

## Structure of 2-Hydroxybiphenyl

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**Abstract.** 2-Biphenylol,  $C_{12}H_{10}O$ ,  $M_r = 170.2$ , monoclinic,  $Cc$ ,  $a = 5.882(2)$ ,  $b = 12.867(2)$ ,  $c = 12.313(3)$  Å,  $\beta = 103.76(3)^\circ$ ,  $V = 905.2(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.249$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.5418$  Å,  $\mu = 5.36$  cm<sup>-1</sup>,  $F(000) = 360$ ,  $T = 293$  K, final  $R = 0.064$  for 751 observed independent diffractometer-measured intensity data. The dihedral angle between the two ring planes is  $57.0(7)^\circ$ . The OH group is disordered over the four *ortho* positions, which leads to short C–O bond lengths. The OH group interacts with the  $\pi$  electrons of the rings to form intramolecular hydrogen bonding.

**Introduction.** The biphenyl molecule has been extensively studied in recent years because of the differences found for the inter-ring torsion angle  $\psi$  in the gas phase and in the solid state (Almenningen & Bastiansen, 1958; Trotter, 1961; Robertson, 1961; Hargreaves & Rizvi, 1962; Charbonneau & Delugeard, 1976, 1977). On the other hand, among the hydroxybiphenyl derivatives, only the structure of 4-hydroxybiphenyl is known, showing two crystal modifications: monoclinic and orthorhombic (Brock & Haller, 1984) in which the inter-ring torsion  $\psi$  is very small, about  $2^\circ$ . In the case of 2-hydroxybiphenyl, the ultraviolet and infrared spectra have been examined indicating an O–H $\cdots\pi$  interaction (Oki & Iwamura, 1967; Schaefer, Wildman, Sebastian & McKinnon, 1984). To elucidate the stereochemistry of the intramolecular O–H $\cdots\pi$  bond, the structure of this compound was studied by X-ray diffraction.

**Experimental.** Suitable crystals obtained from cyclohexane. A needle approximately  $0.3 \times 0.3 \times 0.6$  mm was used first for film studies of space group:  $Cc$ , then for data collection with an automatic Nonius CAD-4 four-circle diffractometer; unit-cell parameters refined by a least-squares fit of 25 reflections in the range  $14.9 < \theta < 50.6^\circ$ ;  $\omega$ - $2\theta$  scan technique used to collect intensities of 1045 reflections with  $\theta < 73^\circ$  (range of  $hkl$ :  $h0 \rightarrow 7$ ,  $k0 \rightarrow 15$ ,  $l-15 \rightarrow 15$ ), 853 independent ( $R_{int} = 0.08$ ), 751 of which considered as observed [ $I > 3\sigma(I)$ ]. One standard reflection measured every 60 min to control the intensity and, at intervals of 100 reflections, the orientation of the crystal. Lorentz and

polarization corrections made. Structure determined by direct methods and refined on  $F$  by *SHELX76* (Sheldrick, 1976). 150 independent parameters; the  $E$  map showed all non-H atoms of the molecule. The difference Fourier synthesis showed the H atoms and other peaks at *ortho* positions: these peaks were assumed to be O atoms with fractional occupation and introduced into the refinement. C atoms refined first isotropically, then anisotropically; the other atoms refined with isotropic constant  $U$ , except the two O atoms having occupation 0.4 which were refined anisotropically. The H atoms of the hydroxyl groups were not positioned due to the low electron density at the fractional H.

$(\Delta/\sigma)_{max} = 0.877$  for  $z$  coordinate of O(46);  $(\Delta/\sigma)_{av} = 0.292$ . Residual electron density in final difference Fourier synthesis:  $0.07$  e Å<sup>-3</sup>. Unit weight used,  $R = 0.064$ ,  $wR = 0.057$ , goodness of fit: 0.645. Atomic scattering factors from *SHELX76*.

**Discussion.** The final positional and thermal parameters are given in Table 1.\* Fig. 1 is a plot of the molecule by *PLUTO* (Motherwell, 1978) indicating the numbering scheme. The two atoms O(5) and O(42) have occupancy 0.40 whereas the two others, O(3) and O(46), have occupancy 0.10. Bond distances and angles are listed in Table 2. We note the unusual values of the C–O bonds, all smaller than the 1.36 Å found in phenols, and this is a consequence of disorder. For two of them C(3)–O and C(46)–O, the electron density of the O or H atoms is quite similar due to occupation, so the distance is the average between 1.08 (C–H) and 1.36 Å (C–O), that is to say about 1.22 Å. On the other hand, for C(5)–O and C(42)–O the electron density for the O atoms is larger, so the distance has a value near to 1.36 Å. Some torsional angles have been calculated; among them C(3)–C(4)–C(41)–C(46) and C(5)–C(4)–C(41)–C(46) have the values  $-54.3(8)$  and  $123.4(6)^\circ$ , respectively, showing that the two

\* Lists of structure factors, anisotropic vibration parameters, H-atom coordinates, torsional angles and deviations of atoms from selected mean planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43666 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ( $\times 10^4$ ) and equivalent isotropic thermal factors for non-H atoms, with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i a_j a_i^* a_j^*$$

	x	y	z	$U_{eq}(\text{\AA}^2)$
C(1)	-2071 (13)	3469 (5)	7659 (5)	0.079 (3)
C(2)	63	3292 (4)	8389	0.077 (3)
C(3)	405 (11)	2418 (4)	9067 (5)	0.066 (2)
C(4)	-1425 (9)	1725 (4)	9030 (4)	0.058 (2)
C(5)	-3561 (10)	1912 (4)	8293 (5)	0.065 (2)
C(6)	-3905 (12)	2772 (5)	7593 (5)	0.079 (2)
C(41)	-1049 (10)	782 (4)	9743 (4)	0.056 (2)
C(42)	-2462 (10)	590 (4)	10502 (5)	0.065 (2)
C(43)	-2099 (12)	-268 (5)	11171 (5)	0.078 (3)
C(44)	-318 (13)	-982 (5)	11154 (5)	0.079 (2)
C(45)	1094 (13)	-786 (5)	10400 (6)	0.080 (3)
C(46)	747 (11)	73 (4)	9725 (5)	0.066 (2)
O(5)	-5277 (15)	1217 (8)	8132 (8)	0.076 (4)
O(42)	-4041 (17)	1314 (7)	10626 (8)	0.079 (4)
O(3)	2364 (58)	2256 (28)	9650 (29)	0.07
O(46)	1954 (63)	240 (28)	9016 (28)	0.07

Table 2. Bond distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

C(1)–C(2)	1.378 (7)	C(41)–C(42)	1.413 (9)
C(2)–C(3)	1.386 (7)	C(42)–C(43)	1.364 (9)
C(3)–C(4)	1.391 (8)	C(43)–C(44)	1.397 (10)
C(4)–C(5)	1.385 (7)	C(44)–C(45)	1.407 (11)
C(5)–C(6)	1.387 (9)	C(45)–C(46)	1.369 (8)
C(6)–C(1)	1.391 (10)	C(46)–C(41)	1.400 (8)
C(3)–O(3)	1.222 (32)	C(42)–O(42)	1.349 (12)
C(5)–O(5)	1.328 (11)	C(46)–O(46)	1.268 (40)
C(4)–C(41)	1.482 (7)		
O(3)–C(3)–C(2)	118 (2)	O(42)–C(42)–C(41)	118.9 (1)
O(3)–C(3)–C(4)	122 (2)	O(42)–C(42)–C(43)	120.2 (1)
C(4)–C(3)–C(2)	120.0 (1)	C(41)–C(42)–C(43)	120.6 (1)
C(4)–C(3)–C(4)	121.4 (1)	C(41)–C(46)–C(45)	121.4 (1)
C(5)–C(4)–C(3)	119.0 (1)	C(42)–C(43)–C(44)	122.2 (1)
C(5)–C(4)–C(1)	118.8 (1)	C(42)–C(41)–C(46)	117.5 (1)
C(6)–C(1)–C(2)	120.3 (1)	C(43)–C(44)–C(45)	117.1 (1)
C(1)–C(2)–C(3)	120.5 (1)	C(44)–C(45)–C(46)	121.2 (1)
C(5)–C(4)–C(41)	121.0 (1)	C(46)–C(41)–C(4)	122.1 (1)
C(3)–C(4)–C(41)	120.0 (1)	C(42)–C(41)–C(4)	120.4 (1)
O(5)–C(5)–C(4)	121.3 (1)	O(46)–C(46)–C(41)	117 (2)
O(5)–C(5)–C(6)	116.8 (1)	O(46)–C(46)–C(45)	122 (2)

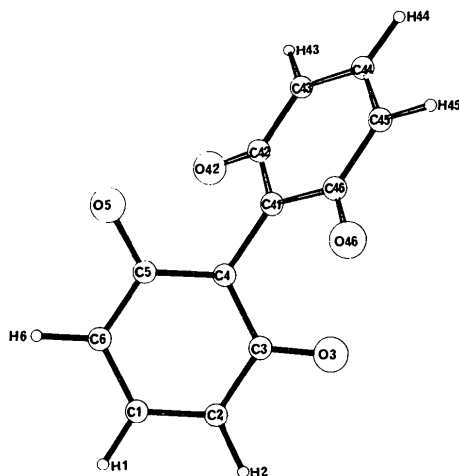


Fig. 1. Molecule viewed perpendicular to C(3)C(4)C(41) and numbering scheme.

Table 3. Main distances ( $\text{\AA}$ ) involving O atoms

Plane I: C(1)–C(2)–C(3)–C(4)–C(5)–C(6).

Plane II: C(41)–C(42)–C(43)–C(44)–C(45)–C(46).

	C(3)	C(4)	C(5)	C(41)	C(42)	C(46)	Plane I	Plane II
O(3)	—	—	—	2.78	—	2.97	0.09	-1.88
O(5)	—	—	—	2.84	3.10	—	0.14	2.03
O(42)	—	2.82	3.05	—	—	—	-2.04	-0.14
O(46)	2.95	2.76	—	—	—	—	1.96	0.04

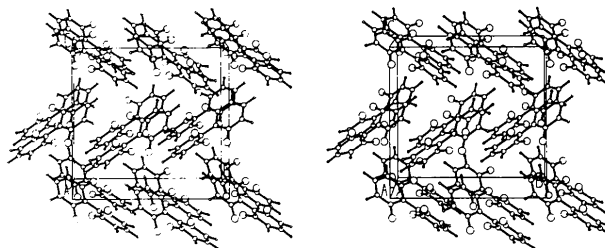


Fig. 2. Stereoscopic view of the structure seen along [100] drawn by PLUTO (Motherwell, 1978).

phenyl rings are not coplanar as found for 4-hydroxybiphenyl (Brock & Haller, 1984). The two rings are planar ( $\chi^2 = 2.57$  and  $9.78$ ) and the angle between the two planes is  $57.0 (7)^\circ$ . This value is consistent with that estimated from the ultraviolet spectral data:  $50^\circ$  (Oki & Iwamura, 1967).

Table 3 gives most relevant distances involving the O atoms. It is clear that these distances are calculated with the coordinates found by refinement, O-atom positions being the average between O and H. These calculated distances have values quite similar to those found in 2,6-diphenylphenol (Nakatsu, Yoshioka, Kunitomo, Kinugasa & Ueji, 1978). This means that the O–H group probably interacts with the  $\pi$  electrons of the rings giving an intramolecular hydrogen bond of the type O–H $\cdots\pi$  as observed in the IR spectrum (Oki & Iwamura, 1967). These authors showed that the strength of the OH $\cdots\pi$  hydrogen bonding increases with increasing dihedral angle of the two phenyl rings.

The crystal structure is illustrated in Fig. 2. No close intermolecular contacts between O atoms with the same numbering were found in the crystal. However, some intermolecular bonds are formed occasionally between O atoms with different numbering.

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## Structure of an *N*-Monomethylated Cyclic Dipeptide, *cyclo*(-*N*-Methyl-L-phenylalanyl-L-phenylalanyl-)

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**Abstract.** 1-Methyl-3,6-bis(phenylmethyl)-2,5-piperazinedione,  $C_{19}H_{20}N_2O_2$ ,  $M_r = 308.3$ , orthorhombic,  $P2_12_12_1$ ,  $a = 10.254$  (2),  $b = 13.370$  (3),  $c = 24.294$  (4) Å,  $V = 3330$  (1) Å<sup>3</sup>,  $Z = 8$ ,  $D_x = 1.23$  g cm<sup>-3</sup>,  $\lambda(\text{Cu } K\alpha) = 1.54178$  Å,  $\mu = 5.6$  cm<sup>-1</sup>,  $F(000) = 1312$ , room temperature,  $R = 0.052$  for 1697 observed reflections. Two crystallographically independent molecules joined through a pair of N–H...O hydrogen bonds form dimers as distinct units in the crystal lattice. The general molecular conformation is similar to that of *cyclo*(L-Phe)<sub>2</sub> [Gdaniec & Liberek (1986). *Acta Cryst.* **C42**, 1343–1345]. In molecule *B* the aromatic side chain of the *N*-methylated phenylalanine residue folds over the diketopiperazine moiety [ $\chi_1^1 = 61.1$  (7)°] while the other side chain is in extended conformation [ $\chi_2^1 = -62.5$  (6)°]. The opposite conformation of the side chains is observed in molecule *A* [ $\chi_1^1 = -65.9$  (6),  $\chi_2^1 = 68.7$  (6)°].

**Introduction.** In the crystal structures of *cyclo*(*N*-Me-L-Phe)<sub>2</sub> (Benedetti, Marsh & Goodman, 1976) and *cyclo*(L-Phe)<sub>2</sub> (Gdaniec & Liberek, 1986) none of the molecules adopts a conformation with  $C_2$  symmetry postulated on the basis of NMR data (Kopple & Marr, 1967; Deslauries, Grzonka, Schaumburg, Shiba & Walter, 1975). Introduction of a methyl group at one of the 2,5-piperazinedione (hereafter DKP) N atoms destroys the potential symmetry and makes the two phenylalanine residues nonequivalent. <sup>1</sup>H NMR data of such monomethylated cyclic dipeptides (Liberek, Bednarek, Kitowska & Macikowska, 1977) speak in favour of a conformation in which the DKP ring is boat, the

aromatic ring of the *N*-methylamino-acid residue bends over the DKP nucleus and the other aromatic ring is extended towards the N atom.

The crystal structure of *cyclo*(*N*-Me-L-Phe-L-Phe) has been solved to find out if the preference of an *N*-methylamino-acid residue to fold over the DKP ring is preserved in the solid state as well as to provide more structural data on cyclic dipeptides with two aromatic amino-acid residues.

**Experimental.** Colourless crystal 0.1 × 0.2 × 0.3 mm from methanol–water,  $D_m$  not determined, Syntex *P2*<sub>1</sub> diffractometer, graphite monochromator, lattice parameters from 15 reflections in  $2\theta$  13–22°, profiles measured for 2563 unique reflections with  $2\theta \leq 115^\circ$  ( $h$  0→11,  $k$  0→14,  $l$  0→26),  $\omega$ – $2\theta$  scan technique, variable scan rate, profile analysis according to Lehmann & Larsen (1974), no significant intensity variation for two standard reflections, absorption ignored, 1697 reflections with  $I \geq 1.96\sigma(I)$ . Structure solved by direct methods with *SHELX76* (Sheldrick, 1976), full-matrix least-squares refinement on  $F$ ,  $w = 1/\sigma^2$ , H atoms bonded to C in calculated positions, H atoms bonded to N located on a  $\Delta F$  map, final refinement: anisotropic non-H atoms and empirical isotropic extinction parameter  $x$  used to correct  $F_c$  according to  $F_c' = F_c(1 - xF_c^2/\sin\theta)$ ,  $x$  converged at  $1.15(3) \times 10^{-6}$ ;  $R = 0.052$  and  $wR = 0.046$ ;  $S = 3.09$ ; in final refinement cycle max.  $\Delta/\sigma \leq 0.1$ , largest peak in final  $\Delta F$  map 0.14, largest hole  $-0.16$  e Å<sup>-3</sup>; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); computer programs: *SHELX76*