Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

1,2-Bis[bis(4-methoxyphenyl)hydroxymethyl]benzene

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Received 27 January 2003
Accepted 28 January 2003
Online 7 February 2003

Key indicators

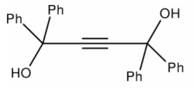
Single-crystal X-ray study
T = 160 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.052
wR factor = 0.132
Data-to-parameter ratio = 13.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

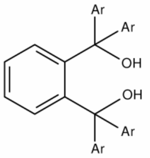
The title diol, $C_{36}H_{34}O_6$, has approximate twofold rotation symmetry in its crystal structure. It forms both intramolecular and intermolecular hydrogen bonds through its twofold disordered OH groups, linking most of the molecules into pairs with a chain of three O—H···O hydrogen bonds. As a result of the disorder, these dimers have an average centrosymmetric structure, and 12 (3)% of the molecules have only an intramolecular hydrogen bond, with no dimer formation.

Comment

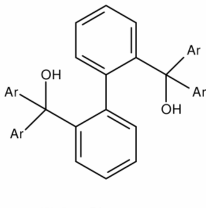
Molecules with two diarylmethanol groups close to each other, either with their relative positions fixed by a rigid framework, as in (1) and (2), or where proximity can be achieved through rotation about a single bond, as in (3), are of interest in two chemical contexts. They are potentially useful as inclusion compounds for host–guest complexes, as in the case of (1) (Toda *et al.*, 1989) and the TADDOLs reported by Seebach (von dem Bussche-Huennefeld *et al.*, 1992; Seebach *et al.*, 1993), and they are potential precursors of bis(diarylmethyl) dications, as in the cases of (1), (2) and (4) (Olah *et al.*, 1976; Hart *et al.*, 1963; Suzuki *et al.*, 1997; Carey *et al.*, 2002).



(1)



(2) Ar = Ph
(5) Ar = 4-MeO-C_6H_4



(3) Ar = Ph
(4) Ar = 4-MeO-C_6H_4

We recently prepared diols (3) and (4) as precursors for bis(diarylmethyl) dications for use as protecting groups for primary amines (Carey *et al.*, 2002); in an extension to that work, we prepared compound (5) and now report its crystal structure.

The asymmetric unit contains a single molecule of (5), which is ordered except for the H atoms of the two hydroxy groups. Each of these OH groups has two alternative orientations with almost equal occupancies. The disorder of the two groups is correlated, as a result of intramolecular hydrogen bonding. Moreover, the correlation extends, through an intermolecular hydrogen bond, to a second molecule related by inversion symmetry.

Fig. 1 shows a general view of one molecule, with only the major disorder component. An alternative view, in Fig. 2, illustrates the close approximation of the molecule to non-

DOI: 10.1107/S1600536803002514

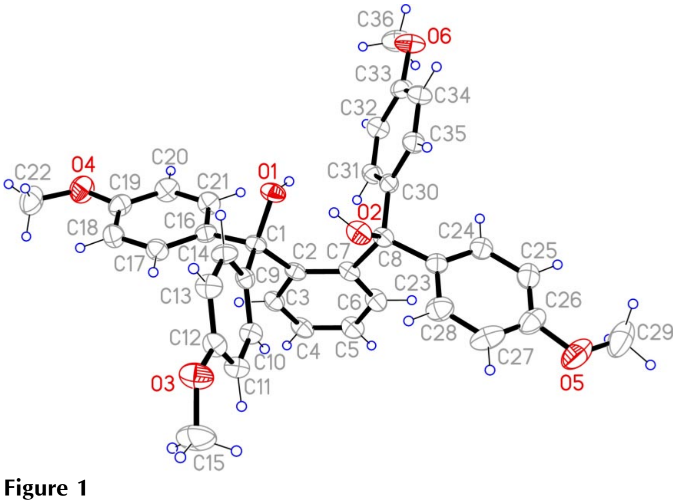


Figure 1
The molecular structure with atom labels and 50% probability ellipsoids for non-H atoms. Only the major disorder component is shown for the OH groups.

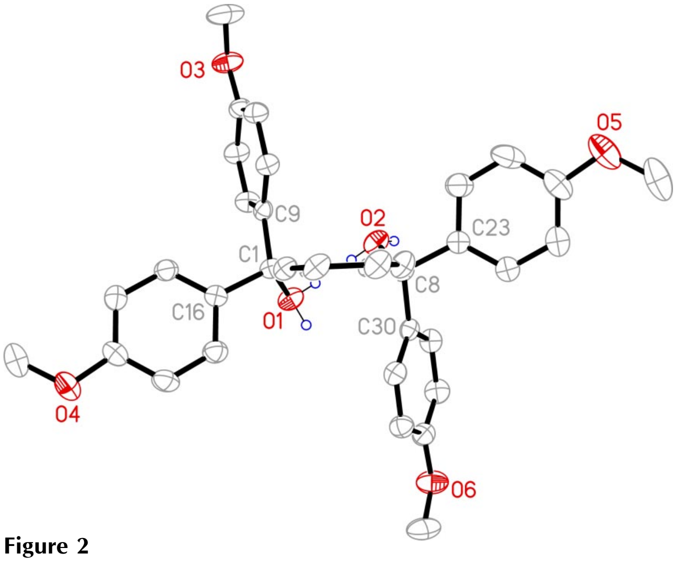


Figure 2
A view of the molecule along the non-crystallographic twofold rotation axis. Both positions are included for the disordered OH groups, and selected atoms are labelled. H atoms bonded to C atoms have been omitted.

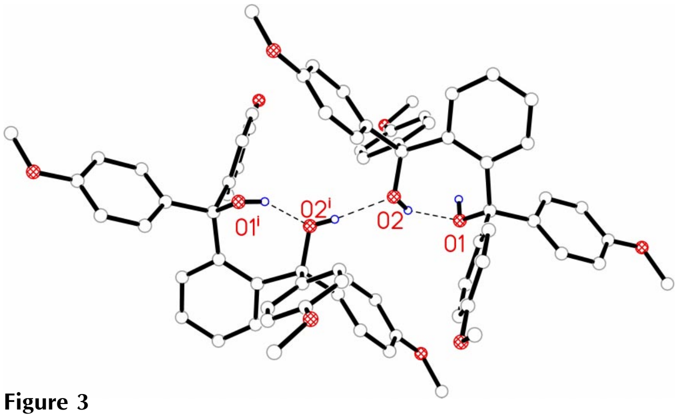


Figure 3
Two molecules, related by an inversion centre (symmetry code in Table 2), showing one correlated set of the twofold disordered OH groups with their intramolecular and intermolecular hydrogen bonds.

crystallographic twofold rotation symmetry, the axis running through the plane of the central aromatic ring. In this view, both orientations of each OH group are shown, while other H atoms have been omitted for clarity. All the aromatic rings are essentially planar and all four methoxy groups lie approximately in the respective ring planes. Selected molecular geometry parameters are given in Table 1.

The hydrogen bonding is shown in Fig. 3, with details given in Table 2. The correlated orientations of the four OH groups of two inversion-related molecules generate a chain of three O—H···O hydrogen bonds, two intramolecular and one intermolecular. The last OH group in the chain (O1 in Fig. 3) does not act as a hydrogen-bond donor, so discrete dimers are formed. Refinement of the occupancy factors of the OH groups indicates that most of the molecules are paired in this way, with random choice of the hydrogen-bond chain direction within each dimer. However, 12 (3)% of the molecular pairs have the two intramolecular hydrogen bonds but no intermolecular bond, the OH groups of O2 being directed away from each other, with a true inversion centre between them.

Structures of compounds in which a benzene ring is *ortho*-substituted by two C*sp*^{3}—OH groups that are not part of a further ring are surprisingly rare; a search of the Cambridge Structural Database (CSD, Version 5.23, April 2002, and 3 updates; Allen, 2002) gives only four. Of these, two (Kaize *et al.*, 1979; Rheingold & Allen, 1996) include no H atoms for the OH groups, because of low precision and/or structural disorder, and it is not possible to assign hydrogen-bonding patterns unambiguously. In the complex of a dihydroxy ligand complexed to Cr(CO)$_3$ (Dusausoy *et al.*, 1975), exclusively intermolecular hydrogen bonds among the OH groups form cyclic (OH)$_4$ tetrads and molecules are thus linked into a double chain. In the trigonal crystal structure of a hydrated organic diol (Paquette & Zhou, 1999), molecules form hydrogen-bonded trimers, with one OH of each molecule linked to the corresponding group of the next molecule, and the other OH linked to a water molecule disordered on the threefold rotation axis. Neither of these structures involves intramolecular hydrogen bonding, unlike the title compound, and it is clear from the positions of the OH groups that the same is true of the other two previously characterized diols. In our study of diols with a biphenyl unit between the two C*sp*^{3}—OH groups, we found intermolecular, but no intramolecular, hydrogen bonds (Carey *et al.*, 2002).

Experimental

n-Butyllithium (2.2 mol dm^{-3} in hexanes, 10 ml, 22 mmol) was diluted with THF (20 ml) under nitrogen, and cooled to 195 K. *p*-Bromoanisole (4.0 g, 21 mmol) was added, whereupon a white precipitate formed; after 10 min, dimethyl phthalate (0.71 g, 3.7 mmol) was added, to give an orange solution. The reaction was kept at 195 K for 30 min, shaken intermittently, then allowed to come to room temperature. Solvents were removed on a rotary evaporator and the residual oil was partitioned between water and dichloromethane. The organic phase was dried (Na$_2$SO$_4$), filtered, and evaporated, to give an orange oil, which, on standing for 48 h, deposited orange crystals. The supernatant liquid was removed by pipette and the remaining crystals were triturated with ether–petrol (50:50) and then dried under reduced pressure, to give colourless crystals (m.p. 498–499 K). Analysis: C 77.2, H 6.2%; calculated: C 76.9, H 6.1%. ^{1}H NMR (300 MHz, CD_3CN): δ 3.83 (12H, *s*, methyl), 4.1 (2H, *s*, OH), 6.72 (2H, *mult*, C3 and C6 of central ring), 6.95 (16H, *mult*, H of MeO-substituted phenyl groups), 7.12 p.p.m. (2H, *mult*, C4 and C5 of central ring). A sample of the product was recrystallized from toluene/petrol for crystal structure determination.

Crystal data

$C_{36}H_{34}O_6$
$M_r = 562.63$
Triclinic, $P\overline{1}$
$a = 10.584$ (3) Å
$b = 11.437$ (3) Å
$c = 13.510$ (3) Å
$\alpha = 84.45$ (2)°
$\beta = 71.11$ (2)°
$\gamma = 72.96$ (2)°
$V = 1479.4$ (7) Å^3

$Z = 2$
$D_x = 1.263$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 47 reflections
$\theta = 21.0$–24.8°
$\mu = 0.69$ mm^{-1}
$T = 160$ (2) K
Plate, colourless
0.36 × 0.22 × 0.04 mm

Data collection

Stoe–Siemens diffractometer
ω/θ scans with on-line profile fitting (Clegg, 1981)
Absorption correction: ψ scan (*XPREP* in *SHELXTL*; Sheldrick, 2001)
$T_{\min} = 0.789$, $T_{\max} = 0.991$
5605 measured reflections
5182 independent reflections

3615 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.083$
$\theta_{\max} = 67.7°$
$h = -11 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = -9 \rightarrow 16$
5 standard reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.132$
$S = 1.04$
5182 reflections
397 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 0.7787P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.21$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.0014 (2)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.448 (3)	C8—O2	1.442 (3)
O1—C1—C2	112.68 (19)	C2—C7—C6	117.7 (2)
C1—C2—C3	115.0 (2)	C2—C7—C8	126.8 (2)
C1—C2—C7	126.8 (2)	C6—C7—C8	115.3 (2)
C3—C2—C7	118.0 (2)	C7—C8—O2	109.78 (19)
O1—C1—C2—C7	39.6 (3)	C2—C7—C8—O2	39.8 (3)
C1—C2—C7—C8	−9.5 (4)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*B*···O2	0.81 (3)	1.88 (5)	2.601 (3)	148 (7)
O2—H2*A*···O1	0.81 (3)	1.87 (4)	2.601 (3)	149 (6)
O2—H2*B*···O2$^{\rm i}$	0.81 (3)	1.94 (3)	2.745 (4)	168 (8)

Symmetry code: (i) $1 - x, 2 - y, -z$.

Methyl and aromatic H atoms were placed geometrically and refined with a riding model (including free rotation about O—C bonds), and with $U_{\rm iso}$ constrained to be 1.2 (1.5 for methyl groups) times $U_{\rm eq}$ of the carrier atom. Hydroxy H atoms were located in a difference map, with two disordered alternative positions for each OH group; they were refined with all four O—H distances restrained to be approximately equal, with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm O})$, and with correlated occupancy factors [refined values 0.56 (3):0.44(3)].

Data collection: *DIF*4 (Stoe & Cie, 1988); cell refinement: *DIF*4; data reduction: local programs; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

We thank the EPSRC for financial support.

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