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Optical crystallographic properties of the 4-phenyl- and 4-cyclohexylcyclohexanols.

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The *cis* and *trans* isomers of 4-phenylcyclohexanol have been shown by thermal analysis to form a system with a single eutectic point in which solid solutions are absent below 10 % and above 90 %. The *cis* and *trans* isomers of 4-cyclohexylcyclohexanol form a system with two eutectic points which is indicative of compound formation and miscibility (Ungnade, 1948). The unexpected differences in the two pairs of isomers are in agreement with the optical crystallographic properties of the substances.

trans-4-Phenylcyclohexanol (I) is biaxial, positive in character, with $2V$ about 75–80°, whereas *cis*-4-phenylcyclohexanol (II) is uniaxial and negative in optical character. The two isomers necessarily crystallize individually in different crystal systems and result in the formation of a eutectic when mixed. (I) is probably monoclinic and (II) is probably hexagonal, but the crystal morphology is too imperfectly developed to permit definite determination.

cis-4-Cyclohexylcyclohexanol (IV) is biaxial, positive in character with $2V$ about 70–75° and birefringence about 0·038, whereas *trans*-4-cyclohexylcyclohexanol (III) is biaxial, with $2V$ so close to 90° that the optical character is indeterminate or probably ranges from positive to negative across 90°, and has a birefringence of about 0·026. Both isomers crystallize in needles. Crystals of (III) are elongated parallel to X, those of (IV) are elongated parallel to Y. Both crystallize in the monoclinic system and exhibit a degree of similarity in optical character.

The optical properties given in Table 1 were measured with a petrographic microscope. Refractive indices were determined by comparison in white light with standardized immersion aqueous solutions of potassium mercuric iodide. Optic angles were estimated from interference figures well centered in orientation.

Reference

Ungnade, H. E. (1948). *J. Organ. Chem.* **13**, 361.

Table 1. *Optical properties*

Compound	Refractive indices* X	Y	Z	Optical character	$2V$ (°)†	Axial dispersion	Elongation
I	1·549	1·595	1·688	+	75–80	r > v	–
II	$E=$ 1·550	.	$O=$ 1·581	–	0	.	.
III	1·542	1·555	1·568	– ? + ?‡	87–90	r > v§	–
IV	1·534‖	1·549	1·572	+	70–75	r > v	±

* Precision 0·002 except where noted.

† Estimated, ±5°.

‡ The optical character was not distinguishable, for the optic axis interference figures appeared as practically straight bars. Some figures suggested (+), others (–); it is probably (–).

§ If the optical sign is negative.

‖ Accuracy 0·004.

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Relative phases of diffraction maxima by multiple reflection.

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The occurrence of 'forbidden' maxima in the diffraction of X-rays (Renninger, 1937*a*, *b*; Davisson & Haworth, 1944; Pabst, 1939; Collin & Lipscomb, 1949) and electrons (Raether, 1932; Darbyshire & Cooper, 1935) has been observed by several investigators. Most often this phenomenon is due to a second diffraction $(h_2k_2l_2)$ following a high-intensity first diffraction $(h_1k_1l_1)$. The second diffraction emerges from the crystal in the direction of another diffraction $(h_3k_3l_3)$ whose indices are related to the first two by the equation $\mathbf{h}_3-\mathbf{h}_1=\mathbf{h}_2$, where the $\mathbf{h}_i$ are reciprocal-lattice vectors.* It is the purpose of this note to discuss some of the more obvious factors in connection with one experimental arrangement using X-rays to investigate the determination of the relative phases of $(h_2k_2l_2)$ and $(h_3k_3l_3)$ when the latter is of relatively low but not zero intensity.

Such an arrangement would rotate the crystal about $\mathbf{h}_1$ as an axis, with the angle between incident beam and axis of rotation such as to maintain the reciprocal-lattice point $(h_1k_1l_1)$ on the sphere of reflection for all angular positions of the crystal. Simultaneous to diffraction from any other reflecting reciprocal-lattice point $(h_3k_3l_3)$ there would then be diffraction in the same direction from a corresponding reciprocal-lattice point $(h_2k_2l_2)$ by the mechanism described. Such simultaneous diffractions would show interference effects depending, at least in part, on how the phase change of $(h_3k_3l_3)$ compares with the sum of the phase changes of $(h_1k_1l_1)$ and $(h_2k_2l_2)$. The intensities of the diffraction maxima so obtained could be compared with those obtained after slight displacement of the axis of rotation so that $(h_1k_1l_1)$, and subsequently $(h_2k_2l_2)$, were no longer diffracting. If the phase change of $(h_1k_1l_1)$ is considered constant for all orientations of the crystal, the information obtained might be presumed to be related to the relative phases of $(h_2k_2l_2)$ and $(h_3k_3l_3)$.

Although experimental results have so far been in-

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* A more complete statement would include the contribution of the intensity of $(h_3k_3l_3)$ to $(h_1k_1l_1)$ because of the relation $\mathbf{h}_3-\mathbf{h}_1=-\mathbf{h}_2$, but this is not important for the present discussion.

conclusive,* it seemed desirable to point out that the method has some very serious objections which are related to non-parallelism of the incident wave vectors $\mathbf{s}_0$ and to the mosaic character of crystals.

With an incident beam defined within a very small fraction of a second of arc and a perfect crystal oriented within the same degree of precision, it seems possible that interference phenomena might be observable. Let us suppose, however, that the incident wave vectors for various directions correspond to a slightly non-parallel set of $\mathbf{s}_0$'s. The various spheres of reflection for the various $\mathbf{s}_0$'s will all intersect the origin (by definition) but not simultaneously the end-points of the vectors $\mathbf{h}_1$ and $\mathbf{h}_3$. In fact all $\mathbf{s}_0$'s corresponding to displacement about $\mathbf{h}_3$ of the center of the sphere of reflection going through the reciprocal-lattice point $(h_3k_3l_3)$ will give diffractions $(h_3k_3l_3)$, but only a very small fraction of these would also give the two successive diffractions $(h_1k_1l_1)$ and $(h_2k_2l_2)$, and interference effects of any kind would ordinarily be completely obliterated.

If one substitutes a mosaic crystal for the perfect crystal, only a small fraction of the crystal could possibly be lined up precisely enough to show interference effects with a given $\mathbf{s}_0$, but a very much larger fraction of the crystal could be expected to contribute by single diffraction to $(h_3k_3l_3)$ when the crystal is rotated about some average $\mathbf{h}_1$. This effect contributes an additional component to $(h_3k_3l_3)$ which could not show interference effects. When the effect of variation of $\mathbf{s}_0$ is superimposed it is seen that the obliteration of the interference effects would be considerably greater for a mosaic crystal than for a perfect crystal.

Finally, even in a perfect crystal the interference effects which would actually occur may not be those due to the structure factor only. It has been pointed out to me* that if one makes a variation of $\mathbf{s}_0$ even small enough, say of the order of a few seconds of arc, so that all three diffractions may still be occurring, the interference effects due to geometrical details related to the precise directions of the beams through the crystal might blot out any trace of the influence of the phase relations due to the structure factor. The different polarization effects for the different beams and the boundary conditions at the crystal surface introduce additional complicating factors in the interpretation of the interference effects.

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* The idea and experiments suggested here have been independently conceived by Prof. I. Fankuchen and by Dr Hans Ekstein. Their investigations included similar experiments of this type on pentaerythritol, with inconclusive results with respect to phase relations (private communications). In this laboratory, Mr R. L. Collin and I have carried out experiments in which (040) of glycine was maintained on the sphere of reflection and the {*h*0*l*} zone was photographed with the use of Cu *K* radiation and a Weissenberg goniometer. Three forbidden reflections, (100), (102) and (10$\bar{2}$), were observed, with relative intensities 50, 12 and 16, respectively, on the scale (040) = 5000, given by Albrecht & Corey (1939). No information concerning phase relations was obtained.

* I am very much indebted to Prof. P. P. Ewald for this suggestion. Cf. Lamla (1939); also von Laue (1941, § 27, especially pp. 262–4).

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