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# The Crystal Structure of α-Naphthol

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Crystals of α-naphthol are monoclinic, space group $P2_1/a$, with 4 molecules in a unit cell of dimensions $a=13{\cdot}20$, $b=4{\cdot}78$, $c=13{\cdot}20$ Å, $\beta=117°3'$. The structure has been refined by two-dimensional methods. The molecules are linked through hydroxyl bonds, each of length 2·79 Å, into chains which run parallel to the symmetry axis.

## Introduction

In previous X-ray examinations of the structure of α-naphthol, Kitaijgorodskij (1945, 1949) gave the coordinates of the centre of the naphthalene ring and the orientation of the molecule. It was suggested that there is strong bonding between the hydroxyl groups: the oxygen–oxygen separation was stated to be 2·54 Å, an unusually short distance for hydroxyl bonding, and one much shorter than the distances of 2·72 and 2·79 Å found for similar bonds in β-naphthol (Watson & Hargreaves, 1958). The present examination shows that the arrangement of the molecules differs substantially from that proposed by Kitaijgorodskij and that the hydroxyl bonds are normal in length.

## Experimental

Platy crystals, sufficiently thick for quantitative X-ray examination, were prepared by dissolving the material in hot water, to which a little ethanol had been added, and allowing the solution to cool to room temperature over a period of days. They closely resemble the crystals described by Kitaijgorodskij. The plate face (001) of the monoclinic crystals is elongated in the direction of the symmetry (*b*) axis.

Crystals examined by X-rays were coated with gelatine to reduce evaporation. The unit-cell dimensions, deduced from rotation photographs about the *a*, *b* and *c* axes and zero-layer Weissenberg photographs with rotation about the *a* and *b* axes, with estimated limits of error, are:

$$a=13{\cdot}20\pm0{\cdot}15,\ b=4{\cdot}78\pm0{\cdot}02,\ c=13{\cdot}20\pm0{\cdot}15\ \text{Å},$$
$$\beta=117°\,3'\pm9'.$$

With 4 molecules in the unit cell the calculated density (1·29 g.cm$^{-3}$) agrees with the density measured by flotation in an aqueous solution of strontium chloride (1·292 g.cm$^{-3}$).

The space group is uniquely determined by systematic absences as $P2_1/a$.

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Reflexions *h0l* and 0*kl*, recorded in zero-layer multiple-film Weissenberg photographs with Cu $K\alpha$ radiation, provided the data from which the atomic positions were deduced. Within the circles of reflexion there were 152 observed and 56 unobserved *h0l* reflexions, 60 observed and 24 unobserved 0*kl* reflexions. Intensities were measured by visual comparison with crystal-reflected calibration spots of known relative exposures. Absorption errors are negligible for the small crystal specimens used.

## Determination of the structure

The short *b* axis is of considerable help in solving the [010] projection. The orientation of the molecule was determined by optical methods (Hanson, Lipson & Taylor, 1953). Packing considerations and a few simple structure-factor calculations were then used to locate the centre of the naphthalene group and the position of the oxygen atom. The first trial structure gave a discrepancy index $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ of 0·32. All carbon atoms and the oxygen atom were distinctly resolved in the first electron-density map and *R* fell to 0·25 with atomic positions suggested by this map. Refinement by the method of least squares and by difference syntheses reduced *R* to 0·17 with a temperature constant $B=4{\cdot}1$ Å$^2$ for all atoms. With individual isotropic temperature factors and assumed hydrogen positions *R* fell to 0·14 for all observed *h0l* reflexions. Fig. 1 shows the final $\varrho_o$ and $(\varrho_o-\varrho_c)$ maps. Molecular vibration effects are evident in Fig. 1(*b*), anisotropic thermal vibration of the oxygen atom being particularly pronounced.

The first trial structure for the [100] projection gave $R=0{\cdot}24$. Refinement was difficult because none of the atoms is completely resolved in this projection. In five difference syntheses, with assumed hydrogen positions, *R* was reduced to 0·15. At this stage several atoms lay in substantial troughs in the $(\varrho_o-\varrho_c)$ map. On adjusting the isotropic temperature factors of these atoms *R* fell to 0·12. The final electron-density maps for this projection are shown in Fig. 2.

The standard deviations ($\sigma$) of the atomic coordinates

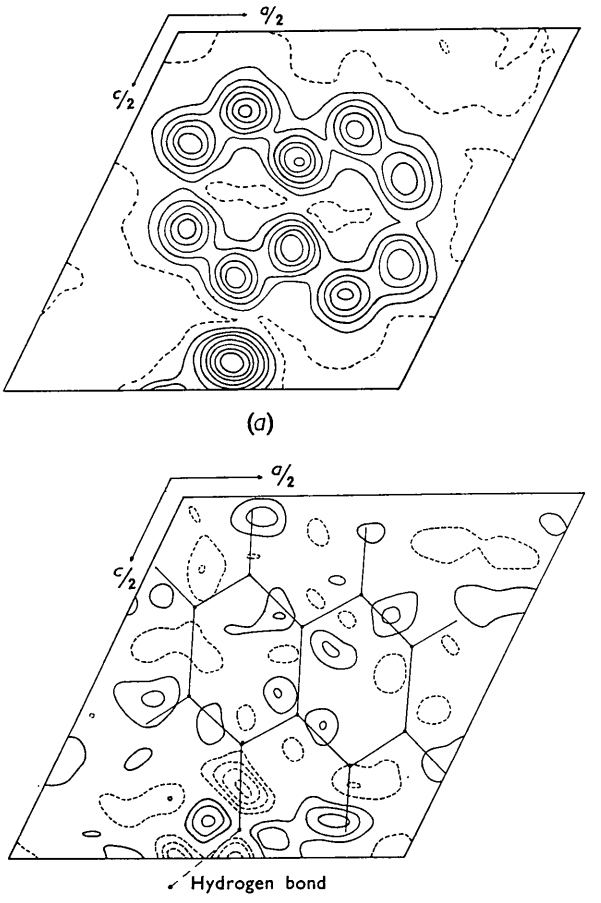


Fig. 1. (*a*) Projection of electron density along [010]. Contours are at intervals of 1 e.Å$^{-2}$; the 1 e.Å$^{-2}$ contour is broken. (*b*) Projection of $(\varrho_o - \varrho_c)$ along [010]. Contours are at intervals of 0·2 e.Å$^{-2}$; negative contours are broken and the zero contour is omitted.

Table 1. *Atomic coordinates*

| Atom | *x/a* | *y/b* | *z/c* |
|---|---|---|---|
| O | 0·2747 | 0·277 | 0·4611 |
| C(1) | 0·2258 | 0·296 | 0·3427 |
| C(2) | 0·1307 | 0·129 | 0·2750 |
| C(3) | 0·0836 | 0·181 | 0·1544 |
| C(4) | 0·1320 | 0·359 | 0·1083 |
| C(5) | 0·2833 | 0·696 | 0·1365 |
| C(6) | 0·3784 | 0·866 | 0·2071 |
| C(7) | 0·4227 | 0·833 | 0·3253 |
| C(8) | 0·3755 | 0·634 | 0·3725 |
| C(9) | 0·2762 | 0·485 | 0·3002 |
| C(10) | 0·2286 | 0·503 | 0·1818 |
| H(2) | 0·092 | 0·975 | 0·312 |
| H(3) | 0·007 | 0·050 | 0·096 |
| H(4) | 0·094 | 0·395 | 0·017 |
| H(5) | 0·274 | 0·725 | 0·045 |
| H(6) | 0·418 | 0·025 | 0·173 |
| H(7) | 0·497 | 0·957 | 0·380 |
| H(8) | 0·410 | 0·605 | 0·465 |

were estimated, for both [010] and [100] projections, by a least-squares program:

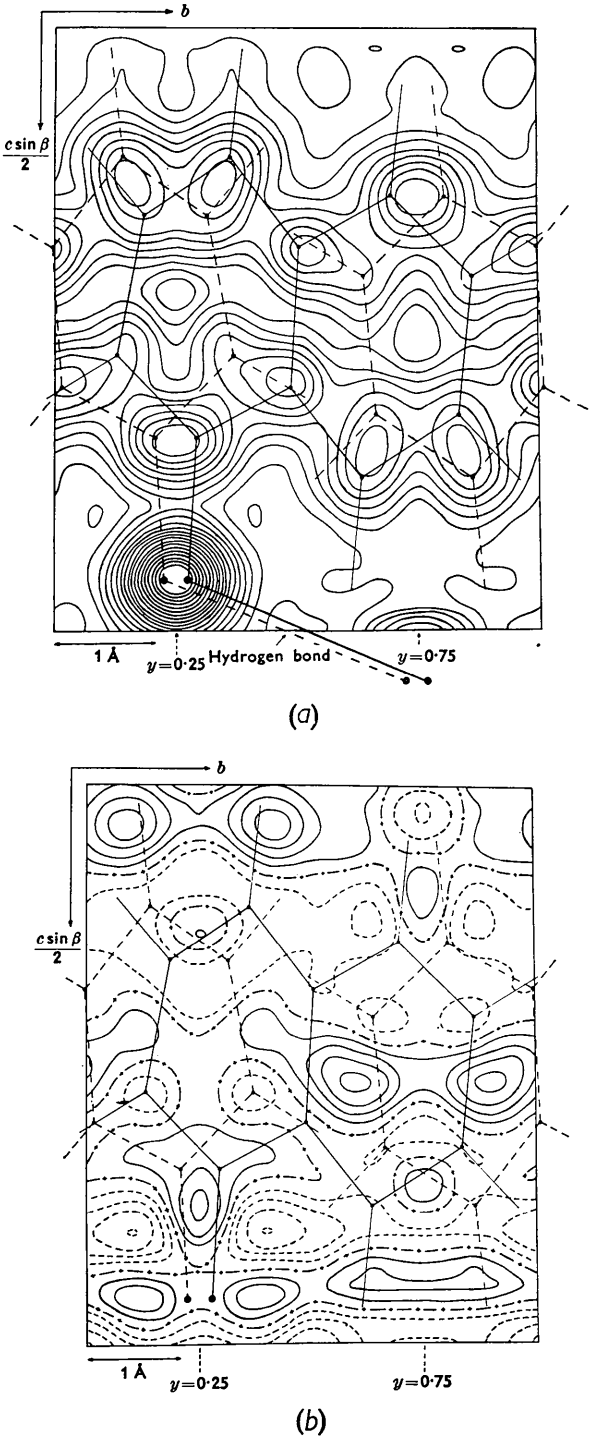


Fig. 2. (*a*) Projection of electron density along [100]. Contours are at intervals of 1 e.Å$^{-2}$. (*b*) Projection of $(\varrho_o - \varrho_c)$ along [100]. Contours are at intervals of 0·2 e.Å$^{-2}$; negative contours are broken; zero contour $- + - + -$.

$[010]: \sigma(x) = \sigma(z) =$ 0·022 Å for carbon,
0·015 Å for oxygen
$[100]: \sigma(y) = \sigma(z) =$ 0·048 Å for carbon,
0·038 Å for oxygen.

With weighted mean values for the $z$ coordinates, the final atomic coordinates are given in Table 1. Tables of structure factors for all $h0l$ and $0kl$ reflexions, calculated with the coordinates given in Table 1, are available for comparison with the observed structure factors (Robinson, 1961); the atomic scattering factors used are those given in analytical form by Forsyth & Wells (1959).

## Discussion

The carbon–oxygen bond length is 1·40 Å with a standard deviation of 0·03 Å. The intramolecular carbon–carbon bond lengths are very inaccurate because of the molecular overlap in the [100] projection: the mean length of these bonds is 1·41 Å and the mean standard deviation 0·05 Å.

Kitaijgorodskij's structure is compared with that determined here in Fig. 3. It can be seen that the molecular orientations differ substantially and that the oxygen atom is attached to different carbon atoms in the two structures.

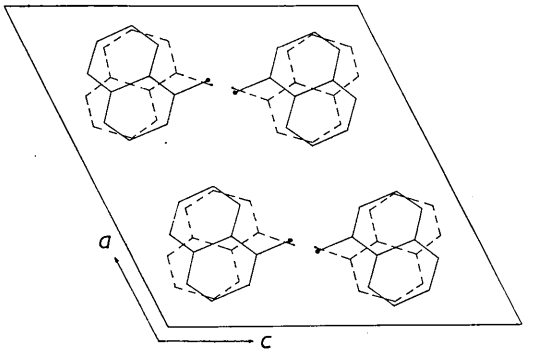


Fig. 3. Comparison between Kitajgorodskij's structure (dashed lines) and present structure (full lines). The pairs of black dots indicate hydrogen bonds.

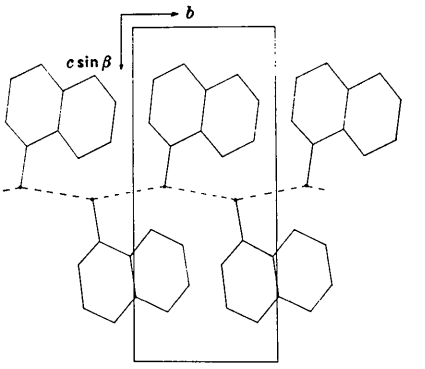


Fig. 4. Hydroxyl-bond formation.

The molecules are linked by hydroxyl bonds into chains running parallel to the $b$ axis as shown in Fig. 4. Since the linked oxygen atoms are related by a two-fold screw axis, their separation in the $y$ direction can be determined much more accurately from the length of the $b$ axis than from the [100] projection. The hydroxyl bond length is 2·79 Å with a standard deviation of 0·013 Å. This length is within the usual range for hydroxyl bonds and much greater than the 2·54 Å determined by Kitaijgorodskij.

The van der Waals distances are of the usual order, the closest distance of approach of atoms in neighbouring molecules being 3·5 Å.

## References

Forsyth, J. B. & Wells, M. (1959). *Acta Cryst.* **12**, 412.
Hanson, A. W., Lipson, H. & Taylor, C. A. (1953). *Proc. Roy. Soc.* A, **218**, 371.
Kitaijgorodskij, A. I. (1945). *Dokl. Akad. Nauk SSSR*, **50**, 319.
Kitaijgorodskij, A. I. (1949). *Izvest. Akad. Nauk SSSR, Khim. Nauk*, **3**, 263.
Robinson, B. (1961). Thesis for the degree of M. Sc. Tech., University of Manchester.
Watson, H. C. & Hargreaves, A. (1958). *Acta Cryst.* **11**, 556.