Crystal and Molecular Structure of an OH ··· π Hydrogen-Bonded System: 2,2-Bis-(2-hydroxy-5-methyl-3-t-butylphenyl)propane

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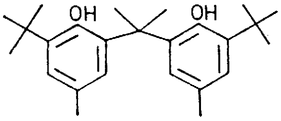
The crystal structure of the title compound (I) has been determined by three-dimensional X-ray analysis. Crystals are orthorhombic, a = 14.089, b = 18.190, c = 8.896 Å, Z = 4, space group $P2_12_12_1$. The structure was solved by direct methods employing 1 646 significant diffractometer data, and refined by least-squares methods to a final R of 0.038. The structure possesses two independent intramolecular OH ··· π hydrogen bonds, mean 2.09 Å, for the perpendicular distance between the hydroxy-hydrogen atom and its corresponding π-electron-dono rring.

THE existence of hydrogen bonds between hydroxy-groups and the π-electrons of aromatic systems has been firmly established by spectroscopic methods.[1] However, little detailed structural information [2,3] is yet available about this type of interaction. We have therefore undertaken an X-ray crystallographic examination of the dinuclear bis-phenol (I), for which a unique conformation involving two OH ··· π intramolecular hydrogen bonds had been assigned mainly on the basis of i.r. studies.[4]



(I)

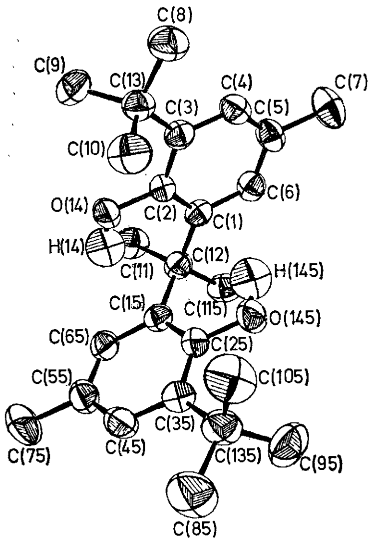
EXPERIMENTAL

Crystal Data.—$C_{25}H_{36}O_2$, $M = 368.6$. Orthorhombic, $a = 14.089$, $b = 18.190$, $c = 8.896$ Å, $Z = 4$, $U = 2\ 280.1$ Å^3, $D_c = 1.07$ g cm^{-3}, $F(000) = 808$. Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 0.66 cm^{-1}. The crystal used was a transparent parallelipiped of dimensions *ca.* 0.90 × 0.52 × 0.50 mm. The compound was recrystallised from ethanol (m.p. 167—168 °C).

Crystallographic Measurements.—Least-squares best cell dimensions were obtained by a treatment of the θ,χ,ϕ, setting angles of twenty-two reflections measured on a Hilger and Watts automatic diffractometer. Intensities were measured by the θ—2θ step scan procedure by use of Zr-filtered Mo-K_α radiation. Background counts were taken at each end of the scan range. The intensities of three standard reflections were monitored after every 40 intensity measurements, and the results used to place the reflections on a common scale; the changes in the standard intensities during data collection were small (<5%). Reflections were surveyed out to $\theta \leqslant 30°$. The intensity values were corrected for Lorentz-polarisation effects, but not for absorption, and 1 646 reflections with $I/\sigma(I) > 2.0$ were obtained.

Structure Analysis.—The structure was solved by direct phase-determining methods using 'MULTAN'[5] and 220 reflections with $|E| \geqslant |1.4|$. An E map computed with that set of phases which gave the highest figure of merit and the lowest residual revealed 25 of the 27 non-hydrogen atom positions in the molecule. A subsequent difference electron-density distribution revealed the remaining two carbon atom positions. These approximate atomic parameters were adjusted by several cycles of full-matrix least-squares calculations employing the program CRYLSQ from the 'X-Ray '72' system,[6] and for anisotropic temperature factors for all the atoms R was reduced to 9.0%.

The thirty-six hydrogen atoms in the molecule were located in a difference electron-density distribution, and were included in subsequent least-squares calculations with isotropic temperature factors. After further cycles of least-squares adjustment on all atomic and thermal parameters the final R value was 3.8% (R' 4.2%). The weighting scheme employed in the least-squares calculations was $w = 1/\sigma^2(F)$.



An ORTEP drawing showing a general view of the molecular structure of (I) in the crystal. (Of the hydrogen atoms only those attached to the oxygen atoms are shown)

Calculations were carried out on an IBM 370/158 com-

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[1] M. D. Joesten and L. J. Schaad, 'Hydrogen Bonding,' Dekker, New York, 1974; G. C. Pimentel and A. L. McClellan, 'The Hydrogen Bond,' Freeman, San Francisco, 1960; L. J. Andrews and R. M. Keefer, 'Molecular Complexes in Organic Chemistry,' Holden–Day, San Francisco, 1964.

[2] A. T. McPhail, G. A. Sim, A. J. Frey, and H. Ott, *J. Chem. Soc.* (*B*), 1966, 377.

[3] For theoretical studies of this type of interaction, see D. Bonchev and P. Cremaschi, *Gazzetta*, 1974, **104**, 1195; and refs. therein.

[4] T. Cairns and G. Eglinton, *J. Chem. Soc.*, 1965, 5906.

[5] G. Germain, P. Main, and M. M. Woolfson, 'MULTAN, A Computer Program for the Automatic Solution of Crystal Structures,' University of York, 1973.

[6] 'X-Ray '72' suit of programmes, eds. J. M. Stewart, G. J. Kruger, M. L. Ammon, C. Dickenson, and S. R. Hall, 1972, Technical Report TR192, Computer Science Center, University of Maryland.

TABLE 1

Fractional atomic co-ordinates, with standard deviations in parentheses, and isotropic parameters; hydrogen atoms are numbered according to the atoms to which they are attached

	X	*Y*	*Z*
C(1)	0.460 9(2)	0.358 1(1)	0.837 9(3)
C(2)	0.525 0(2)	0.314 7(1)	0.754 4(3)
C(3)	0.580 6(2)	0.259 6(1)	0.821 0(3)
C(4)	0.568 3(2)	0.249 0(1)	0.975 7(3)
C(5)	0.508 1(2)	0.290 8(2)	1.061 8(3)
C(6)	0.455 0(2)	0.345 2(1)	0.991 7(3)
C(7)	0.500 3(3)	0.278 8(2)	1.230 6(3)
C(8)	0.706 8(2)	0.160 3(2)	0.827 6(4)
C(9)	0.603 5(2)	0.171 2(2)	0.603 5(3)
C(10)	0.727 8(2)	0.267 7(2)	0.663 8(4)
C(11)	0.322 4(2)	0.372 9(1)	0.671 4(4)
C(12)	0.398 4(2)	0.415 8(1)	0.759 5(3)
C(13)	0.653 1(2)	0.215 3(1)	0.731 1(3)
O(14)	0.534 5(2)	0.323 9(1)	0.601 7(2)
C(15)	0.457 3(2)	0.467 6(1)	0.658 6(2)
C(25)	0.538 8(2)	0.503 3(1)	0.713 6(3)
C(35)	0.591 4(2)	0.552 9(1)	0.626 8(3)
C(45)	0.560 0(2)	0.564 5(1)	0.480 8(3)
C(55)	0.481 4(2)	0.529 7(2)	0.420 3(3)
C(65)	0.430 6(2)	0.481 8(1)	0.510 7(3)
C(75)	0.452 6(3)	0.542 4(2)	0.257 2(3)
C(105)	0.757 0(2)	0.532 8(2)	0.721 4(5)
C(85)	0.724 3(3)	0.643 6(2)	0.569 6(4)
C(95)	0.660 0(3)	0.636 4(2)	0.826 1(4)
C(115)	0.344 6(2)	0.465 3(1)	0.872 5(3)
C(135)	0.681 9(2)	0.590 3(2)	0.686 1(4)
O(145)	0.569 4(1)	0.491 9(1)	0.859 4(2)

	X	*Y*	*Z*	$U \times 10^2$
H(4)	0.611 9(19)	0.210 2(14)	1.024 2(28)	5.7(0.7)
H(6)	0.413 5(18)	0.378 9(13)	1.052 0(28)	5.1(0.7)
H(14)	0.514 2(20)	0.363 3(16)	0.576 4(34)	7.8(1.0)
H(111)	0.277 1(25)	0.404 4(19)	0.620 5(40)	9.5(1.1)
H(112)	0.289 1(21)	0.341 0(17)	0.742 8(34)	7.4(0.9)
H(113)	0.352 6(20)	0.341 7(17)	0.588 4(33)	7.6(0.9)
H(71)	0.490 5(28)	0.319 8(23)	1.281 6(50)	12.4(1.4)
H(72)	0.454 3(35)	0.240 0(24)	1.248 9(54)	15.1(1.7)
H(73)	0.558 9(30)	0.275 2(22)	1.272 5(44)	12.7(1.4)
H(81)	0.737 7(21)	0.184 7(17)	0.910 1(35)	7.7(0.9)
H(82)	0.757 1(23)	0.128 5(19)	0.771 7(39)	8.8(1.1)
H(83)	0.664 9(22)	0.124 1(16)	0.879 3(36)	7.8(1.0)
H(91)	0.644 1(20)	0.144 4(15)	0.555 6(31)	6.4(0.8)
H(92)	0.561 4(30)	0.129 9(21)	0.646 1(46)	12.2(1.3)
H(93)	0.566 3(24)	0.202 3(18)	0.537 4(36)	9.1(1.0)
H(101)	0.701 6(23)	0.298 4(17)	0.603 9(36)	8.0(0.9)
H(102)	0.758 3(24)	0.294 9(19)	0.742 7(39)	9.0(1.1)
H(103)	0.782 5(24)	0.243 3(18)	0.601 1(39)	9.2(1.0)
H(45)	0.587 8(19)	0.599 6(14)	0.422 3(29)	5.8(0.7)
H(65)	0.375 6(19)	0.453 2(14)	0.468 0(29)	5.9(0.8)
H(145)	0.547 2(23)	0.451 0(17)	0.890 7(37)	8.7(1.0)
H(1 151)	0.391 9(21)	0.497 2(15)	0.934 8(30)	7.3(0.9)
H(1 152)	0.304 8(17)	0.501 0(12)	0.815 9(28)	5.0(0.7)
H(1 153)	0.298 6(20)	0.436 2(15)	0.932 2(31)	6.2(0.8)
H(751)	0.483 5(58)	0.571 9(40)	0.204 9(86)	21.7(3.3)
H(752)	0.428 1(42)	0.586 9(30)	0.252 5(60)	14.4(1.9)
H(753)	0.379 0(43)	0.520 9(33)	0.230 3(60)	18.8(2.1)
H(1 051)	0.736 8(33)	0.499 3(25)	0.797 1(47)	12.5(1.4)
H(1 052)	0.768 5(24)	0.503 3(19)	0.641 2(39)	9.3(1.0)
H(1 053)	0.814 7(27)	0.556 2(21)	0.753 3(42)	11.6(1.2)
H(851)	0.732 4(29)	0.626 1(22)	0.481 1(45)	12.2(1.4)
H(852)	0.786 7(27)	0.665 4(21)	0.614 7(44)	10.9(1.2)
H(853)	0.672 7(32)	0.689 4(25)	0.545 6(49)	13.8(1.6)
H(951)	0.714 3(27)	0.668 0(21)	0.872 4(43)	10.8(1.2)
H(952)	0.613 6(30)	0.676 1(23)	0.796 8(46)	13.3(1.4)
H(953)	0.635 4(21)	0.607 8(17)	0.910 6(34)	7.8(0.9)

TABLE 2

Interatomic distances (Å) and valency angles (°), with standard deviations in parentheses

(*a*) Bond lengths

C(1)–C(2)	1.410(4)	C(15)–C(25)	1.408(3)
C(1)–C(6)	1.391(4)	C(15)–C(65)	1.392(4)
C(1)–C(12)	1.538(3)	C(15)–C(12)	1.542(3)
C(2)–C(3)	1.403(4)	C(25)–C(35)	1.400(4)
C(2)–O(14)	1.376(3)	C(25)–O(145)	1.383(3)
C(3)–C(4)	1.400(4)	C(35)–C(45)	1.389(4)
C(3)–C(13)	1.527(4)	C(35)–C(135)	1.538(4)
C(4)–C(5)	1.372(4)	C(45)–C(55)	1.383(4)
C(5)–C(6)	1.389(4)	C(55)–C(65)	1.386(4)
C(5)–C(7)	1.521(4)	C(55)–C(75)	1.525(4)
C(8)–C(13)	1.520(4)	C(85)–C(135)	1.540(5)
C(9)–C(13)	1.543(4)	C(95)–C(135)	1.533(5)
C(10)–C(13)	1.541(4)	C(105)–C(135)	1.521(5)
C(11)–C(12)	1.540(4)	C(115)–C(12)	1.547(4)
O(14)–H(14)	0.803(29)	O(145)–H(145)	0.855(31)

Means: C(sp^3)–H 0.974
C(sp^2)–H 0.988

(*b*) Valency angles

C(1)–C(2)–C(3)	122.3(2)	C(15)–C(25)–C(35)	122.5(2)
C(1)–C(2)–O(14)	121.0(2)	C(15)–C(25)–O(145)	120.8(2)
C(3)–C(2)–O(14)	116.7(2)	C(35)–C(25)–O(145)	116.6(2)
C(2)–C(3)–C(4)	116.4(2)	C(25)–C(35)–C(45)	116.4(2)
C(2)–C(3)–C(13)	121.9(2)	C(25)–C(35)–C(135)	122.3(2)
C(4)–C(3)–C(13)	121.7(2)	C(45)–C(35)–C(135)	121.2(2)
C(3)–C(4)–C(5)	123.3(2)	C(35)–C(45)–C(55)	123.3(3)
C(4)–C(5)–C(6)	118.5(2)	C(45)–C(55)–C(65)	118.4(2)
C(4)–C(5)–C(7)	121.1(3)	C(45)–C(55)–C(75)	120.9(3)
C(6)–C(5)–C(7)	120.4(3)	C(65)–C(55)–C(75)	120.6(3)
C(5)–C(6)–C(1)	122.0(2)	C(55)–C(65)–C(15)	121.7(2)
C(6)–C(1)–C(2)	117.5(2)	C(65)–C(15)–C(25)	117.6(2)
C(6)–C(1)–C(12)	121.8(2)	C(65)–C(15)–C(12)	121.2(2)
C(2)–C(1)–C(12)	120.7(2)	C(25)–C(15)–C(12)	121.2(2)
C(3)–C(13)–C(8)	112.6(2)	C(35)–C(135)–C(85)	111.7(3)
C(3)–C(13)–C(9)	110.5(2)	C(35)–C(135)–C(95)	110.7(2)
C(3)–C(13)–C(10)	109.5(2)	C(35)–C(135)–C(105)	110.1(2)
C(8)–C(13)–C(9)	106.9(2)	C(85)–C(135)–C(95)	106.3(3)
C(8)–C(13)–C(10)	106.6(2)	C(85)–C(135)–C(105)	107.5(3)
C(9)–C(13)–C(10)	110·5(2)	C(95)–C(135)–C(105)	110.4(3)
C(1)–C(12)–C(11)	106·4(2)	C(15)–C(12)–C(115)	106.7(2)
C(1)–C(12)–C(115)	112.5(2)	C(15)–C(12)–C(11)	112.8(2)
C(1)–C(12)–C(15)	111.9(2)	C(11)–C(12)–C(115)	106.5(2)

Means: C(sp^2)–O–H 109.6
C(sp^2)–C(sp^2)–H 118.6
C(sp^2)–C(sp^3)–H 111.9
C(sp^3)–C(sp^3)–H 111.9

TABLE 3

Some short intramolecular separations (<3.0 Å)

C(1) · · · O(145)	2.88	C(15) · · · O(14)	2.87
C(1) · · · H(145)	2.13	C(15) · · · H(14)	2.19
C(2) · · · H(145)	2.78	C(25) · · · H(14)	2.85
C(6) · · · H(145)	2.49	C(65) · · · H(14)	2.52

TABLE 4

Some torsion angles (°)

C(1)–C(2)–O(14)–H(14)	19	C(15)–C(25)–O(145)–H(145)	22
C(6)–C(1)–C(12)–C(115)	10	C(65)–C(15)–C(12)–C(11)	11
C(2)–C(1)–C(12)–C(115)	−171	C(25)–C(15)–C(12)–C(11)	−170
C(6)–C(1)–C(12)–C(11)	−106	C(65)–C(15)–C(12)–C(115)	−106
C(2)–C(1)–C(12)–C(11)	72	C(25)–C(15)–C(12)–C(115)	73
C(6)–C(1)–C(12)–C(15)	130	C(65)–C(15)–C(12)–C(1)	131
C(2)–C(1)–C(12)–C(15)	−51	C(25)–C(15)–C(12)–C(1)	−51
C(2)–C(3)–C(13)–C(10)	60	C(25)–C(35)–C(135)–C(105)	62
C(2)–C(3)–C(13)–C(9)	−62	C(25)–C(35)–C(135)–C(95)	−60
C(2)–C(3)–C(13)–C(8)	178	C(25)–C(35)–C(135)–C(85)	−178

puter at Edinburgh. Observed and calculated structure factors and anisotropic thermal parameters are listed in Supplementary Publication No. SUP 21665 (16 pp., 1 microfiche).* Scattering factors employed for O and C atoms were those listed in ref. 7, those for H in ref. 8. Atomic fractional co-ordinates and isotropic temperature

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* For details of supplementary publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

[7] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[8] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

factors are listed in Table 1, and various parameters connected with the compound's molecular geometry are listed in Tables 2—5. The Figure shows a general view of the structure of (I) in the crystal (for clarity all hydrogen atoms have been omitted except those bonded to the two oxygen atoms).

TABLE 5

Displacements (Å) of atoms from planes through various sets of atoms

Plane (*A*): C(1)—(6)
C(1) −0.009, C(2) 0.001, C(3) 0.009, C(4) −0.012, C(5) 0.003, C(6) 0.007, C(7) 0.034, C(12) −0.073, C(13) 0.084, O(14) −0.021, O(145) 2.752, H(145) 2.077

Plane (*B*): C[(1—7)5]
C(15) −0.006, C(25) 0.008, C(35) −0.002, C(45) −0.005, C(55) 0.006, C(65) −0.001, C(75) 0.057, C(12) −0.057, C(135) 0.050, O(145) 0.002, O(14) 2.752, H(14) 2.118

Plane (*C*): C(1), C(4), C(12), C(15)
C(1) −0.021, C(4) 0.008, C(12) 0.013, C(15) 0.000, C(45) −0.084, C(2) 0.895, C(25) −0.958, C(6) −0.923, C(65) 0.920

Plane (*D*): C(15), C(45), C(12), C(1)
C(15) 0.015, C(45) −0.005, C(12) −0.009, C(1) 0.000, C(4) 0.104, C(2) 0.963, C(25) −0.897, C(6) −0.910, C(65) 0.920

Angles (°) between plane normals (*A*)–(*B*) 97.7, (*C*)–(*D*) 2.7

DISCUSSION

A striking overall feature of the molecule is the non-crystallographic two-fold symmetry axis which passes through the centrally situated carbon atom C(12) (see Tables 2—5 for a comparison of relevant molecular parameters). A consideration of the relevant torsion angles for the two non-equivalent t-butyl groups shows them both to be staggered with respect to their adjacent hydroxy-oxygen atoms.[9]

The most interesting feature of the molecular conformation is the existence of two OH $\cdots \pi$ hydrogen bonds in this highly hindered molecule. The average perpendicular distance from a hydroxy-hydrogen atom to the plane of its corresponding π-electron donor ring is 2.09 Å, which should be regarded as an upper limit for this perpendicular distance. A neutron diffraction study of (I) is underway in order to eliminate the artificial shortening of the O–H bonds known to occur in an *X*-ray analysis, and thereby obtain a more accurate perpendicular distance. The mean angle between the O–H vectors and the normals to the benzene rings in this constrained system is 37.9°, this being somewhat larger than the corresponding angle predicted for an unconstrained OH $\cdots \pi$ hydrogen bond.[3] The hydroxy-hydrogen atoms are situated such that they appear to interact with the π-electron density associated with the C(1)–C(6) and C(15)–C(65) bonds of the molecule.

None of the intermolecular contacts in the crystal structure is significantly shorter than the appropriate van der Waals contacts.

Previous spectroscopic evidence[4] indicated that this conformation is maintained in solvents normally capable of intermolecular hydrogen bond formation. However, i.r. measurements in hexamethylphosphoramide $[(CH_3)_2N]_3PO$ (a powerful σ-electron donor[1]) suggest a significant amount of conformational disruption, due to intermolecular bonding.

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[5/1945 *Received*, 6*th October*, 1975]

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[9] For similar staggered arrangements, see *e.g.* M. Maze and C. Rerat, *Compt. rend.*, 1964, **259**, 4612.