

2,6-Diphenylphenol: A Structure Containing an Intramolecular O—H... π Hydrogen Bond

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Abstract. C₁₈H₁₄O, orthorhombic, $P2_12_12_1$, $a = 11.165$ (1), $b = 18.399$ (2), $c = 6.368$ (1) Å, $Z = 4$, $D_x = 1.251$ g cm⁻³, $\mu(\text{Mo } K\alpha) = 0.89$ cm⁻¹. The stereochemistry of the intramolecular O—H... π hydrogen bond in the title molecule has been established by single-crystal X-ray analysis. The hydroxyl H atom is favourably located in the proximity of two of the 2-phenyl C atoms, at distances of 2.43 (4) and 2.40 (4) Å, to interact with their π electrons. The 2- and 6-phenyl rings are twisted from the phenol ring by 52 and 44° respectively.

Introduction. Hitherto many spectroscopic studies have been carried out on hydrogen bonds in which π electrons are involved as the acceptor base. However, only a few unequivocal X-ray studies on such hydrogen bonds have been reported (Hardy & MacNicol, 1976; Aubry, Protas, Moreno-Gonzalez & Marraud, 1977). To elucidate the stereochemistry of the intramolecular O—H... π bond the structure of the present compound was studied by X-ray diffraction. Spectroscopic studies on CCl₄ solutions of the compound (Ōki, Hosoya & Iwamura, 1961; Ueji, Ueda & Kinugasa, 1976) showed an intramolecular interaction between the hydroxyl group and the π electrons of the *o*-phenyl group. The IR spectrum of the crystals (CsI disc) indicated a single hydroxyl stretching band at 3524 cm⁻¹, which was red-shifted by 88 cm⁻¹ from that of phenol in a dilute CCl₄ solution. This strongly suggests the presence of an O—H... π bond in the crystals.

The compound was prepared by a different method from that described by Luttringhans & Ambros (1956). Single crystals grown from a cyclohexane solution were pale-pink prisms elongated along *c*. A specimen approximately 0.28 × 0.14 × 0.12 mm was used for the X-ray data collection on a computer-controlled four-circle diffractometer equipped with a graphite

monochromator. 1754 independent reflexions with 2θ less than 55° were measured with Mo *K* α radiation in the ω - 2θ scanning mode; of these, 1271 with $|F_o| > 3\sigma(F)$ were used for the structure determination.

The structure was solved by an application of the symbolic addition procedure (Karle & Karle, 1966), and refined by the block-diagonal least-squares method. Anisotropic thermal vibrations were assumed for the non-hydrogen atoms. All the H atoms, including the hydroxyl H atom, were clearly found on a difference Fourier map and their positional and isotropic thermal parameters were refined. The final residuals were $R = \sum (|F_o| - |F_c|) / \sum |F_o| = 0.052$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2} = 0.059$. The weighting scheme used in the final least-squares cycle was $1/w = \sigma^2(F) + 0.00090|F_o|^2$. Atomic scattering factors for C and O were taken from *International Tables for X-ray Crystallography* (1974); for H those of Stewart, Davidson & Simpson (1965) were used. All computations were carried out on a FACOM 270/20 computer of Kwansai Gakuin University with the programs developed by the authors.

The final positional parameters are given in Table 1.*

Discussion. Fig. 1 shows the stereochemistry of the molecule. Table 2 lists the bond lengths and angles. The phenyl rings, (II) and (III), are twisted about the bonds connecting them to ring (I) in opposite directions; the dihedral angles between the planes of (I) and (II), and (I) and (III) are 52 and 44° respectively. O(1) is coplanar with ring (I), while H(1) slightly protrudes

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33470 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Final fractional atomic coordinates ($\times 10^4$, for H $\times 10^3$)

	x	y	z
O(1)	2834 (2)	1589 (1)	480 (4)
C(1)	3108 (3)	1207 (2)	2284 (5)
C(2)	4239 (3)	874 (2)	2518 (5)
C(3)	4446 (3)	491 (2)	4382 (6)
C(4)	3596 (3)	453 (2)	5935 (6)
C(5)	2506 (3)	786 (2)	5657 (5)
C(6)	2230 (3)	1169 (2)	3826 (5)
C(7)	5173 (3)	904 (2)	872 (5)
C(8)	5716 (3)	269 (2)	157 (6)
C(9)	6594 (3)	288 (2)	-1380 (7)
C(10)	6937 (3)	938 (2)	-2243 (6)
C(11)	6426 (3)	1576 (2)	-1557 (7)
C(12)	5561 (3)	1562 (2)	10 (6)
C(13)	1022 (3)	1500 (2)	3613 (5)
C(14)	494 (3)	1864 (2)	5298 (6)
C(15)	-652 (3)	2137 (2)	5163 (7)
C(16)	-1307 (3)	2051 (2)	3350 (8)
C(17)	-805 (3)	1696 (2)	1653 (7)
C(18)	355 (3)	1425 (2)	1772 (6)
H(1)	343 (4)	154 (2)	-50 (7)
H(3)	531 (3)	22 (2)	465 (5)
H(4)	373 (3)	19 (1)	723 (5)
H(5)	193 (3)	77 (2)	663 (6)
H(8)	540 (3)	-19 (2)	64 (6)
H(9)	696 (3)	-16 (2)	-190 (5)
H(10)	754 (3)	97 (2)	-326 (6)
H(11)	666 (3)	205 (2)	-225 (6)
H(12)	521 (3)	204 (2)	54 (6)
H(14)	95 (3)	192 (2)	654 (6)
H(15)	-104 (4)	239 (2)	650 (8)
H(16)	-219 (3)	225 (2)	320 (7)
H(17)	-123 (3)	163 (2)	26 (5)
H(18)	72 (3)	118 (2)	57 (6)

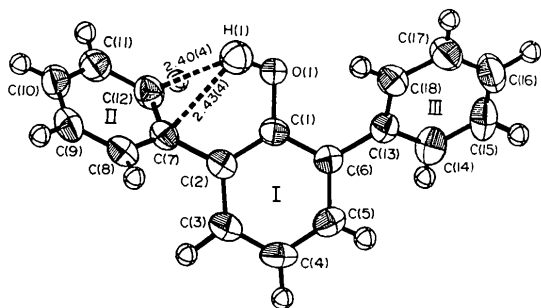


Fig. 1. The molecular structure of 2,6-diphenylphenol viewed perpendicular to ring (I). Thermal ellipsoids are drawn to include the 50% probability level, except those for the aromatic H atoms, which are represented by spheres of an arbitrary fixed radius.

from plane (I) by 0.09 Å and approaches C(7) and C(12). The O—H bond direction is almost parallel to ring (II) and the perpendicular distances from O(1) and H(1) to ring (II) are 1.924 and 1.90 Å respectively. The distances H(1)···C(7) [2.43 (4) Å] and H(1)···C(12) [2.40 (4) Å] are almost the same. The corresponding distances found in 2,2-bis(2-hydroxy-5-methyl-3-*tert*-butylphenyl)propane are 2.13, 2.19, 2.49, and 2.52 Å (Hardy & MacNicol, 1976). The

Table 2. Bond lengths (Å) and bond angles (°)

O(1)—H(1)	0.92 (4)	C(10)—C(11)	1.377 (5)
C(1)—O(1)	1.381 (4)	C(11)—C(12)	1.390 (5)
C(1)—C(2)	1.412 (4)	C(12)—C(7)	1.397 (5)
C(2)—C(3)	1.400 (5)	C(6)—C(13)	1.486 (4)
C(3)—C(4)	1.372 (5)	C(13)—C(14)	1.396 (5)
C(4)—C(5)	1.374 (5)	C(14)—C(15)	1.376 (5)
C(5)—C(6)	1.397 (5)	C(15)—C(16)	1.376 (7)
C(6)—C(1)	1.389 (4)	C(16)—C(17)	1.382 (6)
C(2)—C(7)	1.480 (4)	C(17)—C(18)	1.390 (5)
C(7)—C(8)	1.394 (4)	C(18)—C(13)	1.396 (5)
C(8)—C(9)	1.386 (5)		
C(9)—C(10)	1.371 (5)	C—H (mean)	0.99 (3)
C(1)—O(1)—H(1)	111 (3)	C(7)—C(8)—C(9)	121.2 (3)
C(2)—C(1)—O(1)	120.4 (3)	C(8)—C(9)—C(10)	120.2 (3)
C(6)—C(1)—O(1)	117.3 (3)	C(9)—C(10)—C(11)	120.1 (3)
C(2)—C(1)—C(6)	122.3 (3)	C(10)—C(11)—C(12)	120.0 (3)
C(1)—C(2)—C(3)	117.1 (3)	C(7)—C(12)—C(11)	120.9 (3)
C(1)—C(2)—C(7)	122.7 (3)	C(6)—C(13)—C(14)	120.7 (3)
C(3)—C(2)—C(7)	120.2 (3)	C(6)—C(13)—C(18)	121.3 (3)
C(2)—C(3)—C(4)	121.5 (3)	C(14)—C(13)—C(18)	117.9 (3)
C(3)—C(4)—C(5)	119.8 (3)	C(13)—C(14)—C(15)	121.3 (4)
C(4)—C(5)—C(6)	121.9 (3)	C(14)—C(15)—C(16)	120.3 (4)
C(1)—C(6)—C(5)	117.4 (3)	C(15)—C(16)—C(17)	119.6 (4)
C(1)—C(6)—C(13)	123.7 (3)	C(16)—C(17)—C(18)	120.4 (4)
C(5)—C(6)—C(13)	118.9 (3)	C(13)—C(18)—C(17)	120.5 (3)
C(2)—C(7)—C(8)	120.4 (3)		
C(2)—C(7)—C(12)	121.9 (3)	C—C—H (mean)	120 (2)
C(8)—C(7)—C(12)	117.6 (3)		

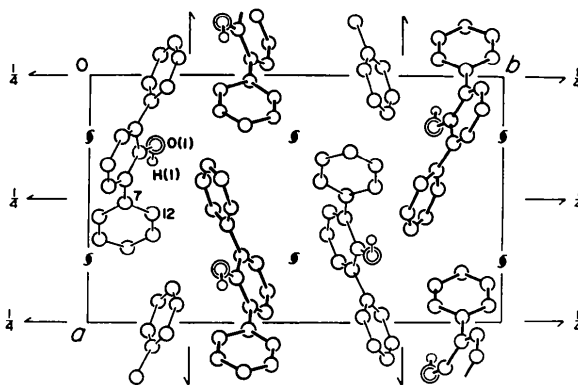


Fig. 2. The crystal structure viewed along *c*. C(7) and C(12) are indicated by numbers only.

distance between H(1) and the midpoint of the bond C(7)—C(12) is 2.31 Å and the angle O(1)—H(1)···(midpoint) is 122°. Thus the O—H group is favourably located to interact equally with the π electrons on both C(7) and C(12).*

*The stereochemistry of the O—H··· π bond in the present molecule is different from that found in the crystal of tributylammonium tetraphenylborate monohydrate (Aubry, Protas, Moreno-Gonzalez & Marraud, 1977), where each water H atom is located almost immediately above the centre of an aromatic ring to form the O—H··· π bond, the H···C(aromatic) distances ranging from 2.49 (3) to 2.91 (3) Å. In the X-ray study of *aci-p*-iodobenzoylamino-cyclol (McPhail & Sim, 1965; McPhail, Sim, Frey & Ott, 1966) similar bonding has been found, but the relevant H atom has not been definitely located.

The molecular structure thus established substantiates an intramolecular hydrogen bond of the type O—H... π . The present results are consistent with the observations based on the IR spectrum, and also with the inferred location of the H atom in the O—H... π interaction (Öki & Iwamura, 1961, 1967).

The crystal structure is illustrated in Fig. 2. No close intermolecular contact involving the O—H group was found in the crystal structure [H(1)...H > 2.86, H(1)...C > 3.00, O(1)...H > 2.96, and O(1)...C > 3.43 Å].

References

- AUBRY, A., PROTAS, J., MORENO-GONZALEZ, E. & MARRAUD, M. (1977). *Acta Cryst.* B33, 2572–2578.
- HARDY, A. D. U. & MACNICOL, D. D. (1976). *J. Chem. Soc. Perkin Trans. 2*, pp. 1140–1142.
- International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–98. Birmingham: Kynoch Press.
- KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* 21, 849–859.
- LUTTRINGHANS, A. & AMBROS, D. (1956). *Chem. Ber.* 89, 463–474.
- MCPHAIL, A. T. & SIM, G. A. (1965). *J. Chem. Soc. Chem. Commun.* pp. 124–126.
- MCPHAIL, A. T., SIM, G. A., FREY, A. J. & OTT, H. (1966). *J. Chem. Soc. B*, pp. 377–395.
- ÖKI, M., HOSOYA, H. & IWAMURA, H. (1961). *Bull. Chem. Soc. Jpn*, 34, 1391–1395.
- ÖKI, M. & IWAMURA, H. (1961). *Bull. Chem. Soc. Jpn*, 34, 1395–1401.
- ÖKI, M. & IWAMURA, H. (1967). *J. Am. Chem. Soc.* 89, 576–579.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.
- UEJI, S., UEDA, N. & KINUGASA, T. (1976). *J. Chem. Soc. Perkin Trans. 2*, pp. 178–180.

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(2*RS*,4*RS*)-2-Hydroxy-4-aminovaleric Acid Hydrochloride, a Structural Analogue of GABA

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Abstract. C₅H₁₁NO₃·HCl, *M_r* = 169.61, m.p. 175.5–176.5°C (dec.), triclinic, *P*1̄, *a* = 6.368 (2), *b* = 8.111 (2), *c* = 9.590 (2) Å, α = 70.83 (2), β = 67.67 (3), γ = 98.64 (3)°, *V* = 406.4 Å³, *Z* = 2, *D_m* (flotation) = 1.38, *D_x* = 1.386 g cm⁻³. The structure was refined to *R* = 0.055. The crystal structure is stabilized by hydrogen bonds.

Introduction. 2-Hydroxy-4-aminovaleric acid (Honoré, Hjeds, Krogsgaard-Larsen & Christiansen, 1978) and 2-hydroxy-4-aminovalerohydroxamic acid (Hjeds & Honoré, 1978) were synthesized as part of an investigation of the relationship between structure and biological activity of analogues of γ -aminobutyric acid (GABA). Two diastereomeric racemates of each compound were obtained and the relative stereochemistries of the hydroxamic acids and the amino acids were synthetically related (Hjeds & Honoré, 1978). This X-ray analysis of the title compound has been carried out in order to establish the relative stereochemistries of these racemates.

Platelet crystals of the title compound were grown from acetic acid. Intensities were measured on a

Nonius three-circle automatic diffractometer with graphite-monochromated Mo *K* α (λ = 0.71069 Å) radiation. The ω -scan technique with a scan speed of 1.2° min⁻¹ was employed. Background counts were taken for half the scanning time at each of the scan-range limits. The crystal (0.34 × 0.37 × 0.12 mm) was sealed in a glass capillary and oriented with *c* parallel to the ϕ axis of the goniostat. Of the 2346 independent reflections measured in the range 2.5 ≤ θ ≤ 30.0°, 1652 had net intensities >3.0 $\sigma(I)$, where $\sigma(I)$ is the standard deviation from counting statistics. These were regarded as observed and used in the refinement. Lorentz and polarization corrections were applied but no absorption corrections were made [$\mu(\text{Mo } K\alpha)$ = 4.07 cm⁻¹]. Cell dimensions were obtained by least-squares refinement from the 2 θ values of 30 reflections measured on the diffractometer. The coordinates of the Cl⁻ ion were deduced from a Patterson function, and an electron density map phased on the contribution of the Cl⁻ ion gave the positions of all other non-hydrogen atoms. Refinement, first with isotropic, then anisotropic thermal parameters, proceeded smoothly. The coordinates of all 12 H atoms were located in a