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Structure of 2,6-Bis(hydroxymethyl)-4-isopropylphenol

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Abstract. $C_{11}H_{16}O_3$, $M_r = 196{\cdot}2$, orthorhombic, *Pcab*, $a = 12{\cdot}897\,(2)$, $b = 18{\cdot}978\,(3)$, $c = 8{\cdot}497\,(3)$ Å, $V = 2079{\cdot}7\,(9)$ Å^3, $Z = 8$, $D_x = 1{\cdot}253$ g cm^{-3}, $\lambda(\text{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 6{\cdot}52$ cm^{-1}, $F(000) = 848$, $T = 293$ K. Final $R = 0{\cdot}047$ for 1207 observed independent diffractometer-measured intensity data. The two hydroxymethyl groups have different orientations about the ring plane: one being nearly coplanar [$-0{\cdot}133\,(3)$ Å] and the other strongly tilted [$-1{\cdot}253\,(3)$ Å out of plane]. The dihedral angle between the ring plane and the plane of the isopropyl group is $98{\cdot}6\,(5)$°. Molecules are held together by hydrogen bonds forming sheets inter-related by van der Waals contacts.

Introduction. The chemistry of phenolic resins is complex owing to the great number of products obtained during polycondensation reactions. Relations between composition and properties of these materials can be determined by the study of their precursors.

Among the possible series with different substituted phenols, only a few studies have been made with 4-isopropylphenol derivatives, *i.e.* two patents (Azrak, Ancker & Bertolucci, 1975; Kaneko, 1976) dealing with them because of their interesting thermosetting properties.

The title compound is the first member of one of the series and the determination of its structure was undertaken to discover the molecular conformation about the hydroxymethyl groups and the hydrogen bonds between molecules in the crystal.

Experimental. X-ray diffraction study on a single crystal at room temperature. Needle approximately $0{\cdot}3 \times 0{\cdot}3 \times 1$ mm used for data collection with automatic Nonius CAD-4 four-circle diffractometer, graphite monochromator, Cu $K\alpha$ radiation; cell dimensions obtained by least squares from setting angles of 25 reflections. ω–2θ scan technique used to collect intensities of 1751 independent reflections with $2\theta < 73°$ (range of *hkl*: $h\,0\rightarrow16$, $k\,0\rightarrow23$, $l\,0\rightarrow10$), 1207 of which considered as observed [$I > 3\sigma(I)$]. One standard reflection measured every 60 min to control the intensity and the same was measured at 100-reflection intervals to control the orientation of the crystal. Lorentz and polarization corrections applied but no absorption correction made [$1{\cdot}39 < A(\theta) < 1{\cdot}40$]. Systematic absences in orthorhombic system indicated space group *Pcab*. Structure determined by direct methods and refined on *F* by *SHELX*76 (Sheldrick, 1976). Number of independent parameters: 191. An *E* map showed clearly all non-H atoms of the molecule. H positions determined by a difference Fourier synthesis and introduced into the refinement. Each H atom assigned an isotropic temperature factor corresponding to that of the heavy atom to which it is bonded. They were fixed during first stages of anisotropic refinement then refined isotropically. $(\Delta/\sigma)_{\max} = 1{\cdot}7$ for U_{33} of O(1), $(\Delta/\sigma)_{\text{average}} = 0{\cdot}06$. Residual electron density in final difference Fourier synthesis $0{\cdot}18$ e Å^{-3}. Unit weights used, $wR = 0{\cdot}047$, $S = 1{\cdot}04$, final $R = 0{\cdot}047$. Atomic scattering factors from *SHELX*76.

Discussion. Fig. 1 shows the molecule and the numbering of the atoms. The final atomic coordinates with their e.s.d.'s and the isotropic thermal parameters are given in Table 1. The bond distances and angles resulting from refinement are listed in Table 2.*

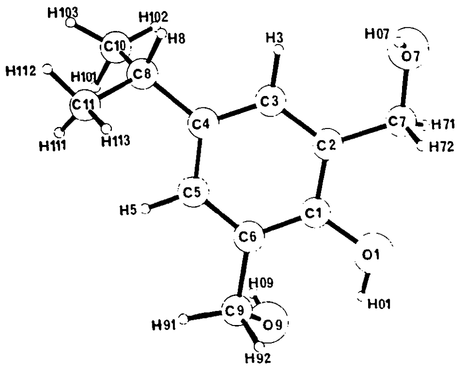

Fig. 1. View along the [100] axis and numbering scheme.

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* Lists of structure factors, anisotropic thermal parameters for non-H atoms and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42369 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional coordinates* ($\times 10^4$; *for* H $\times 10^3$) *and equivalent isotropic temperature factors for non-*H *atoms and isotropic temperature factors for* H *atoms*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}\mathbf{a}_i.\mathbf{a}_j a_i^* a_j^*.$$

	x	*y*	*z*	*U* or U_{eq}(Å^2)
C(1)	1129 (2)	4903 (2)	8209 (4)	0·032 (1)
C(2)	1430 (2)	5051 (2)	9767 (4)	0·030 (1)
C(3)	1562 (3)	4481 (2)	10782 (4)	0·034 (1)
C(4)	1397 (3)	3792 (2)	10322 (4)	0·036 (1)
C(5)	1071 (3)	3672 (2)	8771 (4)	0·037 (1)
C(6)	934 (3)	4224 (2)	7708 (4)	0·035 (1)
C(7)	1586 (3)	5802 (2)	10235 (4)	0·039 (1)
C(8)	1543 (3)	3187 (2)	11473 (4)	0·045 (1)
C(9)	559 (3)	4081 (2)	6058 (4)	0·044 (1)
C(10)	499 (5)	2925 (3)	12090 (7)	0·069 (2)
C(11)	2199 (6)	2595 (3)	10801 (7)	0·077 (2)
O(1)	1076 (2)	5486 (1)	7240 (3)	0·038 (1)
O(7)	1839 (2)	5897 (1)	11864 (3)	0·039 (1)
O(9)	−431 (2)	4390 (2)	5768 (3)	0·052 (1)
H(3)	183 (3)	458 (2)	1193 (5)	0·06 (1)
H(5)	94 (3)	318 (2)	842 (4)	0·05 (1)
H(8)	193 (3)	339 (2)	1237 (5)	0·05 (1)
H(71)	92 (3)	604 (2)	1012 (5)	0·04 (1)
H(72)	218 (3)	601 (2)	967 (5)	0·06 (1)
H(91)	53 (3)	354 (2)	589 (5)	0·05 (1)
H(92)	106 (3)	429 (2)	523 (5)	0·06 (1)
H(101)	4 (3)	270 (2)	1120 (5)	0·09 (1)
H(102)	7 (3)	333 (2)	1253 (5)	0·10 (2)
H(103)	61 (3)	247 (2)	1268 (5)	0·07 (1)
H(111)	175 (4)	233 (2)	1020 (5)	0·08 (2)
H(112)	229 (3)	222 (2)	1165 (5)	0·10 (1)
H(113)	293 (4)	280 (2)	1025 (5)	0·10 (1)
H(O1)	75 (4)	536 (2)	656 (5)	0·13 (1)
H(O7)	253 (4)	580 (2)	1202 (5)	0·05 (1)
H(O9)	−84 (3)	425 (2)	643 (5)	0·08 (1)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)–C(2)	1·408 (4)	C(6)–C(9)	1·508 (4)
C(2)–C(3)	1·394 (4)	C(4)–C(8)	1·522 (4)
C(3)–C(4)	1·381 (4)	C(8)–C(10)	1·527 (6)
C(4)–C(5)	1·402 (4)	C(8)–C(11)	1·517 (6)
C(5)–C(6)	1·395 (4)	C(1)–O(1)	1·380 (3)
C(6)–C(1)	1·380 (4)	C(7)–O(7)	1·433 (3)
C(2)–C(7)	1·494 (4)	C(9)–O(9)	1·426 (4)

O(1)–C(1)–C(2)	114·5 (3)	C(4)–C(5)–C(6)	121·6 (3)
O(1)–C(1)–C(6)	123·7 (3)	C(1)–C(6)–C(5)	118·6 (3)
C(6)–C(1)–C(2)	121·8 (3)	C(5)–C(6)–C(9)	120·5 (3)
C(1)–C(2)–C(3)	117·4 (3)	C(1)–C(6)–C(9)	120·9 (3)
C(1)–C(2)–C(7)	118·5 (2)	C(2)–C(7)–O(7)	114·0 (2)
C(3)–C(2)–C(7)	124·0 (2)	C(4)–C(8)–C(10)	111·0 (3)
C(2)–C(3)–C(4)	122·7 (3)	C(4)–C(8)–C(11)	112·7 (3)
C(3)–C(4)–C(5)	117·8 (3)	C(10)–C(8)–C(11)	112·3 (4)
C(3)–C(4)–C(8)	120·9 (3)	C(6)–C(9)–O(9)	112·0 (3)
C(5)–C(4)–C(8)	121·2 (3)		

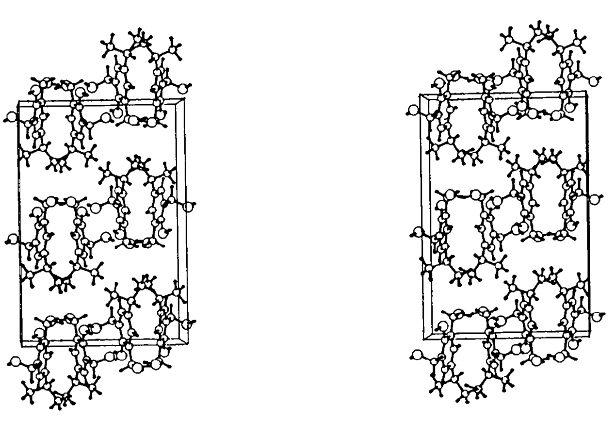

Fig. 2. Stereoscopic view of the structure seen along [001] drawn by *PLUTO* (Motherwell, 1978).

Table 3. *Intermolecular hydrogen bonds*

	D···*A*	*D*–H	H···*A*	*D*–H···*A*
O(1)–H(O1)···O(9^{i})	2·698 (4) Å	0·75 (4) Å	2·07 (4) Å	140 (4)°
O(7)–H(O7)···O(1^{ii})	2·818 (4)	0·92 (4)	1·90 (4)	173 (4)
O(9)–H(O9)···O(7^{iii})	2·765 (4)	0·82 (4)	1·96 (4)	169 (4)

Symmetry code: (i) $\bar{x}, 1-y, 1-z$; (ii) $\frac{1}{2}-x, y, z+\frac{1}{2}$; (iii) $\bar{x}, 1-y, 2-z$.

The aromatic C—C bond distances are normal and vary from 1·380 (4) to 1·408 (4) Å with a mean value of 1·393 (4) Å. The C—H bond distances vary from 0·93 (4) to 1·12 (4) Å with a mean value of 1·02 (4) Å.

In the benzene ring, the internal angles at the substituted C atoms deviate from the mean value (120°) as expected in substituted benzene derivatives; endocyclic-angle values are more than 120° at the OH group, less than 120° at the hydroxymethyl and isopropyl groups.

Indeed the regular hexagonal geometry of the benzene ring is slightly modified by substituents; this could be connected with the σ-electron-withdrawing or -releasing character of the substituents that respectively increase and decrease the angles (Domenicano, Vaciago & Coulson, 1975).

The C—O bond distances have values of 1·380 (3) Å for the phenolic substituent and average 1·430 (3) Å in the hydroxymethyl groups. These values are in good agreement with those found in similar products (Perrin, Lamartine, Vicens, Bernard, Brigandat, Perrin, Thozet, Hanton & Fugier, 1985).

As in other phenols, the angles C(2)—C(1)—O(1) and C(6)—C(1)—O(1) have different values and are larger than 120° on the side of the phenolic H atom.

The equation of the benzene-ring plane and the deviations of atoms from it have been deposited (program used: *NRC*22, Ahmed, Hall, Pippy & Huber, 1966).* The H(O1) atom of the phenolic group is near the ring plane [−0·14 (4) Å].

The O(7) atom is near this plane too: the distance from it is −0·133 (3) Å and the torsional angle C(3)—C(2)—C(7)—O(7) is 2·8 (5)°. Otherwise the O(9) atom is out of the ring plane: the distance to the plane is −1·253 (3) Å and the torsional angle C(5)—C(6)—C(9)—O(9) is 115·5 (4)°. The possibly significant distortion ($\chi^2 = 46{\cdot}04$) from planarity of the benzene ring could be an effect of the dissymmetry of the substituents.

The dihedral angle between the ring plane and the plane of the isopropyl group is 98·6 (5)° with C(10) and C(11) on different sides with respect to the ring plane. The packing of the molecules in the cell is shown in Fig. 2. Hydrogen bonds are observed between symmetrical molecules: they are given in Table 3 with the symmetry code. Each O atom is involved in two hydrogen bonds, one as a donor and the second as an acceptor. These hydrogen-bonded molecules form

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* See previous footnote.

sheets almost parallel to the [410] direction connected by van der Waals interactions. The intramolecular distance O(1)···O(9) has a value of 3·109 (4) Å, a little too long for a hydrogen bond.

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Structure of 3*H*-1,2-Dithiole-3-thione*

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Abstract. $C_3H_2S_3$, $M_r = 134{\cdot}241$, tetragonal, $P4_2/mbc$, $a = b = 10{\cdot}654$ (3), $c = 9{\cdot}304$ (3) Å, $V = 1056{\cdot}1$ Å^3, $Z = 8$, $D_m = 1{\cdot}66$ (2), $D_x = 1{\cdot}688$ g cm^{-3}, $\lambda(\text{Mo } K\alpha_1) = 0{\cdot}7093$ Å, $\mu = 11{\cdot}85$ cm^{-1}, $F(000) = 544$, $T = 296$ (1) K. Final $R(F) = 0{\cdot}049$ for 571 unique nonzero reflections. The two H atoms were located and their positional parameters refined. Molecules are nearly planar, to within 0·004 (2) Å (H atoms excluded), and the plane normal of the five-membered ring makes an angle of 91·2 (1)° with the z axis. The disordered-crystal model successfully utilized in the refinement assumes a random distribution of each molecule in the two orientations related to each other by a crystallographic mirror plane.

Introduction. To understand the relationship between chemotherapeutic properties and structure, Bueding, Dolan & Leroy (1982) have studied the antischistosomidal effects on mice of several drugs, including the drug oltipraz, the structure of which was reported from this laboratory (Wei, 1983), and its analogs. Because of their structural similarities a detailed comparison of these compounds affords considerable stereochemical insight concerning the chemotherapeutic value, and one of our systematic investigations on 5-(*p*-methoxyphenyl)-3*H*-1,2-dithiole-3-thione has been reported (Wang, Lin & Wei, 1985).

In most cases drugs of this class contain 3*H*-1,2-dithiole-3-thione as a building unit, and it is considered by Bueding *et al.* (1982) as a necessary unit to make these drugs function. Investigation of the structure of this basic fragment is clearly desirable in view of its important role. A similar structure, that of 4-methyl-1,2-dithia-4-cyclopentene-3-thione, has previously been reported in detail by Jeffrey & Shiono (1959).

Experimental. Orange crystals having leek-like smell grown from an ethyl acetate solution. Crystal density determined by flotation in mixtures of bromobenzene and 2-bromobutyric acid. A crystal with approximate dimensions 0·66 × 0·24 × 0·22 mm mounted on a Picker four-circle diffractometer with **c** approximately parallel to the φ axis of the diffractometer; lattice parameters refined by least-squares method from angle measurements of 10 strong reflections in 2θ range 41–50° (Busing, Ellison, Levy, King & Roseberry, 1968); systematic absences $0kl$, $k = 2n + 1$ (or $h0l$, $h = 2n + 1$) and hhl, $l = 2n + 1$, consistent with $P4_2bc$ or $P4_2/mbc$. Intensity data collected by θ–2θ step scans in 2θ range 1–55° ($0 \le h \le 13$, $0 \le k \le 9$, $0 \le l \le 12$; $h \ge k$). All 646 unique reflections including 571 nonzero and 75 zero intensities used for final least-squares refinement. Absorption corrections calculated analytically by the method of Busing & Levy (1957); transmission range 0·765–0·788. No extinction corrections applied. Maximum mosaic spread of crystal used estimated to be 0·8°.

Interpretation of a Patterson map inconclusive. Structure solved instead with *MULTAN* (Germain, Main & Woolfson, 1971), which gave positions of all non-H atoms except C(5). Centrosymmetric space

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