axis were read on a stereogram.

As predicted by theory, if the constituent molecules of a crystal are arranged parallel to a plane, but not parallel to each other, the optical sign will be negative whether the molecules are plate-like or rod-shaped. Such is precisely the case with the monoclinic form of *p*-dichlorobenzene and, in fact a negative sign has been observed.

APPENDIX

For the calculation of the B_i in the monoclinic form of *p*-dichlorobenzene we proceeded as follows: In a stereographic projection $\mathbf{a},\mathbf{b},\mathbf{c}$, $\mathbf{a}^*,\mathbf{b}^*,\mathbf{c}^*$, and the directions of the b_i for each of the two molecules of the crystal cell, were located.

An orthogonal coordinate system was chosen so that $Z\|\mathbf{b}$, $X\|\mathbf{a}$ and $Y\perp X$ and Z; the angles formed by the b_i with the X,Y,Z, axis were read and introduced into the formula

$$b_{xy}=\sum_{i=1}^{3} b_i \cos(b_i,x)\cos(b_i,y)\,,$$

which gives the components of the tensors of the polarizabilities b_{M1} and b_{M2} corresponding to each of the two molecules in the crystal cell.

We define

$$\mathbf{B}=\frac{\mathbf{b}_{M1}+\mathbf{b}_{M2}}{2}\,.$$

By diagonalization of $\mathbf{B}$ the values and the directions of the principal polarizabilities for the monoclinic phase are obtained.

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Table 4. *Calculated and measured refractive indices for the monoclinic crystals of p-dichlorobenzene*

B_i	(*a*)* Orientation, calculated	(*a*)* n_i calc.	(*b*)† Orientation, calculated	(*b*)† n_i calc.	(*c*) Orientation, measured	(*c*) n_i meas.
B_2	$B_2 \| \mathbf{b}$	$\beta=1{\cdot}67$	$B_2 \| \mathbf{b}$	$\beta=1{\cdot}67$	$B \| \mathbf{b}$	$\beta=1{\cdot}64$
B_1	$B_1 \wedge \mathbf{c}=20{\cdot}5°$	$\alpha=1{\cdot}425$	$B_1 \wedge \mathbf{c}=11°$	$\alpha=1{\cdot}46$	$\alpha \wedge \mathbf{c}=19{\cdot}5°$	$\alpha=1{\cdot}52$
B_3	$B_3 \perp B_1$	$\gamma=1{\cdot}86$	$B_3 \perp B_1$	$\gamma=1{\cdot}79$		$\gamma=1{\cdot}75$ calc.

* Calculated from B_i in Table 3, column (*a*).
† Calculated from B_i in Table 3, column (*b*).

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