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The Crystal Structure of 7-Acenaphthenol, $C_{12}H_9OH$

BY M. P. GUPTA AND T. N. P. GUPTA

Department of Physics, University of Ranchi, Ranchi 834008, *India*

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The crystal structure of 7-acenaphthenol has been determined by X-ray diffraction and refined by least-squares calculations to an R of 0·078. The crystals are monoclinic with $a=15{\cdot}72_2$, $b=4{\cdot}95_2$, $c=12{\cdot}97_0$ Å, $\beta=119{\cdot}3°$, space group $P2_1/a$, $Z=4$. The molecules are arranged in the form of spirals, held together by hydrogen bonds of 2·78 Å between the hydroxyl groups and by van der Waals forces.

The title compound was studied as part of a programme in this laboratory of investigations of hydrogen-bonded systems.

Experimental

Single crystals were grown from benzene solution. The crystals are acicular in habit, the long edge corresponding to [010], with (001) and (100) as side faces. The cell dimensions were derived from high sin θ reflexions on Weissenberg films with Ag lines superimposed as internal standards.

Crystal data

Monoclinic, $a=15{\cdot}72_2$, $b=4{\cdot}95_2$, $c=12{\cdot}97_0$ Å, $\beta=119{\cdot}3°$, $d_o=1{\cdot}31$, $d_c=1{\cdot}28$ g cm^{-3}, $Z=4$, space group $P2_1/a$, μ(Cu $K\alpha$) = 6·40 cm^{-1}.

657 independent reflexions were collected by Weissenberg photography around [010], [100] and [001], estimated visually, and brought to approximate absolute scale by statistical methods. Large thermal motion of atoms imposed a cut-off on observed high sin θ reflexions.

Determination and refinement of the structure

The structure was solved from a sharpened Patterson projection down [010] which gave the orientation of the molecule. Packing considerations and Fourier syntheses gave a set of parameters for full-matrix least-squares refinement (Busing, Martin & Levy, 1962). R fell to 13·1%. The hydrogen atoms were located from a difference synthesis and their inclusion reduced R to 11·9%. An extinction correction (Zachariasen, 1967) and the weighting scheme ($\sqrt{W}F=a+b\bar{F}_o$, a and b being

Table 1. *Atomic and thermal parameters*

(*a*) Final atomic coordinates and their e.s.d.'s ($\times 10^4$, and for hydrogen atoms $\times 10^3$).

	x/a	*y/b*	*z/c*
C(1)	3722 (6)	1201 (18)	4070 (7)
C(2)	2590 (6)	1293 (18)	3567 (7)
C(3)	2241 (6)	3464 (17)	2610 (7)
C(4)	1328 (7)	4445 (18)	1878 (8)
C(5)	1217 (7)	6457 (22)	1028 (8)
C(6)	2000 (8)	7414 (21)	937 (9)
C(7)	2953 (7)	6369 (19)	1671 (8)
C(8)	3846 (8)	7167 (19)	1714 (9)
C(9)	4709 (8)	5955 (21)	2509 (11)
C(10)	4746 (7)	3958 (20)	3316 (9)
C(11)	3930 (6)	3173 (18)	3341 (8)
C(12)	3037 (6)	4401 (16)	2519 (7)
O	2330 (4)	1996 (11)	4443 (5)
H(1)	394	−74	396
H(2)	221	−41	319
H(3)	75	343	200
H(4)	63	736	62
H(5)	197	890	43
H(6)	378	869	109
H(7)	533	684	255
H(8)	534	307	391
H(9)	404	168	487
H(10)	245	407	479

Table 1 (*cont.*)

(*b*) Thermal parameters and their e.s.d.'s ($\times 10^4$ Å^2), $T=\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{13}hl+2b_{23}kl)]$

	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	54 (6)	324 (49)	68 (8)	3 (14)	26 (6)	21 (17)
C(2)	56 (6)	291 (46)	64 (8)	−20 (13)	32 (6)	−34 (17)
C(3)	47 (6)	244 (47)	60 (7)	−16 (13)	25 (6)	−40 (17)
C(4)	62 (8)	262 (44)	78 (9)	1 (14)	24 (8)	−27 (18)
C(5)	65 (7)	386 (54)	63 (8)	24 (17)	12 (7)	−20 (19)
C(6)	90 (9)	387 (56)	64 (8)	−16 (18)	37 (8)	−19 (18)
C(7)	57 (7)	344 (50)	77 (9)	−31 (15)	32 (7)	−27 (19)
C(8)	96 (9)	265 (49)	88 (9)	−29 (16)	55 (8)	−8 (18)
C(9)	87 (9)	405 (57)	137 (12)	−78 (18)	70 (9)	−20 (23)
C(10)	62 (7)	404 (54)	104 (10)	−14 (16)	46 (7)	−17 (21)
C(11)	49 (6)	313 (51)	70 (8)	−4 (14)	31 (6)	−13 (17)
C(12)	46 (6)	236 (44)	54 (8)	−10 (13)	27 (6)	−16 (15)
O	71 (4)	257 (38)	69 (5)	−6 (9)	43 (4)	−30 (11)

Table 3. *Bond lengths and bond angles*

C(7)—C(12)	1·43 (1) Å	C(3)—C(2)	1·53 (1) Å
C(12)–C(11)	1·42 (1)	C(1)—C(2)	1·57 (1)
C(12)–C(3)	1·39 (1)	C(2)—O	1·43 (1)
C(7)—C(8)	1·43 (2)	C(1)—H(1)	1·05
C(7)—C(6)	1·42 (1)	C(2)—H(2)	1·01
C(8)—C(9)	1·38 (1)	C(4)—H(3)	1·11
C(6)—C(5)	1·38 (2)	C(5)—H(4)	0·92
C(5)—C(4)	1·43 (1)	C(6)—H(5)	0·97
C(9)—C(10)	1·42 (2)	C(8)—H(6)	1·07
C(10)–C(11)	1·36 (2)	C(9)—H(7)	1·05
C(4)—C(3)	1·37 (1)	C(10)–H(8)	0·97
C(11)–C(1)	1·50 (1)	C(1)—H(9)	0·94
		O---H(10)	1·10

C(1)—C(2)—C(3)	104·0 (8)°
C(2)—C(3)—C(12)	108·9 (7)
C(3)—C(12)–C(11)	113·2 (8)
C(12)–C(11)–C(1)	108·1 (9)
C(11)–C(1)—C(2)	105·8 (7)
C(3)—C(4)—C(5)	118·2 (10)
C(4)—C(5)—C(6)	121·9 (8)
C(5)—C(6)—C(7)	120·7 (10)
C(6)—C(7)—C(12)	115·7 (10)
C(7)—C(12)–C(3)	123·1 (7)
C(12)–C(3)—C(4)	120·4 (9)
C(11)–C(10)–C(9)	121·2 (9)
C(10)–C(9)—C(8)	121·7 (12)
C(9)—C(8)—C(7)	119·8 (11)
C(8)—C(7)—C(12)	116·1 (8)
C(7)—C(12)–C(11)	123·8 (9)
C(12)–C(11)–C(10)	117·4 (9)
C(8)—C(7)—C(6)	128·1 (10)
C(4)—C(3)—C(2)	130·7 (10)
C(10)–C(11)–C(1)	134·5 (8)
C(1)—C(2)—O	112·7 (6)
C(2)—O---O	125·0 (6)
C(3)–C(2)–O	110·3 (7)
C(2)–O—H(10)	119·9
H(1)–C(1)–H(9)	110·8
H(1)–C(1)–C(11)	108·7
H(1)–C(1)–C(2)	110·2
H(2)–C(2)–O	105·0
H(2)–C(2)–C(3)	107·8
H(2)–C(2)–C(1)	117·0
H(3)–C(4)–C(3)	113·2
H(3)–C(4)–C(5)	128·4
H(4)–C(5)–C(6)	117·7
H(4)–C(5)—C(4)	119·5
H(5)–C(6)—C(5)	124·3
H(5)–C(6)—C(7)	114·8
H(6)–C(8)—C(9)	124·5
H(6)–C(8)—C(7)	115·7
H(7)–C(9)—C(8)	114·1
H(7)–C(9)—C(10)	123·6
H(8)–C(10)–C(11)	113·8
H(8)–C(10)–C(9)	125·0
H(9)–C(1)—C(11)	112·0
H(9)–C(1)—C(2)	109·3

constants for the group) were applied in the last stage of refinement, with anisotropic thermal factors for the carbon and oxygen atoms. This brought R down to 0·078.

The numbering of atoms in the molecule is given in Fig. 1, positional and thermal parameters in Table 1. Observed and calculated structural factors are in Table 2.* Bond lengths and bond angles are in Table 3.

The equation for the weighted least-squares plane through the 12 carbon atoms in the molecule is:

$$-0{\cdot}2070X+0{\cdot}7157Y+0{\cdot}6670Z-2{\cdot}8007=0,$$

where X, Y, Z are coordinates of atoms referred to orthogonal axes a, b, c' (c' normal to a and b). Deviations from the plane are given in Table 4. The direction

Table 4. *Deviations of atoms from the weighted least-squares plane and their e.s.d.'s.*

C(1)	0·019 (10) Å	C(7)	−0·025 (10) Å
C(2)	−0·026 (9)	C(8)	0·006 (10)
C(3)	0·010 (9)	C(9)	0·000 (12)
C(4)	0·006 (10)	C(10)	−0·005 (11)
C(5)	0·003 (11)	C(11)	0·004 (10)
C(6)	0·006 (10)	C(12)	0·002 (8)

cosines of the normal to the plane are ($l=-0{\cdot}2070$, $m=0{\cdot}7157$, $n=0{\cdot}6670$).

The crystal and molecular structure

The molecules are linked by hydrogen bonds of 2·78 Å between the hydroxyl groups related by a twofold screw axis and as a consequence form spirals. The hydrogen-bond distances are similar to those of 2·731 and 2·717 Å found in α-resorcinol (Bacon & Jude, 1973) and the 2·720 and 2·700 found in *cis*-1,2-acenaphthenediol (Trotter & Mak, 1963). Other linkages between the molecules are of van der Waals type, the shortest contact being 3·30 Å.

The bond lengths and angles reported in this work are similar to those found in *cis*-1,2-acenaphthenediol (Trotter & Mak, 1963), acenaphthene (Ehrlich, 1957), and in acenaphthenequinone (Mak & Trotter, 1963). The angles C–O–H have values of 112·1 and 111·2° in α-resorcinol, similar to the 119·9° found in this structure. There is an angle of 5·1° between O–H and O–O

* Table 2 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30600 (15 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

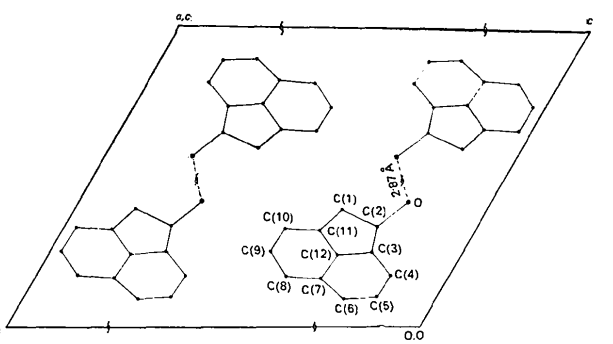

Fig. 1. The structure looking down the [010] axis.

compared with similar values of 2·6 and 9·2° found in α-resorcinol (Bacon & Jude, 1973).

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Hydrogen Bonding in $Ca(H_2PO_4)_2.H_2O$ as Determined by Neutron Diffraction*

BY L. W. SCHROEDER,† E. PRINCE AND B. DICKENS‡

Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234, *U.S.A.*

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The hydrogen positions in $Ca(H_2PO_4)_2.H_2O$ have been determined and the structure refined to $R_w=0{\cdot}068$ and $R=0{\cdot}055$ using 1045 neutron data. No evidence is found for any disorder of the protons. The two crystallographically distinct $H_2PO_4^-$ ions are hydrogen bonded to each other and to the water molecule. The oxygen atom of the water coordinates to a calcium ion and a hydrogen atom from $H_2PO_4^-$ along its lone-pair orbital directions with distances $Ca\cdots O_w=2{\cdot}479$ Å and $H\cdots O_w=1{\cdot}679$ Å. One of the hydrogen atoms of the water molecule is 2·106 and 2·315 Å from two oxygen atoms, with O_w–$H\cdots O$ angles of 110·9 and 147·5°. The distances and angles indicate that only the stronger of these two interactions is structurally significant. The other hydrogen atom of the water molecule is involved in a hydrogen bond with $H_w\cdots O=1{\cdot}823$ Å and the angle O_w–$H\cdots O=160{\cdot}4°$.

Introduction

On the basis of a refinement of the structure of $Ca(H_2PO_4)_2.H_2O$ from X-ray diffractometer data, Dickens & Bowen (1971) located the hydrogen atoms approximately and calculated idealized positions. An electron-density difference synthesis based on the X-ray data suggested that one hydrogen bond involving the water molecule was bifurcated. Allowing each of the possible hydrogen bonds to be linear in turn gave rise to two possible idealized positions, which were, however, incompatible with the difference synthesis. However, disorder of the water molecule would be compatible with Berry's (1968) interpretation of the infrared spectrum of $Ca(H_2PO_4)_2.H_2O$.

We undertook a neutron-diffraction study in order to determine definitely the orientation of the water molecule and to establish the arrangement of hydrogen bonds formed by the water molecule.

Experimental

Crystals of $Ca(H_2PO_4)_2.H_2O$ were grown from solutions (Elmore & Farr, 1940). Most exhibited polysynthetic twinning, as is common for this material (Smith, Lehr & Brown, 1955), with (010) as the composition plane. A crystal was chosen whose twin components were approximately four-fifths and one-fifth of the total volume. The smaller component was removed by polishing the twin with pumice. The remaining part of the crystal was examined under a polarizing microscope to ensure that removal of the small component was complete. The resulting plate had dimensions $3\times5\times0{\cdot}367$ mm (volume $\sim5{\cdot}5$ mm^3) and was used for data collection after examination of the crystal by precession photography had shown no evidence of twinning. The cell constants, $a=5{\cdot}6261$ (5), $b=11{\cdot}889$ (2), $c=6{\cdot}473$ (8), $\alpha=98{\cdot}633$ (6), $\beta=118{\cdot}2$ (6), $\gamma=83{\cdot}344$ (6)°, are taken from Dickens & Bowen

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† Research Associate of the American Dental Association Health Foundation at the National Bureau of Standards, Washington, D.C. 20234, U.S.A.

‡ Dental Research Section, National Bureau of Standards, Washington, D.C. 20234, U.S.A. and presently Research Associate, American Dental Association Health Foundation.