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The Crystal Structure of *cis*-1,2-Acenaphthenediol

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cis-1,2-Acenaphthenediol crystallizes in the monoclinic system with four molecules in the unit cell, which has dimensions $a=12{\cdot}77$, $b=4{\cdot}845$, $c=15{\cdot}74$ Å, $\beta=111°\,50'$. The space group is $P2_1/c$. The structure has been determined by Patterson methods, and refined by (F_o-F_c) syntheses utilizing partial three-dimensional data.

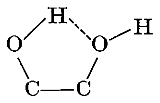
The carbon skeleton is planar and the valency-angle distortions are similar to those found in related compounds. The *peri* bonds are significantly shortened (average value $1{\cdot}48\pm0{\cdot}01_0$ Å) while the $1{\cdot}60\pm0{\cdot}01_4$ Å C(1)–C(2) bond distance shows the effect of ring strain and steric repulsion of the oxygen atoms. The crystal structure consists of zigzag chains of intermolecular hydrogen bonds formed between molecules related by a screw axis, the intermolecular O · · · O distances being 2·72 and 2·70 Å.

Introduction

X-ray analyses of acenaphthene (Ehrlich, 1957) and pyracene (Simmons & Lingafelter, 1961) and acenaphthenequinone (Mak & Trotter, 1963) have shown that the carbon skeleton of the acenaphthene system is planar, and that the strain caused by the fusion of a five-membered ring to the naphthalene moiety is reflected in the distortion of valency angles rather than lengthening of the aliphatic C–C bond. As a consequence of the planarity of the *peri* ring, *cis*-1,2-substituents are syn-periplanar and *trans*-1,2-substituents are anti-clinal at $\tau=\pm120°$ on the aliphatic C–C bond (Klyne & Prelog, 1960).

For *cis*-1,2-acenaphthenediol molecular models show that the oxygen–oxygen distance is less than the normal van der Waals separation. There is some evidence that an internal hydrogen bond exists between the eclipsed OH groups. Study of the infrared spectrum of *cis*-1,2-acenaphthenediol in carbon tetrachloride solution (Moriconi, O'Connor, Kuhn, Keneally & Wallenberger, 1959) revealed two OH absorption bands: a well-resolved peak at $\nu=3584$ cm^{-1} and a broad shoulder at $\nu=3543$ cm^{-1}. Moriconi *et al.* assigned the higher frequency to a weak OH...π interaction and the lower frequency to stronger intramolecular hydrogen bonding between *vic*-OH groups. Similarly, infrared measurements on the crystalline solid (Csizmadia & Hayward, 1962) showed the presence of two absorption bands of approximately equal intensity: the lower frequency at 3190 cm^{-1} indicating intramolecular hydrogen bonding of considerable strength, in agreement with the assignment of Moriconi *et al.*, and the higher frequency at 3333 cm^{-1} being ascribed, more appropriately in this case, to intermolecular hydrogen bonding.

Simple consideration of molecular geometry, however, suggests that the hydrogen bond between OH groups on adjacent carbon atoms, if formed at all, can at most be a weak one. For the five-membered intramolecular chelate ring



the angle φ between the O–H bond and the O · · · O line is at least 30° if standard values are assumed for the bond distances and valency angles. Since the proton is far from the internuclear O · · · O line a large strain energy is expected for the bending of the hydrogen bond (Pauling, 1960), so that its formation is rather unlikely. As a first step towards resolving this anomaly, we have felt it desirable to determine the crystal structure of *cis*-1,2-acenaphthenediol.

Experimental

A sample of *cis*-1,2-acenaphthenediol consisted of colourless needles elongated along the *b* axis, with the (001) face well developed. All the crystals examined were twinned on (100). The density was measured by flotation in aqueous potassium iodide. The unit-cell dimensions and space group were determined from rotation and oscillation photographs of a crystal mounted about the *b* axis, *h*0*l* and *h*1*l* Weissenberg films, and *hk*0 and 0*kl* precession films.

Crystal data

cis-1,2-Acenaphthenediol, $C_{12}H_{10}O_2$; $M=186{\cdot}2$; m.p. 218–219·5 °C.
Monoclinic,
$a=12{\cdot}77\pm0{\cdot}02$, $b=4{\cdot}845\pm0{\cdot}003$,
$c=15{\cdot}74\pm0{\cdot}02$ Å; $\beta=111°\,50'\pm5'$.
Volume of the unit cell: 904·0 Å^3.
Density calculated (with $Z=4$): 1·368, measured: 1·35 g.cm^{-3}.

Absorption coefficients for X-rays, $\lambda=1{\cdot}5418$ Å, $\mu=8{\cdot}93$ cm^{-1}; $\lambda=0{\cdot}7107$ Å, $\mu=1{\cdot}13$ cm^{-1}.

Total number of electrons per unit cell: $F(000)=392$.

Absent spectra: $h0l$ when l is odd, $0k0$ when k is odd. Space group is $P2_1/c$ (C_{2h}^5).

For the collection of intensity data a needle crystal of cross-section $0{\cdot}09\times0{\cdot}06$ mm was mounted about the b axis. The intensities of the $h0l$ and $h1l$ reflections were recorded on Weissenberg photographs, using Cu $K\alpha$ radiation, and multiple-films to correlate strong and weak reflections. The ranges of $h0l$ and $h1l$ intensities were about 7460 to 1 and 18400 to 1 respectively, the estimates being made visually. Twinning of the crystal resulted in the appearance of two sets of reflections on a Weissenberg film (different c^* axis) with occasional overlap. Fortunately one component of the twin was appreciably bigger than the other (intensity ratio 8 to 3), so that the spots from the two components could be distinguished, although often with some difficulty. No absorption corrections were considered necessary. The structure amplitudes were derived by the usual formulae, the absolute scale being established later by correlation with the calculated structure factors. 138 independent $h0l$ reflections and 246 $h1l$ reflections were observed, representing 56% and 49% respectively of the possible number observable under the experimental conditions.

Structure analysis

[010] *projection*

Since the b axis is reasonably short (4·845 Å) a good view of the molecule was expected in this projection. The orientation of the aromatic nucleus was deduced first from the weighted reciprocal lattice and confirmed later from examination of the Patterson projection along the b axis (Fig. 1). The well-resolved intramolecular O–O vector peak indicated that the projection of the molecular axis M (Fig. 3) must be almost parallel to the a axis. The highest peak on the Patterson map corresponded to the interaction between naphthalene rings related by symmetry and led to the coordinates $X=0{\cdot}207$, $Z=0{\cdot}276$ for the molecular origin, defined as the centre of the C(5a)–C(8b) bond. (The final coordinates of the molecular origin are $X=0{\cdot}2008$, $Z=0{\cdot}2761$.) The x and z parameters were then obtained from the projection of a CENCO Petersen molecular model held in the deduced orientation. Structure amplitudes for $h0l$ reflections were calculated with the use of carbon and oxygen scattering factors from *Tabellen zur Röntgenstrukturanalyse* (Sagel, 1958) and an overall isotropic temperature factor $B=4{\cdot}5$ Å^2. The discrepancy factor for 193 reflections, including 55 unobserved reflections with intensities taken at half the minimum observable limit, was somewhat high ($R=51{\cdot}7\%$). However, there were no serious disagreements between the observed and unobserved structure amplitudes and their calculated values. It was possible to allocate signs to 94 observed reflections for a Fourier synthesis, and the resulting map showed good resolution of all the atoms. Recalculation of the $h0l$ structure factors with the x and z coordinates of the electron-density maxima lowered R (observed reflections only) to 34·4%. Refinement of the atomic parameters was carried out by means of successive (F_o-F_c) syntheses, and after six cycles R was 14·8%.

The final difference map had a number of electron density maxima which could be attributed to the presence of hydrogen atoms. Although the electron density was negative in the region between oxygen atoms in the same molecule and positive in the proximity of the intermolecular O · · · O lines, this should not be taken as definite evidence against internal hydrogen bonding since hydrogen atoms in O–H · · · O bonds are difficult to locate by X-ray methods. Since the locations of the hydroxyl hydrogens were uncertain, positional parameters were deduced only for the eight hydrogen atoms attached to the carbon skeleton. When these hydrogen atoms were included in the structure factor calculation, R was lowered to 13·1%. The measured and calculated

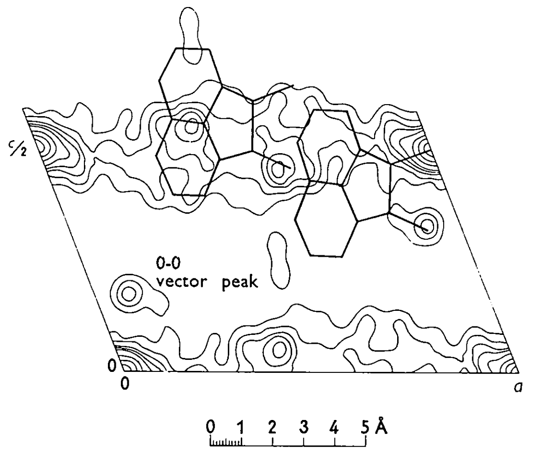


Fig. 1. Patterson projection along [010]. Contour-line scale arbitrary. A diagram of two molecules is superimposed.

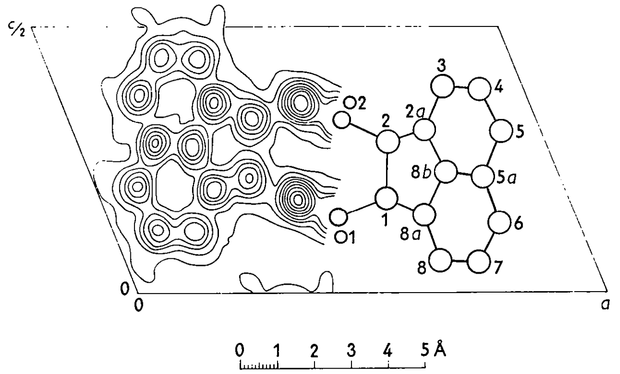


Fig. 2. Electron-density projection along [010]. Contour lines are drawn at intervals of 1 e.Å^2 starting with 1 e.Å^2.

Table 1. *Measured and calculated structure factors*

*h*0*l*

h	l	F_o	F_c	h	l	F_o	F_c	h	l	F_o	F_c	h	l	F_o	F_c
0	0	not obs.	392	-10	4	32.2	-26.1	-12	8	4.1	-4.7	-9	12	<2.3	-3.1
1	0		-30.1	-9	4	13.4	12.7	-11	8	3.3	4.7	-8	12	<2.3	-0.1
2	0	52.8	-61.5	-8	4	24.5	24.4	-10	8	<2.2	2.7	-7	12	4.5	4.0
3	0	22.3	-22.5	-7	4	12.8	12.5	-9	8	<2.0	-2.5	-6	12	12.6	-14.8
4	0	14.2	-19.4	-6	4	8.4	-9.2	-8	8	5.0	5.6	-5	12	12.4	15.5
5	0	7.4	-7.3	-5	4	18.8	-16.4	-7	8	13.5	-9.9	-4	12	<2.2	-1.1
6	0	2.3	2.1	-4	4	7.2	-7.7	-6	8	39.6	32.4	-3	12	<2.2	3.2
7	0	13.4	-9.4	-3	4	35.6	36.6	-5	8	6.0	6.4	-2	12	12.5	16.5
8	0	2.5	2.3	-2	4	2.3	-5.7	-4	8	32.4	-27.4	-1	12	11.5	13.0
9	0	4.6	-3.5	-1	4	13.4	-18.6	-3	8	35.8	-38.6	0	12	11.7	-12.9
10	0	<2.2	-1.2	0	4	53.2	-51.0	-2	8	11.9	17.2	1	12	29.9	-31.2
11	0	11.6	-5.5	1	4	44.0	44.4	-1	8	<1.7	2.0	2	12	<2.3	-0.2
12	0	29.4	24.4	2	4	52.6	-55.2	0	8	8.1	-9.0	3	12	7.5	10.6
13	0	<2.0	2.4	3	4	31.2	27.6	1	8	20.2	20.4	-14	14	6.3	-4.3
14	0	10.9	-7.5	4	4	28.4	25.7	2	8	<1.8	-1.2	-13	14	<1.8	-2.7
15	0	4.2	-2.8	5	4	32.9	30.1	3	8	16.3	-19.3	-12	14	9.2	5.2
-15	2	10.1	6.9	6	4	22.9	-19.5	4	8	15.1	17.4	-11	14	<2.2	-4.9
-14	2	<1.8	-0.5	7	4	<2.0	-4.6	5	8	15.0	-15.2	-10	14	3.2	-2.9
-13	2	<2.1	-1.3	8	4	3.3	-4.7	6	8	16.5	18.3	-9	14	<2.3	2.6
-12	2	4.6	-3.0	9	4	4.6	5.8	7	8	<2.3	0.4	-8	14	<2.3	5.7
-11	2	3.3	5.6	10	4	5.7	-3.6	8	8	5.0	-6.0	-7	14	<2.3	1.0
-10	2	<2.1	-2.9	11	4	6.2	-5.9	9	8	4.2	-5.7	-6	14	17.4	17.9
-9	2	3.7	-4.9	12	4	<1.8	0.5	-14	10	4.8	-3.7	-5	14	16.6	-16.8
-8	2	13.4	-13.3	13	4	3.7	3.3	-13	10	<2.1	1.9	-4	14	4.1	4.9
-7	2	5.3	-8.2	-13	6	<2.3	-3.5	-12	10	3.3	0.8	-3	14	<2.3	-0.6
-6	2	<1.6	-0.0	-12	6	4.7	5.8	-11	10	24.0	21.5	-2	14	9.5	-11.5
-5	2	30.9	25.6	-11	6	10.5	-10.7	-10	10	<2.3	-5.3	-1	14	5.3	-6.7
-4	2	<1.2	4.4	-10	6	24.9	22.2	-9	10	<2.2	1.7	0	14	3.6	4.6
-3	2	60.5	55.9	-9	6	18.5	-16.6	-8	10	15.1	-15.3	1	14	<2.2	2.0
-2	2	37.5	41.4	-8	6	<2.0	1.2	-7	10	<2.1	3.8	2	14	<2.1	0.5
-1	2	<0.8	-1.7	-7	6	11.6	9.4	-6	10	14.6	-14.7	3	14	<2.0	1.3
0	2	93.5	-93.1	-6	6	14.0	-14.4	-5	10	<2.0	-2.1	4	14	<1.8	4.9
1	2	22.5	25.3	-5	6	<1.6	-0.3	-4	10	8.6	8.0	5	14	<1.6	-2.2
2	2	24.7	-25.9	-4	6	9.7	9.8	-3	10	<1.9	1.2	6	14	5.6	6.6
3	2	30.5	-31.8	-3	6	10.0	15.6	-2	10	9.4	-12.0	-11	16	2.6	5.3
4	2	17.7	19.7	-2	6	16.0	19.0	-1	10	14.3	13.2	-10	16	<2.0	-0.4
5	2	38.8	-33.7	-1	6	48.4	-45.9	0	10	<2.1	-2.7	-9	16	4.7	6.2
6	2	17.3	17.4	0	6	30.9	26.6	1	10	17.8	21.6	-8	16	<2.2	-2.2
7	2	8.5	8.6	1	6	34.0	-31.2	2	10	<2.2	6.0	-7	16	4.7	-6.6
8	2	3.1	5.8	2	6	39.9	39.0	3	10	6.8	-6.5	-6	16	<2.2	-5.0
9	2	4.3	5.1	3	6	2.4	-2.2	4	10	12.5	-16.7	-5	16	4.7	3.9
10	2	4.3	4.6	4	6	15.6	-18.1	5	10	<2.3	6.3	-5	18	5.4	7.0
11	2	<2.3	1.3	5	6	4.1	7.5	6	10	5.7	-7.2	-4	18	3.7	-2.6
12	2	14.4	-11.5	6	6	7.9	-9.6	-14	12	8.2	8.4	-3	18	<1.8	2.2
13	2	4.5	-2.6	7	6	<2.2	-0.7	-13	12	10.1	8.0	-2	18	<1.7	-3.1
-14	4	7.7	6.4	-16	8	4.9	-5.3	-12	12	8.3	-7.5	-1	18	<1.5	-1.2
-13	4	<2.2	-2.2	-15	8	<1.7	-0.9	-11	12	26.3	-21.0	0	18	3.2	3.0
-12	4	8.8	-8.9	-14	8	<1.9	1.8	-10	12	11.5	10.0	-5	20	4.2	-6.9
-11	4	8.7	9.2	-13	8	<2.0	-2.3								

*h*1*l*

h	l	F_o	F_c	h	l	F_o	F_c	h	l	F_o	F_c	h	l	F_o	F_c
1	0	14.2	-21.3	12	1	<2.5	0.5	-1	3	34.2	-32.5	-10	5	5.6	-6.7
2	0	112.7	106.1	13	1	2.9	3.0	0	3	13.7	16.2	-9	5	2.6	-0.6
3	0	16.6	17.8	14	1	4.8	3.0	1	3	23.1	20.2	-8	5	13.5	-13.9
4	0	<1.0	-3.2	-14	2	3.2	2.2	2	3	4.6	-4.0	-7	5	17.0	15.8
5	0	3.2	2.7	-13	2	<2.4	0.2	3	3	<1.2	0.6	-6	5	4.3	1.5
6	0	12.2	-11.2	-12	2	<2.9	-0.9	4	3	13.1	14.7	-5	5	12.7	-8.9
7	0	3.1	2.5	-11	2	<3.0	0.6	5	3	15.7	-15.3	-4	5	6.6	2.1
8	0	3.0	-4.6	-10	2	<2.9	4.8	6	3	5.8	-5.2	-3	5	12.1	-10.8
9	0	<2.7	3.3	-9	2	<2.6	1.5	7	3	<2.4	1.9	-2	5	6.5	11.8
10	0	21.1	-18.9	-8	2	4.9	4.0	8	3	<2.7	4.4	-1	5	13.7	-16.1
11	0	5.8	4.0	-7	2	9.7	-10.7	9	3	8.7	-8.8	0	5	27.9	32.0
12	0	3.0	3.2	-6	2	3.5	2.8	10	3	<3.0	3.6	1	5	22.0	26.0
13	0	<2.1	0.2	-5	2	81.6	-75.0	-13	4	<2.6	-1.7	2	5	12.7	-13.0
14	0	5.4	4.4	-4	2	8.5	7.1	-12	4	4.6	4.6	3	5	12.1	-14.6
15	0	<0.8	3.2	-3	2	46.0	47.3	-11	4	<3.0	-1.2	4	5	6.6	-11.2
-15	1	3.3	2.0	-2	2	93.1	83.9	-10	4	14.4	-13.7	5	5	4.6	5.6
-14	1	4.0	-4.0	-1	2	39.3	-38.4	-9	4	9.5	10.4	6	5	7.8	10.4
-13	1	8.2	-4.5	0	2	10.3	11.2	-8	4	20.1	-20.0	7	5	7.1	-8.1
-12	1	<2.8	3.3	1	2	6.5	11.8	-7	4	9.7	13.4	8	5	<3.0	1.0
-11	1	<3.0	1.4	2	2	1.9	0.8	-6	4	<1.5	0.4	-14	6	<2.1	-0.3
-10	1	<2.9	-1.5	3	2	2.0	1.9	-5	4	25.8	24.3	-13	6	4.4	4.7
-9	1	<2.6	0.8	4	2	<1.3	-1.9	-4	4	12.1	-10.8	-12	6	8.2	-6.0
-8	1	<2.4	1.8	5	2	26.6	-21.4	-3	4	5.0	9.0	-11	6	4.7	3.8
-7	1	<1.8	-0.2	6	2	10.4	12.7	-2	4	4.2	7.7	-10	6	8.5	7.9
-6	1	5.7	5.5	7	2	35.6	-32.7	-1	4	9.3	-9.2	-9	6	7.5	-8.3
-5	1	9.0	-8.3	8	2	7.1	5.0	0	4	6.9	6.2	-8	6	2.4	3.9
-4	1	15.2	13.7	9	2	8.5	9.0	1	4	11.2	-15.2	-7	6	7.6	-7.4
-3	1	74.4	70.3	10	2	14.9	17.2	2	4	19.2	-21.8	-6	6	<1.7	0.7
-2	1	95.2	-81.9	11	2	3.9	-4.3	3	4	1.9	2.9	-5	6	22.2	22.7
-1	1	35.7	-51.2	12	2	<2.4	-2.4	4	4	3.4	-4.8	-4	6	29.6	-30.2
0	1	4.4	5.3	-13	3	<2.5	-2.3	5	4	4.6	7.0	-3	6	11.5	10.9
1	1	22.5	20.2	-12	3	5.0	-3.3	6	4	<2.3	3.3	-2	6	23.6	-20.3
2	1	25.7	26.8	-11	3	<3.0	3.2	7	4	9.8	11.3	-1	6	37.8	39.6
3	1	5.6	-5.9	-10	3	5.6	5.6	8	4	<2.9	1.8	0	6	18.6	-21.3
4	1	<2.4	-1.3	-9	3	<2.5	-3.6	9	4	<3.0	-1.8	1	6	8.5	8.0
5	1	5.8	6.3	-8	3	20.8	18.4	10	4	<2.8	-1.2	2	6	11.7	14.9
6	1	5.7	-7.9	-7	3	22.6	-22.5	11	4	<2.4	-2.5	3	6	5.7	-6.9
7	1	6.8	6.4	-6	3	3.9	-3.2	12	4	<1.8	1.0	4	6	3.4	-3.0
8	1	6.9	-6.9	-5	3	8.5	9.5	13	4	2.8	-3.3	5	6	6.4	5.9
9	1	10.9	13.8	-4	3	9.1	-8.7	-13	5	<2.7	-2.2	6	6	3.8	-2.6
10	1	10.5	-9.0	-3	3	26.9	-23.9	-12	5	7.4	8.6	7	6	8.0	7.0
11	1	9.6	-7.7	-2	3	24.1	21.8	-11	5	3.8	5.0	8	6	8.7	-10.7

h	l	F_o	F_c	h	l	F_o	F_c	h	l	F_o	F_c	h	l	F_o	F_c
9	6	<2.8	0.5	4	8	5.2	-9.7	-11	11	<2.9	0.2	-8	13	3.7	3.0
-13	7	2.7	2.6	5	8	<2.9	-5.5	-10	11	17.6	13.4	-7	13	2.9	-4.5
-12	7	8.2	-7.6	6	8	12.7	13.1	-9	11	<3.0	2.1	-6	13	<3.0	-0.6
-11	7	4.1	4.0	7	8	2.8	-1.7	-8	11	11.4	-9.7	-5	13	3.6	3.6
-10	7	<2.9	0.7	8	8	<2.7	2.9	-7	11	7.8	6.2	-4	13	6.4	-5.6
-9	7	8.5	-7.9	-9	9	<2.8	-1.6	-6	11	<2.6	-1.9	-3	13	<3.0	0.7
-8	7	<2.4	1.9	-8	9	5.1	8.7	-5	11	3.3	-4.6	-2	13	8.6	-11.3
-7	7	5.6	5.8	-7	9	8.8	-7.1	-4	11	14.2	12.2	-1	13	9.7	10.9
-6	7	2.8	-3.4	-6	9	2.4	2.6	-3	11	12.6	-12.1	0	13	7.7	10.3
-5	7	<1.7	2.8	-5	9	9.2	8.6	-2	11	3.7	7.8	1	13	<3.0	-3.3
-4	7	19.9	-23.8	-4	9	<2.0	3.1	-1	11	<2.6	-4.8	-14	14	4.3	-2.6
-3	7	20.8	23.4	-3	9	5.5	-5.7	0	11	11.0	-11.4	-13	14	<1.6	0.1
-2	7	9.8	10.4	-2	9	2.8	3.2	1	11	<2.8	-0.4	-12	14	<2.1	1.6
-1	7	16.6	19.9	-1	9	5.2	-6.9	2	11	19.7	18.0	-11	14	<2.4	-1.9
0	7	37.0	-32.0	0	9	<2.1	-1.2	3	11	<3.0	1.1	-10	14	<2.7	-0.5
1	7	2.6	-5.9	1	9	<2.3	1.6	4	11	5.0	-4.7	-9	14	<2.9	-4.2
2	7	3.6	4.8	2	9	4.2	-5.5	5	11	<2.8	-1.8	-8	14	6.5	-5.5
3	7	9.7	-9.7	3	9	4.7	5.3	-13	12	8.5	6.8	-7	14	5.1	4.6
4	7	7.5	7.5	4	9	<2.9	-0.5	-12	12	2.6	-2.3	-6	14	<3.0	-0.8
5	7	4.7	5.2	-13	10	<2.5	-3.8	-11	12	14.5	9.2	-5	14	<3.0	2.7
6	7	5.7	-6.3	-12	10	2.5	0.1	-10	12	<3.0	-3.6	-4	14	19.6	21.2
7	7	4.1	5.8	-11	10	7.8	-6.1	-9	12	14.3	-9.1	-3	14	3.7	-4.6
8	7	4.0	-6.6	-10	10	4.1	-0.1	-8	12	4.6	4.2	-2	14	8.7	-9.7
9	7	2.6	2.2	-9	10	16.7	19.8	-7	12	<2.9	-1.7	-1	14	<3.0	-2.3
10	7	3.4	3.4	-8	10	11.5	12.5	-6	12	<2.8	-6.5	0	14	2.8	0.3
-13	8	3.4	-3.5	-7	10	3.9	-3.9	-5	12	3.5	3.0	1	14	<2.8	0.0
-12	8	3.7	3.5	-6	10	14.3	-18.2	-4	12	14.6	-19.3	2	14	3.4	-5.1
-11	8	<3.0	-2.7	-5	10	3.7	3.6	-3	12	6.6	10.6	3	14	<2.3	1.6
-10	8	<2.9	-0.9	-4	10	1.9	1.7	-2	12	<2.8	4.8	4	14	<1.8	-3.2
-9	8	<2.7	-4.2	-3	10	11.3	-11.8	-1	12	13.5	19.3	5	14	2.8	4.0
-8	8	4.1	-6.3	-2	10	6.6	7.6	0	12	4.6	-4.7	-14	15	2.1	-1.9
-7	8	4.2	-5.6	-1	10	7.4	-9.9	1	12	4.0	4.6	-13	15	2.4	1.4
-6	8	30.1	31.2	0	10	4.3	1.6	2	12	<3.0	-2.1	-8	15	7.4	-5.8
-5	8	8.9	-8.6	1	10	6.4	-7.6	3	12	7.0	-9.3	4	15	4.7	-4.0
-4	8	16.9	17.8	2	10	4.9	6.8	4	12	<2.8	-2.1	-13	16	3.7	-3.6
-3	8	5.9	-9.5	3	10	5.5	7.8	-15	13	1.4	-2.0	-10	17	3.0	-3.1
-2	8	5.5	4.8	4	10	11.9	16.6	-14	13	2.0	-2.7	-8	17	3.0	3.5
-1	8	20.8	-24.2	5	10	7.4	-6.7	-13	13	8.4	6.0	-3	18	4.2	4.9
0	8	9.7	12.5	6	10	6.3	-10.2	-12	13	<2.3	1.3	-3	19	3.3	3.4
1	8	<2.0	2.8	7	10	<2.4	0.3	-11	13	<2.6	-0.1				
2	8	8.8	-9.8	-13	11	5.7	-5.4	-10	13	<2.9	-3.0				
3	8	3.7	7.6	-12	11	5.5	-4.9	-9	13	<3.0	1.8				

structure factors are listed in Table 1, and the final electron-density projection on (010) is shown in Fig. 2.

y parameters and final refinement

As good resolution of the individual atoms could not be expected in the [100] and [001] projections, the *y* coordinates were deduced from the *h*1*l* data. Approximate *y* parameters referred to the molecular origin were derived from a molecular model, and the *y* coordinate of the molecular origin was then varied until reasonable agreement was obtained between the calculated and observed structure factors for a few low-order *h*1*l* reflections. Structure factors were calculated for all the *h*1*l* reflections, using the *y*

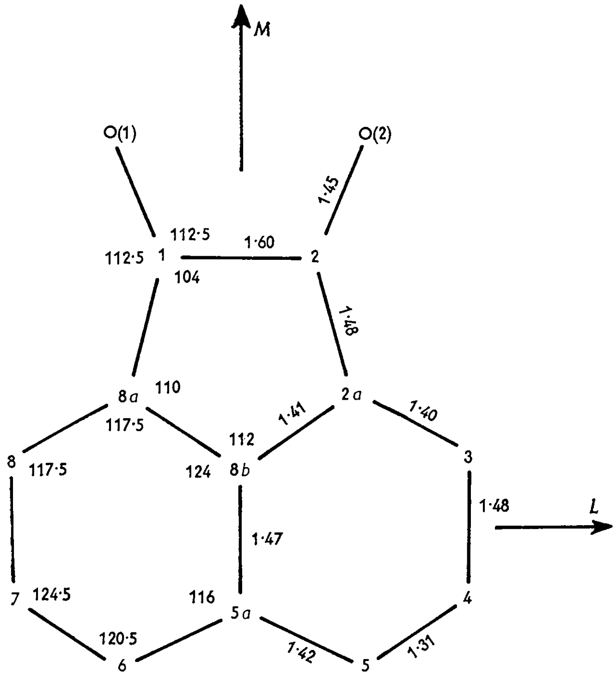


Fig. 3. Numbering and dimensions of the *cis*-1,2-acenaphthenediol molecule.

coordinates thus determined and the x, z and B parameters from the $h0l$ refinement. R was 34·2%.

For further refinement we felt it would be advantageous to use the complete three-dimensional data. However, indexing of the $h2l$ and $h3l$ layers was difficult as a result of the twinning, and in any case the proportion of observable reflections on these upper levels became increasingly smaller. Since the observed $h0l$ and $h1l$ reflections constituted a large part of the observable three-dimensional data, we completed refinement of the structure by computing cosine and sine difference generalized projections, using the $h1l$ data and refining all the x, y, z and B parameters simultaneously (Rossmann & Shearer, 1958). Refinement was complete after six cycles, and R was then 17·3% for the observed $h1l$ reflections. The inclusion of the contributions from the eight hydrogen atoms previously considered led to a significant improvement in the agreement of the observed and calculated structure amplitudes, and the R index was lowered to 15·5%. Measured and calculated $h1l$ structure factors are included in Table 1.

Molecular dimensions and orientation

The final positional and temperature factors are listed in Table 2, where the atomic coordinates are expressed as fractions of the unit cell edges, and x, z and B are the mean of $h0l$ and $h1l$ values. The equation of the mean plane for the carbon atoms is

$$0{\cdot}7039X'+0{\cdot}7101Y+0{\cdot}0152Z'-2{\cdot}5902=0$$

where X', Y and Z' are coordinates expressed in Å and referred to orthogonal axes a, b and c'. The deviations of the atoms from this plane are listed in the last column of Table 2.

Table 2. *Final parameters**

Atom	x	y	z	B (Å^2)	Δ (Å)
C(1)	0·3922	0·104	0·3255	4·1	0·024
C(2)	0·3366	0·110	0·2164	4·6	−0·029
C(2*a*)	0·2484	0·320	0·1931	4·5	−0·008
C(3)	0·1718	0·437	0·1113	5·3	0·025
C(4)	0·0948	0·648	0·1173	4·8	0·036
C(5)	0·0887	0·737	0·1947	4·4	−0·014
C(5*a*)	0·1619	0·640	0·2789	4·1	−0·018
C(6)	0·1687	0·720	0·3705	4·4	−0·038
C(7)	0·2490	0·619	0·4422	5·4	0·057
C(8)	0·3291	0·391	0·4393	5·5	0·002
C(8*a*)	0·3228	0·309	0·3522	4·1	0·003
C(8*b*)	0·2396	0·423	0·2733	4·1	−0·044
O(1)	0·5109	0·167	0·3596	4·6	1·175
O(2)	0·4182	0·170	0·1742	4·4	1·075
H(1)	0·386	−0·100	0·351	6·0	
H(2)	0·305	−0·083	0·191	6·0	
H(3)	0·179	0·329	0·053	6·0	
H(4)	0·040	0·750	0·055	6·0	
H(5)	0·027	0·889	0·202	6·0	
H(6)	0·110	0·874	0·377	6·0	
H(7)	0·254	0·721	0·505	6·0	
H(8)	0·399	0·289	0·493	6·0	

* The numbering of the carbon atoms (Fig. 3) follows the rules recommended by the I.U.P.A.C. (1957). Numbering of the oxygen and hydrogen atoms indicates the carbon atoms to which they are bonded.

Table 3. *Bond lengths, valency angles and some intramolecular approach distances*

Atoms	Bond lengths	Atoms	Bond lengths
1–2	1·596 Å	5–5*a*	1·389 Å
2–2*a*	1·461	5*a*–6	1·464
2*a*–8*b*	1·400	6–7	1·306
8*b*–8*a*	1·413	7–8	1·519
8*a*–1	1·493	8–8*a*	1·401
2*a*–3	1·414	8*b*–5*a*	1·471
3–4	1·446	1–O(1)	1·458
4–5	1·322	2–O(2)	1·440

Atoms	Valency angles	Atoms	Valency angles
1–2–2*a*	106·0°	8*a*–8*b*–5*a*	122·1°
2–2*a*–8*b*	109·6	8*b*–5*a*–6	117·0
2*a*–8*b*–8*a*	111·5	5*a*–6–7	119·4
8*b*–8*a*–1	110·1	6–7–8	124·6
8*a*–1–2	102·6	7–8–8*a*	116·2
2*a*–3–4	118·8	8–8*a*–8*b*	120·0
3–4–5	124·5	1–2–O(2)	112·7
4–5–5*a*	121·3	2*a*–2–O(2)	111·2
5–5*a*–8*b*	114·5	2–1–O(1)	112·5
5*a*–8*b*–2*a*	126·2	8*a*–1–O(1)	114·0
8*b*–2*a*–3	114·7		

Selected intramolecular approach distances:

Atoms	Distances
O(1)–O(2)	2·71 Å
1–O(2)	2·54
2–O(1)	2·53
8*a*–O(1)	2·46
2*a*–O(2)	2·41

The dimensions of the molecule, calculated from the atomic coordinates of Table 2, are given in Table 3. Since differences between chemically equivalent bonds are of doubtful significance, mean values for the bond distances and valency angles were obtained by assuming symmetry *m* for the molecule (Fig. 3).

Table 4. *Molecular orientation in the crystal*

$\chi_L = 90{\cdot}9°$	$\chi_M = 44{\cdot}5°$	$\chi_N = 45{\cdot}3°$
$\psi_L = 87{\cdot}8°$	$\psi_M = 134{\cdot}5°$	$\psi_N = 44{\cdot}8°$
$\omega_L = 177{\cdot}6°$	$\omega_M = 91{\cdot}8°$	$\omega_N = 89{\cdot}1°$

The orientation of the molecule in the unit cell is given in Table 4 in terms of the angles χ_L, ψ_L, ω_L; χ_M, ψ_M, ω_M; χ_N, ψ_N, ω_N which the molecular axes L, M (Fig. 3) and the plane normal N make with the orthogonal system a, b and c'. The axis L was taken through the centres of the C(3)–C(4) and C(7)–C(8) bonds, and axis M through atom C(5*a*) and the mid-point of the C(1)–C(2) bond. L, M and N are thus not exactly perpendicular to each other, the angles being $\angle LM = 90{\cdot}4°$, $\angle MN = 89{\cdot}8°$, and $\angle LN = 90{\cdot}0°$.

The standard deviations of the mean x and z coordinates (Cruickshank, 1949) are $\sigma(x) = \sigma(z) = 0{\cdot}01_0$ Å for carbon, 0·009 Å for oxygen. $\sigma(y)$ is certainly somewhat greater, but since most of the bonds lie close to the (010) plane and are therefore not very dependent on y, the standard deviations of the measured bond distances are about $0{\cdot}01_4$ Å, and of the valency angles about 0·9°.

Discussion

The packing of the molecules is illustrated in Fig. 4 with the main short approach distances indicated. It is seen that molecules related by a screw axis are linked together by intermolecular hydrogen bonds to form infinite zigzag chains extending in the direction of *b*. The O–H · · · O distances of 2·72 and 2·70 Å are similar to those found in alcohols (Pimentel & McClelland, 1960). A perspective diagram, Fig. 5, illustrates the mode of hydrogen bonding in the crystal.

It is evident from the zigzag chain molecular packing that there is no intramolecular hydrogen bonding between the *vic*-OH groups. The interatomic O(1) · · · O(2) distance is short (2·71 Å) only as a consequence of the molecular geometry. A plausible explanation of the two infrared absorption peaks may be the different angles and environments of the intermolecular hydrogen bonds (Fig. 5).

The carbon skeleton of the *cis*-1,2-acenaphthenediol molecule is probably planar. Some of the apparently significant deviations from planarity (maximum value 0·057 Å for carbon atom C7) are due to the fact that the *y* coordinates have been determined less precisely. Since the *b* axis is short, this should not significantly affect the measured bond lengths and valency angles.

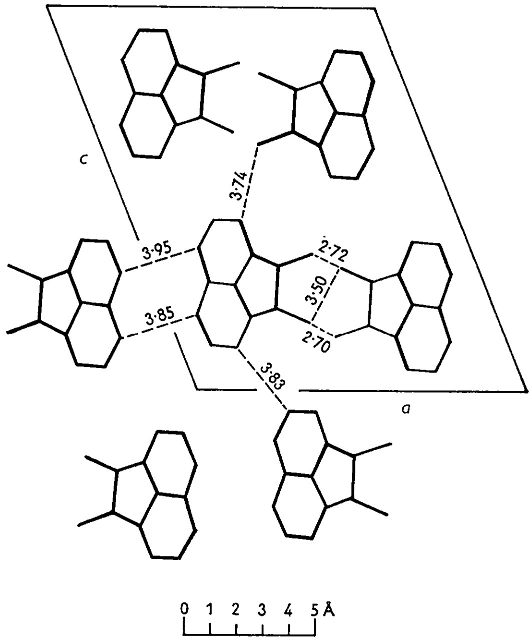


Fig. 4. Projection of the structure along [010], showing the hydrogen bonds and the shorter intermolecular contacts.

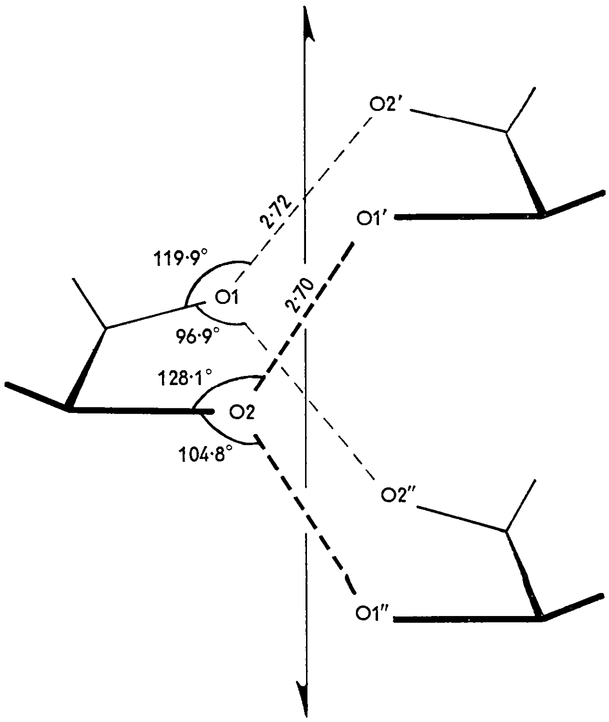


Fig. 5. Perspective diagram showing the hydrogen bonding.

Comparison of the molecular dimensions of *cis*-1,2-acenaphthenediol with the data for other acenaphthene derivatives shows that the valency angles are very similar. The aliphatic C(1)–C(2) bond, however, is significantly lengthened (bond length $1{\cdot}59_6 \pm 0{\cdot}01_4$ Å, projection on (010) 1·59$_4$ Å) probably due to the combined effect of ring strain and steric repulsion of the non-bonded oxygen atoms. It is worthy of note that in pyracene a value of 1·59 ± 0·03 Å was found for this distance, although the authors did not consider it to be significantly stretched. The short *peri*-bond length of 1·48 ± 0·01$_0$ Å is unexpected, and its significance cannot be judged until further data for *cis*-1,2-substituted acenaphthenes are available. It may be pointed out, however, that a similar bond-shortening effect has been observed in *cis*-1,2-dichlorobenzocyclobutene, which has an average *peri*-bond distance of 1·45 ± 0·01 Å (Hardgrove, 1959; Hardgrove & Templeton, 1961). The C–O bond has a length of 1·45 ± 0·01$_0$ Å which is typical of aliphatic alcohols (*Tables of Interatomic Distances and Configurations in Ions and Molecules*, 1958). In the naphthalene ring the C(3)–C(4) and C(4)–C(5) bonds are respectively the longest and the shortest, in agreement with the bond-length variations observed in all acenaphthene derivatives so far examined.

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The Crystal Structure of $LiCuCl_3.2H_2O$*

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$LiCuCl_3.2H_2O$ forms garnet-red, monoclinic crystals, $a = 6{\cdot}078$, $b = 11{\cdot}145$, $c = 9{\cdot}145$ Å (all ± 0·003), $\beta = 108^\circ\ 50'$, space group $P2_1/c$, $Z = 4$. The structure contains planar $[Cu_2Cl_6]^{2-}$ ions joined by longer Cu · · · Cl links to form chains. Half of the water molecules are coordinated to copper.

A final refinement using the Levy–Busing anisotropic temperature factor treatment and least-squares program achieved a discrepancy index, R, of 10·5% for our visually determined intensities. Standard deviations as determined from least squares are about 0·007 Å for oxygen parameters, less for others, while important interatomic distances have been determined with standard deviations of ~0·0025 Å.

The structure has very interesting magnetic properties, reported elsewhere (Vossos, Jennings & Rundle, 1960). Because of this, a neutron diffraction study is under way at Brookhaven by S. C. Abrahams.

An interesting correlation between structure and color of copper chlorides is noted.

Introduction

The garnet-red crystals of $LiCuCl_3.2H_2O$ were first reported by Chassevant (1891), but the composition was settled by Meyerhoffer (1892). Attempts to

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* Contribution No. 934. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission. Taken in part from the thesis presented to Iowa State University (1958) by Peter H. Vossos in partial fulfillment of the requirements for the Master of Science degree.