organic compounds

4,8-Dimethoxy-1-naphthalene-methanol

Roger E. Gerkin

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA
Correspondence e-mail: gerkin@chemistry.ohio-state.edu

The title compound, $C_{13}H_{14}O_3$, crystallized in the centrosymmetric space group $C2/c$ with one molecule as the asymmetric unit. Each hydroxyl O atom is involved in hydrogen bonds with two other hydroxyl O atoms. The resulting chains of interactions propagate along [001]. In these interactions, the hydroxyl H atoms are disordered and the O$\cdots$O distances are 2.648 (2) and 2.698 (2) Å. Two leading intermolecular C—H$\cdots$O interactions have H$\cdots$O distances of 2.80 and 2.84 Å and C—H$\cdots$O angles of 136 and 144°; these interactions form chain and ring patterns. Taken together with the hydrogen bonds, they result in a three-dimensional network.

Comment

This report is one of a series on hydrogen bonding and C—H$\cdots$O interactions in aromatic compounds. The title compound, (I), crystallized in the centrosymmetric space group $C2/c$ with one molecule as the asymmetric unit. The refined molecule and the labeling scheme are given in Fig. 1. Two hydrogen bonds and two leading intermolecular C—H$\cdots$O interactions (Taylor & Kennard, 1982; Steiner & Desiraju, 1998) are present in this structure. The geometric parameters of these are given in Table 2. The results of basic first- and second-level graph-set analysis (Bernstein et al., 1995) involving these interactions, labeled a–d for this purpose in the order of their appearance in Table 2, are given in Table 3. (For this analysis, the hydroxyl H atoms were assigned in turn to ordered positions with unit occupancy, so that each hydroxyl O atom was associated with a single unit-occupancy
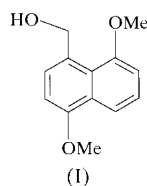
hydroxyl H atom.) At the first level, finite patterns and rings appear. The second-level patterns are all chains, propagating variously along [001], [101], [112] and [103]. Each molecule is linked by these four interactions directly to four other molecules, and a three-dimensional network results.
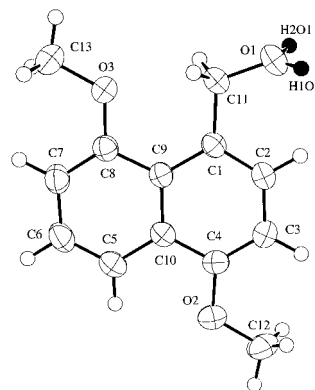

Figure 1
*ORTEP*II (Johnson, 1976) drawing of (I), showing the labeling scheme. Displacement ellipsoids are drawn for 50% probability for all non-H atoms; spheres of arbitrary small radius depict H atoms. Half-occupancy H atoms are shaded.

In the naphthalene ring of (I), the maximum deviation of any of its atoms from the best-fit plane describing them is 0.025 (1) Å, while the average deviation is 0.010 (13) Å. These values are quite similar to the corresponding values for 1,8-dimethoxynaphthalene (Cosmo et al., 1990, corrected by Fitzgerald et al., 1991), but are much smaller than those for, e.g., 1,8-bis(dimethylamino)naphthalene (Einspahr et al., 1973) or naphthalene-1,8-dicarboxylic acid (Fitzgerald et al., 1991), in which the maximum deviations are approximately 0.150 and 0.100 Å, respectively. Further, as also in 1,8-dimethoxynaphthalene, all the non-H atoms in (I) lie roughly in a plane: the maximum deviation of any non-H atom from the best-fit plane describing them is 0.062 (1) Å. In (I), the dihedral angle between naphthalene-ring planes not required by symmetry to be parallel is 71.9 (1)°. Thus, the best-fit planes of the molecules are either strictly parallel or roughly perpendicular. These features are apparent in the packing diagram, Fig. 2.

Selected bond distances and angles of (I) are given in Table 1. All distances and angles fall within normal limits. The methoxy group C—O distances agree well with those in 1,8-dimethoxynaphthalene: 1.372 (1) and 1.365 (1) *versus*
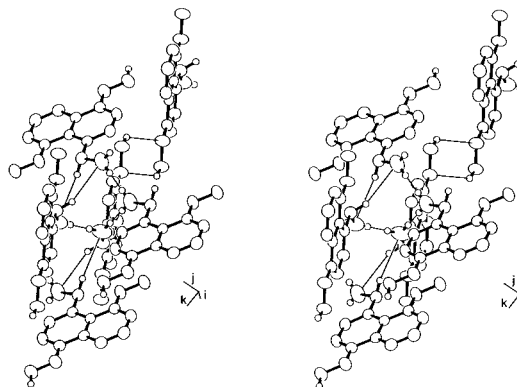

Figure 2
*ORTEP*II (Johnson, 1976) packing diagram of (I) showing a central molecule and its neighbors. Displacement ellipsoids are drawn at 20% probability for all non-H atoms; spheres of arbitrary small radius depict H atoms. Hydrogen bonds and C—H$\cdots$O interactions are depicted by the finer interatomic lines.

1.359 (2) Å, and 1.423 (1) and 1.414 (1) *versus* 1.425 (2) Å. The exterior ring angles C1—C9—C8 and C4—C10—C5 show a consistent pattern in all four of the 1,8-disubstituted molecules discussed above, with C1—C9—C8 values 124.4 (1) for (I) and 125.7, 125.8 and 126.7° for the remaining three, and with C4—C10—C5 values 120.1 (1) for (I) and 119.9, 119.6 and 120.1° for the other three. Further, a consistent pattern of C1···C8 and C4···C5 distances in which the former are ~0.1 Å greater than the latter is shown by all four of these molecules. These patterns document a distortion of the naphthalene cores associated with the 1,8-disubstitution. In (I), the closest intermolecular approaches, excluding pairs of atoms involved in the hydrogen bonding or the tabulated C—H···O interactions, are between C8 and H13$C(x, 1 - y, -\frac{1}{2} + z)$ and fall short of the corresponding Bondi (1964) van der Waals radius sum by 0.04 Å.

Experimental

Compound (I) was obtained as pale ecru thin plates from a sample in Dr D. J. Hart's chemical collection. A solution of this material in a mixed solvent (ether/acetone/ethanol/ethyl acetate) produced suitable, virtually colorless, crystals upon slow evaporation at room temperature. A synthesis is described by Young (1994).

Crystal data

$C_{13}H_{14}O_3$	Mo $K\alpha$ radiation
$M_r = 218.25$	Cell parameters from 30 322
Monoclinic, $C2/c$	reflections
$a = 32.1141$ (6) Å	$\theta = 1.27$–$27.50°$
$b = 10.3464$ (2) Å	$\mu = 0.094$ mm^{-1}
$c = 6.5790$ (1) Å	$T = 291$ K
$\beta = 94.679$ (1)$°$	Irregular polyhedron, colorless
$V = 2178.69$ (6) Å^3	$0.38 \times 0.23 \times 0.23$ mm
$Z = 8$	
$D_x = 1.331$ Mg m^{-3}	

Data collection

Nonius KappaCCD diffractometer	$R_{int} = 0.035$
ω scans with κ offsets	$\theta_{max} = 27.50°$
30 322 measured reflections	$h = -41 \rightarrow 41$
2506 independent reflections	$k = -13 \rightarrow 13$
1950 reflections with $I > 2\sigma_I$	$l = -8 \rightarrow 8$

Refinement

Refinement on F^2	H atoms: see text
$R(F) = 0.048$	$1/[\sigma_{cs}^2 + (0.037I)^2]$
$wR(F^2) = 0.126$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.98$	$\Delta\rho_{max} = 0.24$ e Å^{-3}
2506 reflections	$\Delta\rho_{min} = -0.22$ e Å^{-3}
145 parameters	

Table 1
Selected geometric parameters (Å, °).

O1—C11	1.420 (1)	O3—C8	1.365 (1)
O2—C4	1.372 (1)	O3—C13	1.414 (1)
O2—C12	1.423 (1)	C1—C11	1.517 (2)
C4—O2—C12	117.43 (9)	O2—C4—C10	114.2 (1)
C8—O3—C13	118.74 (9)	O3—C8—C7	122.8 (1)
C2—C1—C11	119.0 (1)	O3—C8—C9	115.25 (9)
C9—C1—C11	122.9 (1)	O1—C11—C1	113.42 (9)
O2—C4—C3	124.8 (1)		

Difference Fourier maps gave the initial locations of the H atoms except for the hydroxyl group. Since two hydroxyl O atoms were

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1O1$\cdots$O1^{i}	0.77	1.87	2.648 (2)	180
O1—H2O1$\cdots$O1^{ii}	0.77	1.93	2.698 (2)	180
C12—H12$C\cdots$O2^{iii}	0.98	2.80	3.572 (2)	136
C11—H11$B\cdots$O1^{iv}	0.98	2.84	3.678 (2)	144

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

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

	a	b	c	d
a	D	$C_2^2(4)$	$C_2^2(17)$	$C_2^2(5)$
b		D	$C_2^2(17)$	$C_2^2(5)$
c			$R_2^2(6)$	$C_2^2(16)$
d				$R_2^2(6)$

found to occur within (short) hydrogen-bonding distances, 2.647 (2) and 2.699 (2) Å, of a given hydroxyl O atom, a model involving a disordered hydroxyl H atom was adopted. Half-occupancy H atoms were fixed 0.77 Å from the hydroxyl O atom along the line of centers to the two hydrogen-bonded hydroxyl O atoms, and with $B = 1.2B_{eq}$ of the hydroxyl O atom. The distance, 0.77 Å, was chosen on the basis that it is the mean of two refined values for similarly disordered half-occupancy H atoms in the hydrogen bonds of naphthalene-1,8-dicarboxylic acid (Fitzgerald *et al.*, 1991).

Data collection: *COLLECT* (Nonius, 1999); cell refinement and data reduction: *DENZO-SMN* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1995); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

References

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Cosmo, R., Hambley, T. W. & Sternhell, S. (1990). *Acta Cryst.* B**46**, 557–562.
Einspahr, H., Robert, J. B., Marsh, R. E. & Roberts, J. D. (1973). *Acta Cryst.* B**29**, 1611–1617.
Fitzgerald, L. J., Gallucci, J. C. & Gerkin, R. E. (1991). *Acta Cryst.* B**47**, 776–782.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1995). *TEXSAN*. Version 1.7. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Steiner, T. & Desiraju, G. R. (1998). *J. Chem. Soc. Chem. Commun.* pp. 891–892.
Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.
Young, D. G. J. (1994). PhD dissertation, The Ohio State University, Columbus, Ohio, USA.