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An X-ray and Physical Study of β-Naphthol

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Evidence is presented to show that the space group and unit-cell dimensions of β-naphthol are different from those previously reported. The space group is *Ia* and a unit cell of dimensions $a = 8{\cdot}185$, $b = 5{\cdot}950$, $c = 36{\cdot}29$ Å, $\beta = 119^\circ\ 52'$ contains two sets of non-equivalent molecules.

1. Introduction

Crystallographic studies of β-naphthol have been described by several workers. The most recent and most detailed reports (Kitaijgorodskij, 1945, 1947) include a discussion of the position and orientation of the molecules and of hydrogen bonding between pairs of molecules.

In the course of an examination of some materials derived from β-naphthol one of us (Hargreaves, 1940) obtained X-ray data for β-naphthol which indicated a unit cell and space group different from those deduced by Kitaijgorodskij. We have now confirmed these results by more extensive measurements. The evidence and its bearing on the results obtained in other examinations of β-naphthol are discussed in this paper.

2. Previous examinations

Groth (1906–19, vol. 5, p. 374) has collected goniometric measurements on crystals of different habits and deduces

$$a:b:c = 1{\cdot}3662:1:2{\cdot}0300,\quad \beta = 119^\circ\ 48'.$$

These values are based on very limited experimental data; none of the crystals examined had more than three forms of faces developed and in all only six interfacial angles were measured. The density is given as 1·217 g.cm.$^{-3}$ and the *C* cleavage is stated to be perfect.

X-ray data have been obtained from powder specimens by Bragg (1921), Bragg & Bragg (1924), Tanaka, Okuno & Tsuji (1931) and Neuhaus (1939), and from single-crystal specimens by Neuhaus (1939) and Kitaijgorodskij (1945, 1947). The later measurements are more reliable and only the results of Neuhaus and Kitaijgorodskij will be quoted—see Table 1.

Table 1. *Crystal data for β-naphthol*

	Neuhaus	Kitaijgo-rodskij	Hargreaves & Watson
a (Å)	8·14	8·09	8·185 ± 0·015
b (Å)	5·92	5·94	5·950 ± 0·003
c (Å)	18·2	17·80	36·29 ± 0·01
β	119° 48′*	119° 48′*	119° 52′ ± 7′
$d_{\text{obs.}}$ (g.cm.$^{-3}$)	1·245	1·23	1·252 ± 0·002
$d_{\text{calc.}}$ (g.cm.$^{-3}$)	1·249	1·29	1·249 ± 0·003
Z	4	4	8
Space group	—	$P2_1/a$	Ia

* The value of β adopted by Neuhaus and by Kitaijgorodskij is that given by Groth.

Both Neuhaus and Kitaijgorodskij took photographs with rotation or oscillation about each of the principal axes and deduced the axial lengths from layer-line spacings; but they experienced difficulty in obtaining reliable values of *c* by this method, and apparently for this reason both used measurements of $c \sin \beta$ to deduce the values of *c* given in Table 1.

3. Present examination

Most of the measurements have been made on material crystallized from carbon disulphide in the form of rhombic plates. X-ray oscillation photographs show that the crystals are monoclinic with the *b* axis lying in the plane of the plate and parallel to the shorter diagonal of the rhomb. The unit cell has been chosen so that the *a* axis is parallel to the longer diagonal of the rhomb and the *c* axis is inclined to *a* at an angle (approximately 120°) equal to the crystallographic angle β determined by Groth. Oscillation photographs about each of the three axes indicate that, to within an accuracy of about 1%, $a=8{\cdot}1$, $b=5{\cdot}95$, $c=36{\cdot}1$ Å. Many reflexions have been examined and indexed satisfactorily using these cell dimensions. It is found that general reflexions *hkl* are present only with $(h+k+l)$ even and that *h0l* reflexions are present only with *h* (or *h* and *l*) even; the space group is therefore either *Ia* or *I2/a*. It will be shown later that additional experimental evidence suggests that the correct space group is *Ia*.

Weissenberg photographs have been taken of the zero layer line with rotation about the *a* axis and of the zero and first layer lines with rotation about the *b* axis. These photographs confirm the systematic absences observed in the oscillation photographs and enable the unit-cell dimensions to be determined more accurately; the cell dimensions are given in Table 1.

The value of the observed density, measured by flotation in a mixture of benzene and chloroform, is in excellent agreement with the calculated density (Table 1) if the unit cell contains 8 molecules. There are 4 equivalent general positions in the space group *Ia*; the 8 molecules in the unit cell must therefore consist of 2 sets of non-equivalent molecules.

The choice between the space groups *Ia* and *I2/a* is based on two sources of evidence:

(i) Tests for the pyroelectric effect using liquid nitrogen appear to indicate that the crystals are weakly polar; this suggests that the centrosymmetric space group *I2/a* should be ruled out and that the correct space group is therefore *Ia*.

(ii) Fig. 1 gives the distributions of the experimentally measured intensities of the *h0l* and *0kl* reflexions. The distribution of the *0kl* reflexions indicates that the [100] projection is non-centrosymmetric (Wilson, 1949; Howells, Phillips & Rogers, 1950) whilst the distribution of the *h0l* intensities lies between the theoretical curves for the centrosymmetric and the hypercentric distributions (Lipson & Woolfson, 1952). The space group *Ia* normally gives rise to non-centrosymmetric distributions for both *h0l* and *0kl* reflexions and the space group *I2/a* to centrosymmetric distributions; the two experimental distributions therefore appear to give conflicting results. However, a preliminary attempt to determine the molecular structure of the crystals suggests that the projections of non-equivalent molecules are very similar in the [010] projection and are so oriented that they can be related in pairs about a pseudo-centre of symmetry; the molecules themselves are also centrosymmetric if the hydroxyl groups are discounted, so that a distribution approaching the hypercentric distribution may be expected. Similar considerations do not apply in the [100] projection. Clearly the balance of evidence from the intensity distributions favours *Ia* rather than *I2/a*.

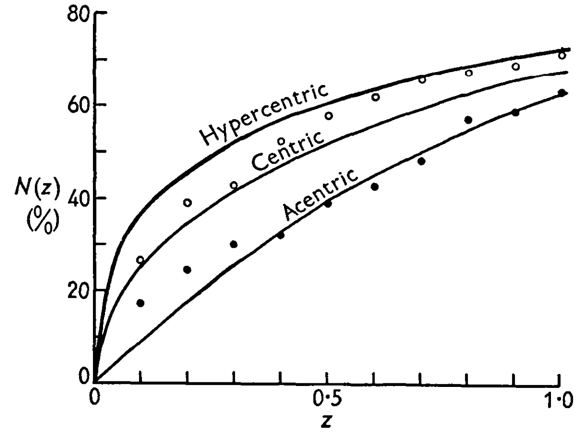

Fig. 1. Comparison of the experimental distributions of the intensities of the *h0l* reflexions (circles) and of the *0kl* reflexions (black spots) with the theoretical acentric, centric and hypercentric distributions (full lines).

4. Discussion

The cell dimensions deduced by Neuhaus and Kitaijgorodskij agree with ours except for the length of the *c* axis, which is only half the length determined by us (Table 1). The space group deduced by Kitaijgorodskij ($P2_1/a$) is also different from that (*Ia*) which we have determined. We shall therefore review some of the evidence which has a bearing on the choice of unit cell and space group.

The monoclinic angle β given by Groth has been adopted by both Neuhaus and Kitaijgorodskij, and agrees with the angle we have calculated from measurements on Weissenberg photographs. Agreement is also obtained with Groth's axial ratios if it is assumed that the length of the *c* axis is one-third of the value determined by us and two-thirds of the value determined by Neuhaus and Kitaijgorodskij. It seems probable that Groth has assigned wrong *l* indices to the small number of planes for which he had goniometric data (§ 2); these data involved only three planes with the index $l \neq 0$.

Our choice of the unit cell and space group is supported by substantial experimental evidence (§ 3). In particular, the reciprocal net of the *h*1*l* reflexions, deduced from a Weissenberg photograph of the first layer line with rotation about the *b* axis, shows quite definitely both that the length of the *c* axis is $\sim 36{\cdot}3$ Å and that the crystal lattice is body-centred. The interpretation of the *c*-axis oscillation photographs is much less easy. It is difficult to pick out the layer-lines on *c*-axis oscillation photographs because there are very few spots in each line and the layer-lines are very close together. Usually one or two row lines are prominent, and since the reflexions in each row line lie on alternate layer lines, because of the systematic absence of *hkl* reflexions with $(h+k+l)$ odd, it is easy to mistake the spacings in the row lines for the layer-line spacings. It seems likely that a misinterpretation of this nature is responsible for the value $c \sim 18$ Å given by Neuhaus and Kitaijgorodskij, particularly since both of them experienced difficulty with the c-axis photographs (§ 2). The true length of the c axis should be revealed, of course, in the process of indexing general reflexions hkl with l odd in the oscillation photographs taken by Kitaijgorodskij; but the c axis in β-naphthol is so long that the spacing of a plane (h, k, l) is nearly the same as that of a plane $(h, k, l\pm1)$ and indexing is not easy if the crystal is slightly mis-set; in any case Kitaijgorodskij does not appear to have indexed general reflexions.

We have presented two independent lines of evidence suggesting that crystals of β-naphthol are polar (§ 3). If the validity of the evidence is accepted then the centrosymmetrical space group $P2_1/a$ determined by Kitaijgorodskij is unacceptable.

It is possible that the material which we have examined has a structure different from that of the crystals examined by Neuhaus and Kitaijgorodskij; thus our material, with two non-equivalent molecules in the unit cell, may be built from molecules closely associated in pairs by hydrogen bonding between the hydroxyl groups whilst that examined by Neuhaus and Kitaijgorodskij may consist of single molecules. We believe this suggestion is unlikely for two reasons. First, our material closely resembles that described by Kitaijgorodskij; both materials are crystallized from carbon disulphide in the form of rhombic plates with $a \sim 8{\cdot}1$ Å parallel to the long diagonal and $b \sim 5{\cdot}95$ Å parallel to the short diagonal of the rhomb and $\beta \sim 119° 50'$. Secondly, we have grown crystals under a variety of conditions from six different solvents and find that powder photographs of all specimens are apparently identical.

Kitaijgorodskij has deduced a structure for β-naphthol, largely from geometrical considerations, which is said to give satisfactory intensities for the $hk0$ and $00l$ reflexions. Some of the geometrical arguments are not valid, however, if applied to our unit cell and space group, and no details are given of the agreement between observed and calculated intensities. We are continuing our X-ray examination of β-naphthol with a view to obtaining full details of the crystal structure.

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The Fourier Transform Method for Normalizing Intensities

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A method for bringing experimental intensities to an absolute scale, based on the value of the electron distribution function in $\mathbf{r} = 0$, is described. Formulas for the normalization constant are given for crystals and samples of spherical and cylindrical symmetry. The formulas represent approximate values. As an example, the percentage error in the normalization constant for cellulose is calculated as a function of the radius of the limiting sphere in reciprocal space, and the calculations are compared with experimental results.

Introduction

The method outlined by Krogh-Moe (1956) for converting experimental X-ray intensities to an absolute scale has been in use for some years at the University of Oslo. The method is described in a study of the cylindrically symmetrical distribution method in X-ray analysis (Norman, 1954*a*, *b*). As the original work is not well known, the formulas for the normalization