Hydrogen bonds and C—H···O interactions in 2,2′-dimethoxybiphenyl-5,5′-dimethanol at 150 K

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The title compound, $C_{16}H_{18}O_4$, crystallized in the centrosymmetric space group $P2_1/c$ with one molecule in the asymmetric unit. The two hydroxyl-H atoms are ordered, and are involved in intermolecular hydrogen bonds with O_{donor}···$O_{acceptor}$ distances of 2.761 (1) and 2.699 (1) Å, and O—H···O angles of 157 (2) and 168 (2)°. Seven leading intermolecular C—H···O interactions have H···O distances ranging from 2.41 to 2.76 Å and C—H···O angles ranging from 125 to 170°. The hydrogen bonds and C—H···O interactions form chain and ring patterns, resulting in a richly three-dimensional network. The biphenyl twist angle is 67.2 (1)°.

Comment

This report on the structure of 2,2′-dimethoxybiphenyl-5,5′-dimethanol, (I), is one of a series on hydrogen bonding and C—H···O interactions in substituted biphenyls, and follows a report on another biphenyl dimethanol, 6,6′-dimethoxy-3,3′,5,5′-tetramethylbiphenyl-2,2′-dimethanol [hereinafter (II); Dobson & Gerkin, 1999].
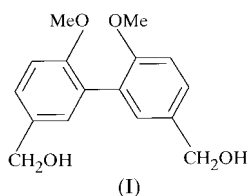
Compound (I) crystallizes in the centrosymmetric space group $P2_1/c$ with one molecule in the asymmetric unit. The refined molecule and the labeling scheme are shown in Fig. 1. The two hydroxyl-H atoms are ordered and are involved in two intermolecular hydrogen bonds. In addition, seven leading intermolecular C—H···O interactions (Taylor & Kennard, 1982; Steiner & Desiraju, 1998) are present in this structure. The geometric parameters of these are given in Table 2. Each molecule is linked by these interactions to ten neighboring molecules. The results of basic first- and second-level graph-set analysis (Bernstein *et al.*, 1995) involving these interactions, labeled *a–i* for this purpose in the order of their
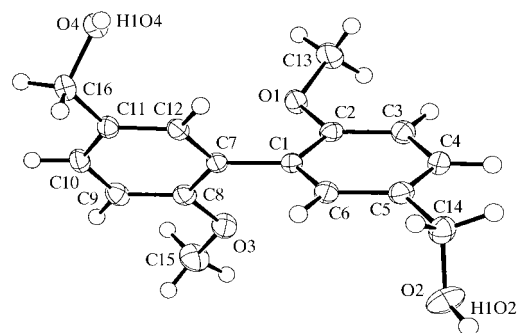

Figure 1
*ORTEP*II (Johnson, 1976) drawing of (I), showing the labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

appearance in Table 2, are given in Table 3. The 45 patterns comprise 27 chains and 18 rings. The chains propagate variously along [100] (2), [010] (12), [001] (7), [201] (3), [1$\bar{1}$0] (2) and [20$\bar{1}$]. A richly three-dimensional network of interactions results.

The individual phenyl rings of (I) are nearly planar; the maximum deviations of any of their C atoms from the best-fit planes describing them are 0.018 (1) and 0.012 (1) Å, while the average deviations are 0.012 (7) and 0.007 (5) Å for the C1–C6 and C7–C12 rings, respectively. These values may be compared with the corresponding values for (II): maximum deviations 0.011 (2) and 0.014 (2) Å, and average deviations 0.007 (3) and 0.008 (4) Å, for the C1–C6 and C7–C12 rings, respectively. The intramolecular dihedral angle between these best-fit planes in (I), the biphenyl twist angle, is 67.2 (1)°. For comparison of the biphenyl twist angle, 2,2′,4,4′,5,5′-hexamethoxybiphenyl (Chattopadhyay *et al.*, 1987) would appear to be quite suitable due to its comparable substituents at the 2,2′- and 5,5′-sites, and with H atoms at the 6,6′-sites. However, in that structure the biphenyl twist angle is 81.1°, which is much closer to the value of 87.3 (1)° found in (II), although (II) has non-H substituents at both the 2,2′- and 6,6′-positions. A packing diagram of (I) is given in Fig. 2.

Selected bond distances and angles in (I) are given in Table 1. All distances and angles fall within normal limits. As Table 1 shows, the geometric parameters of the methoxy
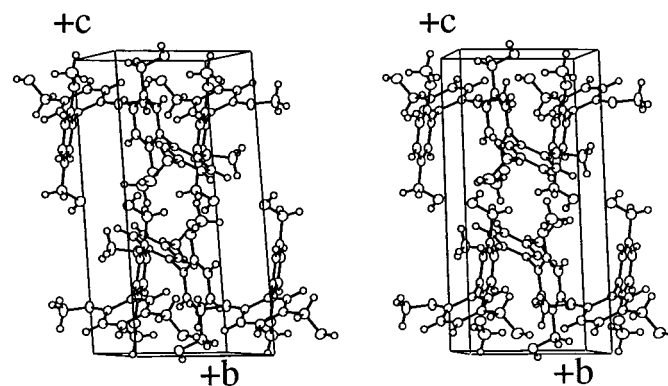

Figure 2
Stereopacking diagram for (I), viewed nearly down **a**.

groups agree quite well with each other, while those of the hydroxymethyl groups are in only reasonable agreement with each other. In (I), the closest intermolecular approaches, excluding pairs of atoms in hydrogen-bonded carboxyl groups in or the tabulated C—H···O interactions, are between C8 and H13$A(x, -1 + y, z)$ and fall short of the corresponding Bondi (1964) van der Waals radius sum by 0.12 Å.

Experimental

Compound (I) was obtained as a colorless column from a sample in Dr D. J. Hart's chemical collection. This was cut to provide the experimental sample. A synthesis is described by Cava *et al.* (1974).

Crystal data

$C_{16}H_{18}O_4$	$D_x = 1.336$ Mg m^{-3}
$M_r = 274.32$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 26 987
$a = 11.4104 (2)$ Å	reflections
$b = 7.4078 (1)$ Å	$\theta = 1.91–27.48°$
$c = 16.9198 (3)$ Å	$\mu = 0.095$ mm^{-1}
$\beta = 107.473 (1)°$	$T = 150$ K
$V = 1364.17 (4)$ Å^3	Cut column, colorless
$Z = 4$	$0.27 \times 0.23 \times 0.19$ mm

Data collection

Nonius KappaCCD diffractometer	$R_{int} = 0.042$
ω scans with κ offsets	$\theta_{max} = 27.50°$
27 579 measured reflections	$h = -14 \rightarrow 14$
3137 independent reflections	$k = -9 \rightarrow 9$
2471 reflections with $I > 2\sigma(I)$	$l = -21 \rightarrow 20$

Refinement

Refinement on F^2	H atoms treated by a mixture of
$R(F) = 0.046$	independent and constrained
$wR(F^2) = 0.099$	refinement
$S = 1.99$	$w = 1/[\sigma^2_{cs} + (0.026I)^2]$
3137 reflections	$(\Delta/\sigma)_{max} < 0.001$
189 parameters	$\Delta\rho_{max} = 0.28$ e Å^{-3}
	$\Delta\rho_{min} = -0.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.374 (1)	O3—C15	1.431 (2)
O1—C13	1.426 (2)	O4—C16	1.434 (2)
O2—C14	1.424 (2)	C5—C14	1.502 (2)
O3—C8	1.370 (1)	C11—C16	1.506 (2)
C2—O1—C13	117.17 (9)	O3—C8—C7	115.7 (1)
C8—O3—C15	117.5 (1)	O3—C8—C9	124.3 (1)
O1—C2—C1	115.7 (1)	O2—C14—C5	108.0 (1)
O1—C2—C3	123.2 (1)	O4—C16—C11	111.2 (1)
C1—C2—O1—C13	160.2 (1)	C2—C1—C7—C12	-111.6 (1)
C2—C1—C7—C8	69.0 (2)	C7—C8—O3—C15	179.1 (1)

Fourier difference methods were used to locate initial H-atom positions, and these H atoms were refined. Refined C—H distances ranged from 0.93 (1) to 1.03 (1) Å, with a mean value of 0.99 (3) Å; their U_{iso} values ranged from 0.9 to 1.5 times the U_{eq} values of the attached C atoms. The H atoms, excepting the hydroxyl-H atoms, were then made canonical, with C—H = 0.98 Å and $U_{iso} = 1.2U_{eq}$ of the attached C atom.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H1O2···O4^i	0.89 (2)	1.92 (2)	2.761 (1)	157 (2)
O4—H1O4···O2^{ii}	0.94 (2)	1.77 (2)	2.699 (1)	168 (2)
C10—H10···O1^{iii}	0.98	2.41	3.201 (1)	137
C3—H3···O4^{iv}	0.98	2.52	3.490 (1)	170
C12—H12···O2^v	0.98	2.67	3.380 (2)	129
C15—H15C···O1^{vi}	0.98	2.69	3.574 (2)	150
C4—H4···O2^{vii}	0.98	2.72	3.377 (2)	125
C14—H14A···O1^i	0.98	2.76	3.637 (2)	149
C13—H13C···O4^{iv}	0.98	2.76	3.557 (2)	139

Symmetry codes: (i) $-x, y - \frac{1}{2}, \frac{3}{2} - z$; (ii) $x, -\frac{1}{2} - y, z - \frac{1}{2}$; (iii) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iv) $x, \frac{1}{2} - y, \frac{1}{2} + z$; (v) $-x, \frac{1}{2} + y, \frac{3}{2} - z$; (vi) $1 - x, -y, 2 - z$; (vii) $-x, -y, 2 - z$.

Table 3
Basic first- and second-level graph-set descriptors involving interactions designated a–i in the order given in Table 2.

	a	b	c	d	e	f	g	h	i
a	$C(11)$	$R_2^4(8)$	$C_2^2(13)$	$R_4^2(16)$	$R_2^2(7)$	$C_2^2(16)$	$C_2^2(12)$	$R_2^2(12)$	$R_2^2(22)$
b		$C(11)$	$R_4^4(26)$	$C_2^2(8)$	$R_2^2(14)$	$C_2^2(17)$	$C_1^2(12)$	$R_4^4(24)$	$C_2^2(11)$
c			$C(8)$	$R_4^4(18)$	$C_2^2(12)$	$C_1^1(8)$	$C_2^2(15)$	$C_2^1(11)$	$R_4^4(16)$
d				$C(9)$	$R_4^2(22)$	$C_2^2(13)$	$C_2^2(14)$	$R_4^4(28)$	$R_2^1(7)$
e					$C(8)$	$C_2^2(14)$	$C_2^2(9)$	$R_2^2(9)$	$R_4^4(28)$
f						$R_2^2(16)$	$C_2^2(15)$	$C_2^1(11)$	$C_2^2(12)$
g							$R_2^2(10)$	$C_2^2(8)$	$C_2^2(17)$
h								$C(7)$	$R_4^4(34)$
i									$C(10)$

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1992–1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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