

Naphthalene-1,7-diol

Bernard Marciniak

Institute of Chemistry and Environment Protection, Jan Dlugosz University, al. Armii Krajowej 13/15, 42-200 Czestochowa, Poland
Correspondence e-mail: crystal@cz.onet.pl

Received 25 November 2006

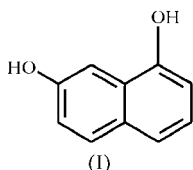
Accepted 23 February 2007

Online 31 March 2007

The asymmetric unit of the title compound, $C_{10}H_8O_2$, contains two planar symmetry-independent molecules linked by an $O-H \cdots O$ hydrogen bond. In the crystal structure, molecules are linked into infinite chains of rings, formed by a combination of $O-H \cdots O$ and $C-H \cdots O$ hydrogen bonds, and additionally reinforced by $\pi-\pi$ stacking interactions. Adjacent chains are connected by weak $C-H \cdots \pi$ interactions.

Comment

Naphthols, naphthalenediols and their derivatives are widely used as intermediates in the synthesis of dyes, tanning agents, antioxidants and antiseptics, as well as as monomers in the preparation of polymers such as polyesters and polynaphthooxazines (Bianchi *et al.*, 1997; Blundell & Buckingham, 1985; Aitken *et al.*, 1992; Shen & Ishida, 1996). Previously, we reported the structures of naphthalene-2,7-diol (Rozycka-Sokolowska *et al.*, 2005) and naphthalene-1,3-diol (Marciniak *et al.*, 2006), and present here the structure of naphthalene-1,7-diol, (I).



In the structure of (I), there are two symmetry-independent molecules, *A* and *B* (Fig. 1), in the asymmetric unit. The geometric parameters of these two molecules are similar; the bond lengths are the same within 3σ , while the bond angles differ by less than 1.1° . The bond lengths and valence angles in (I) have similar ranges to those observed in previously reported naphthalenediols (Rozycka-Sokolowska *et al.*, 2005; Marciniak *et al.*, 2006). The naphthalene rings of molecules *A* and *B* are essentially planar, with the largest r.m.s. deviations from the best least-squares planes being 0.018 (2) Å for the C1A–C10A ring and 0.026 (3) Å for the C1B–C10B ring. Hydroxyl atoms O1A/O2A and O1B/O2B are almost coplanar with the C1A–C10A and C1B–C10B rings, respectively (these

atoms deviate from the ring planes by < 0.1 Å). The dihedral angle between the mean planes of the C1A–C10A and C1B–C10B rings is $78.97(6)^\circ$. This non-coplanar orientation of two symmetry-independent molecules was also observed for naphthalene-2,3-diol (57.9° ; Belskii *et al.*, 1990), and contrasts with the nearly coplanar orientation of the independent molecules observed in naphthalene-2,6-diol [dihedral angle between the mean planes formed by the C atoms of two independent molecules = $4.6(4)^\circ$; Belskii *et al.*, 1990].

As seen in Fig. 1, the two symmetry-independent molecules of (I) are linked through an $O2B-H12B \cdots O1A$ hydrogen

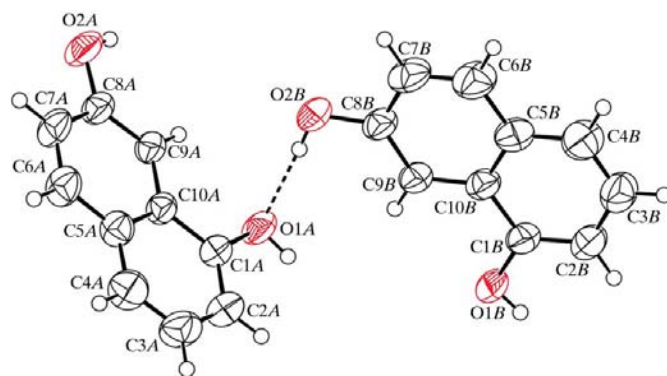


Figure 1

Views of molecules *A* and *B*, showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line depicts the intermolecular hydrogen bond.

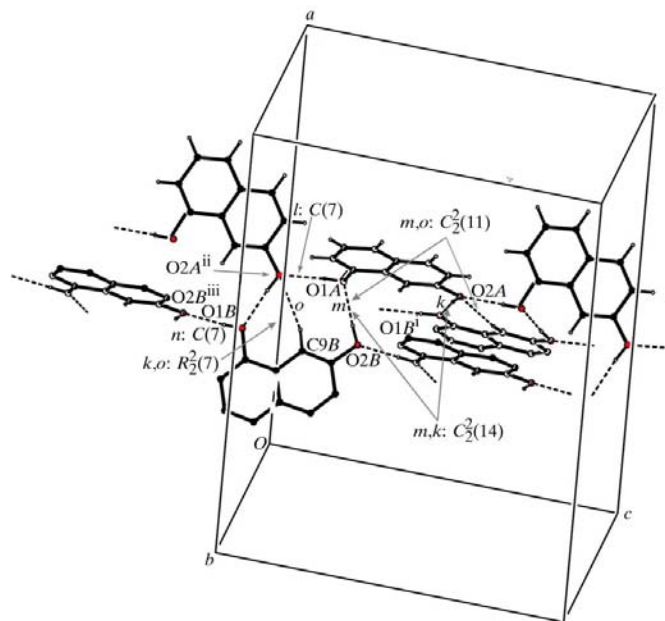


Figure 2

Part of the crystal structure of (I), with the $O-H \cdots O$ (motifs *k*, *l*, *m* and *n*) and $C-H \cdots O$ (motif *o*) interactions shown as dashed lines. Two $C(7)$ chains (*n+l* motif), the $C_2^2(11)$ and $C_2^2(14)$ chains (*m+o* and *k+m* motifs) and the $R_2^2(7)$ ring (*k+o* motif) are depicted. All H atoms of molecules *A* are included for clarity, while for molecules *B*, only atoms H11*B*, H12*B* and H9*B* are included. [Symmetry codes: (i) $x, -\frac{1}{2} - y, \frac{1}{2} + z$; (ii) $x, -\frac{1}{2} - y, -\frac{1}{2} + z$; (iii) $\frac{1}{2} - x, y, -\frac{1}{2} + z$.]

bond (motif *m*; Table 1 and Fig. 2), which can be described by the graph-set notation *D* (Bernstein *et al.*, 1995). In the crystal structure of (I), there are also three intermolecular O—H...O hydrogen bonds and one C—H...O intermolecular hydrogen bond (Table 1 and Fig. 2). On the first-level graph-set, the O2A—H12A...O1Bⁱ (motif *k*, Fig. 2) and C9B—H9B...O2Aⁱⁱ (motif *o*, Fig. 2) hydrogen bonds are also classified as *D* [symmetry codes: (i) $x, -\frac{1}{2} - y, \frac{1}{2} + z$; (ii) $x, -\frac{1}{2} - y, -\frac{1}{2} + z$]. O1A—H11A...O2Aⁱⁱⁱ (motif *l*, Fig. 2) hydrogen bonds link each molecule *A* to adjacent molecules *A*, forming a *C*(7) chain along the *c* axis. A *C*(7) chain parallel to this and in the same direction is also formed by the O1B—H11B...O2Bⁱⁱⁱ

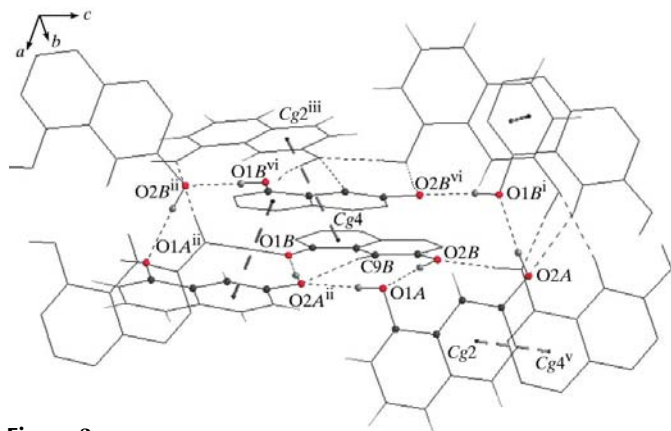


Figure 3

Part of the crystal structure of (I), with the chain of $R_5^3(25)$ and $R_3^3(11)$ rings formed by the O—H...O hydrogen bonds denoted by thin dashed lines (atoms in these rings are spheres), and with π — π stacking interactions indicated by bold dashed lines. Cg2 and Cg4 are the centroids of the C5A—C10A and C5B—C10B rings, respectively, and are shown as small spheres. All H atoms of molecules *A* are included for clarity, while in molecules *B*, only atoms H11B, H12B and H9B are included. [Symmetry codes: (i) $x, -\frac{1}{2} - y, \frac{1}{2} + z$; (ii) $x, -\frac{1}{2} - y, -\frac{1}{2} + z$; (iii) $\frac{1}{2} - x, y, -\frac{1}{2} + z$; (v) $\frac{1}{2} - x, y, \frac{1}{2} + z$; (vi) $\frac{1}{2} - x, -\frac{1}{2} - y, z$.]

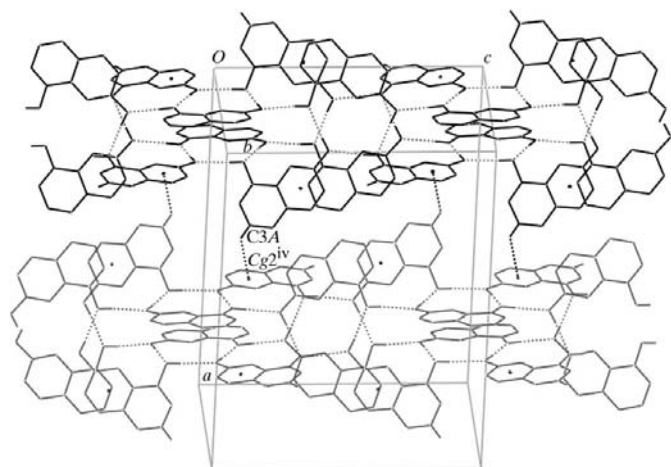


Figure 4

Part of the crystal structure of (I), showing adjacent chains of $R_5^3(25)$ and $R_3^3(11)$ rings formed by O—H...O hydrogen bonds (grey dashed lines) with the intermolecular C—H... π interactions (black dashed lines). The centroids Cg2 of the C5A—C10A rings are denoted by small crosses. All C-bound H atoms, except for atom H3A, have been omitted for clarity. [Symmetry code: (iv) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$.]

hydrogen bond (motif *n*, Fig. 2) between the hydroxyl groups of molecules *B* [symmetry code: (iii) $\frac{1}{2} - x, y, -\frac{1}{2} + z$]. Motifs *m* and *k* form a chain with the $C_2^2(14)$ second-level graph-set descriptor (Fig. 2), while motifs *m* and *o* form a chain with the $C_2^2(11)$ descriptor, and motifs *k* and *o* form a pattern with the $R_2^2(7)$ descriptor (Fig. 2). Information on the binary graph-set descriptors is given in Table 2.

As can be seen from Fig. 3, atoms O1B in the molecules at $(x, -\frac{1}{2} - y, \frac{1}{2} + z)$ and $(\frac{1}{2} - x, -\frac{1}{2} - y, z)$ act as hydrogen-bond donors to atoms O2B at $(\frac{1}{2} - x, -\frac{1}{2} - y, z)$ and $(x, -\frac{1}{2} - y, -\frac{1}{2} + z)$, respectively. This latter atom O2B acts as hydrogen-bond donor to atom O1A at $(x, -\frac{1}{2} - y, -\frac{1}{2} + z)$. These three hydrogen bonds, together with motifs *k* and *l*, form an $R_5^3(25)$ ring, whereas motifs *m* and *l* with O2Aⁱⁱ—H12Aⁱⁱ...O1B form an $R_3^3(11)$ ring, which is reinforced by the C9B—H9B...O2Aⁱⁱ interaction. The combined effect is the formation of a chain of edge-fused rings running parallel to the [001] direction, with $R_5^3(25)$ rings alternating with $R_3^3(11)$ rings (Fig. 3). Additionally, the chain is reinforced by an intermolecular π — π stacking interaction involving the C5A—C10A (centroid Cg2) and C5B—C10B (centroid Cg4) rings (Fig. 3). The perpendicular distance of the ring centroids Cg2 and Cg4 from the symmetry-related centroids at $(\frac{1}{2} - x, y, \frac{1}{2} + z)$ and $(\frac{1}{2} - x, y, -\frac{1}{2} + z)$, *i.e.* Cg4^v and Cg2ⁱⁱⁱ, respectively, is 3.4189 (8) Å, and the centroid-to-centroid separation is 3.782 (1) Å. The planes of these rings are practically parallel, at an angle of 8.21 (7)°. Adjacent chains are linked by C—H... π hydrogen bonds (Fig. 4 and Table 1) into a three-dimensional network.

Experimental

As starting material, commercially available naphthalene-1,7-diol (Sigma Aldrich, purity 99%) was used. Two impurities, namely 1- and 2-naphthol, were detected and identified in this material using gas chromatography. Analyses were performed on a Hewlett–Packard 6890 GC System gas chromatograph with FID detector [fused silica capillary column of dimensions 30 m \times 0.32 mm internal diameter; HP1 methyl silicone stationary phase; split/splitless type injector; helium as carrier gas; 1 μ l sample of 10% solution of (I) in ethanol]. For the identification of these impurities, a Hewlett–Packard 5890 Series II gas chromatograph equipped with an MS detector was also used; this chromatograph operated under nearly the same conditions. To remove the detected impurities, the starting material was purified by twofold crystallization from anhydrous ethanol. Crystals of (I) were grown from a solution in this solvent by slow evaporation at a constant temperature of 293 K.

Crystal data

C ₁₀ H ₈ O ₂	$V = 3182.6 (7) \text{ \AA}^3$
$M_r = 160.16$	$Z = 16$
Orthorhombic, <i>Pccn</i>	Mo $K\alpha$ radiation
$a = 21.423 (3) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$b = 9.5150 (10) \text{ \AA}$	$T = 290 (2) \text{ K}$
$c = 15.613 (2) \text{ \AA}$	$0.24 \times 0.08 \times 0.07 \text{ mm}$

Data collection

Oxford Xcalibur3 CCD area-detector diffractometer	15692 measured reflections
Absorption correction: analytical (<i>CrysAlis RED</i> ; Oxford Diffraction, 2005)	2802 independent reflections
$T_{\min} = 0.930, T_{\max} = 0.998$	1924 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.025$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.123$	
$S = 1.09$	
2802 reflections	$\Delta\rho_{\max} = 0.19 \text{ e \AA}^{-3}$
238 parameters	$\Delta\rho_{\min} = -0.15 \text{ e \AA}^{-3}$

Table 1
Hydrogen-bonding geometry (Å, °).

Cg2 is the centroid of the C5A–C10A ring.

Motif	D–H...A	D–H	H...A	D...A	D–H...A
<i>k</i>	O2A–H12A...O1B ⁱ	0.84 (2)	1.98 (2)	2.812 (2)	175 (3)
<i>l</i>	O1A–H11A...O2A ⁱⁱ	0.84 (2)	1.99 (2)	2.825 (2)	175 (2)
<i>m</i>	O2B–H12B...O1A	0.85 (2)	1.96 (2)	2.806 (2)	176 (3)
<i>n</i>	O1B–H11B...O2B ⁱⁱⁱ	0.83 (2)	1.93 (2)	2.763 (2)	175 (3)
<i>o</i>	C9B–H9B...O2A ⁱⁱ	0.95 (2)	2.55 (2)	3.459 (3)	160 (2)
	C3A–H3A...Cg2 ^{iv}	0.93	2.95	3.634 (3)	131

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

Table 2
First- and second-level graph-set descriptors involving hydrogen bonds designated *k, l, m, n* and *o*.

	<i>k</i>	<i>l</i>	<i>m</i>	<i>n</i>	<i>o</i>
<i>k</i>	<i>D</i>	$D_3^3(12)$	$C_3^2(14)$	$D_3^3(10)$	$R_3^2(7)$
<i>l</i>		$C(7)$	$D_3^3(10)$		$D_3^3(10)$
<i>m</i>			<i>D</i>	$D_3^3(12)$	$C_3^2(11)$
<i>n</i>				$C(7)$	$D_3^3(12)$
<i>o</i>					<i>D</i>

All H atoms, except those on atoms O1A, O2A, O1B, O2B and C9B (involved in hydrogen bonding), were included in the refinement in geometrically calculated positions and refined using a riding model, with C–H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. O-bound H atoms and atom H9B were located in a difference Fourier map and refined with isotropic displacement parameters. All O–H distances for the hydroxyl groups were restrained to 0.83 (3) Å using the DFIX command in *SHELXL97* (Sheldrick, 1997), while the C9B–H9B distance was restrained with a DFIX instruction to 0.93 (3) Å.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *SHELXL97*.

The author is grateful to Dr E. Dziwinski from the Institute of Heavy Organic Synthesis in Kedzierzyn Kozle for help with the gas chromatographic analysis.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3057). Services for accessing these data are described at the back of the journal.

References

Aitken, C. L., McHattie, J. S. & Paul, D. R. (1992). *Macromolecules*, **25**, 2910–2922.

Belskii, V. K., Kharchenko, E. V., Sobolev, A. N., Zavodnik, V. E., Kolomiets, N. A., Prober, G. S. & Oleksenko, L. P. (1990). *Zh. Strukt. Khim. (Russ. J. Struct. Chem.)*, **31**, 116–121. (In Russian.)

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Bianchi, D., Bernardi, A., Bosetti, A., Bortolo, R., Cidaria, D., Crespi, E. & Gagliardi, I. (1997). *Appl. Microbiol. Biotechnol.* **48**, 363–366.

Blundell, D. J. & Buckingham, K. A. (1985). *Polymer*, **26**, 1623–1627.

Brandenburg, K. (2006). *DIAMOND*. Release 3.1d. Crystal Impact GbR, Bonn, Germany.

Marciniak, B., Rozycka-Sokolowska, E. & Pavlyuk, V. (2006). *Acta Cryst.* **C62**, o68–o70.

Oxford Diffraction (2004). *CrysAlis CCD*. Version 1.170. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

Oxford Diffraction (2005). *CrysAlis RED*. Version 1.171. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.

Rozycka-Sokolowska, E., Marciniak, B. & Pavlyuk, V. (2005). *Acta Cryst.* **E61**, o114–o115.

Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Shen, S. B. & Ishida, H. (1996). *J. Appl. Polym. Sci.* **61**, 1595–1605.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.