

## Naphthalene-1,6-diol: a three-dimensional framework built from O—H···O, O—H··· $\pi$ and C—H···O hydrogen bonds

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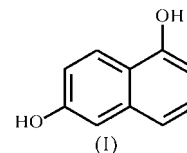
Received 6 April 2007  
Accepted 30 May 2007  
Online 23 June 2007

The asymmetric unit of the title compound, C<sub>10</sub>H<sub>8</sub>O<sub>2</sub>, contains two practically planar symmetry-independent molecules linked by one O—H···O hydrogen bond. Molecules are further linked into a three-dimensional network, which is built from  $R_6^6(36)$ ,  $R_6^6(18)$ ,  $R_6^6(30)$  and  $R_4^4(26)$  rings formed by the combined effect of three O—H···O and one C—H···O hydrogen bond. This network is additionally stabilized by an O—H··· $\pi$  interaction.

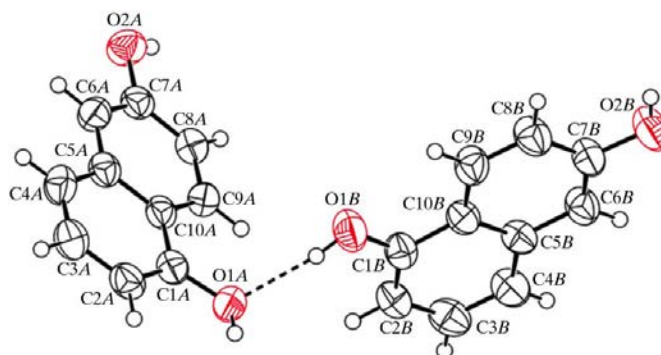
### Comment

This paper is a continuation of our structural studies of mono- and dihydroxynaphthalenes, which are a class of intermediates important for applications in the synthesis of dyes, tanning agents, antioxidants and antiseptics. In the previous papers, the structures of 1-hydroxynaphthalene (1-naphthol; Rozycka-Sokolowska *et al.*, 2004), 2-hydroxynaphthalene (2-naphthol; Marciniak *et al.*, 2003), 1,3-dihydroxynaphthalene

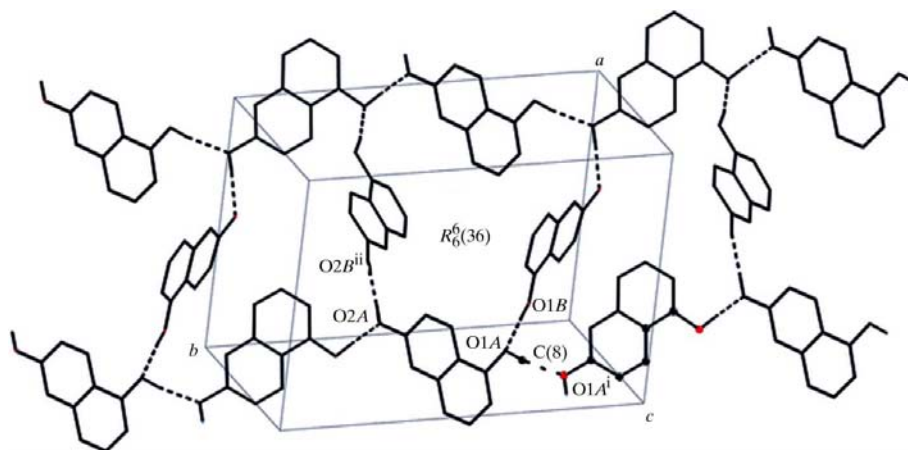
(naphthalene-1,3-diol; Marciniak *et al.*, 2006), 1,7-dihydroxynaphthalene (naphthalene-1,7-diol; Marciniak, 2007) and 2,7-dihydroxynaphthalene (naphthalene-2,7-diol; Rozycka-Sokolowska *et al.*, 2005) have been reported, and the results of structural studies of naphthalene-1,6-diol, (I), are presented here.



As in the case of the other naphthalenediol isomers, such as naphthalene-1,7-diol (Marciniak, 2007), naphthalene-2,3-diol and naphthalene-2,6-diol (Belskii *et al.*, 1990), in the structure of the title compound there are two symmetry-independent molecules, *A* and *B*, in the asymmetric unit, which are linked by an O—H···O hydrogen bond (Fig. 1 and Table 2). The C—C bond distances range from 1.351 (3) to 1.425 (3) Å in molecule *A* and from 1.337 (3) to 1.413 (3) Å in molecule *B* (Table 1). In each molecule, four C—C bonds, *viz.* C1A—C2A,

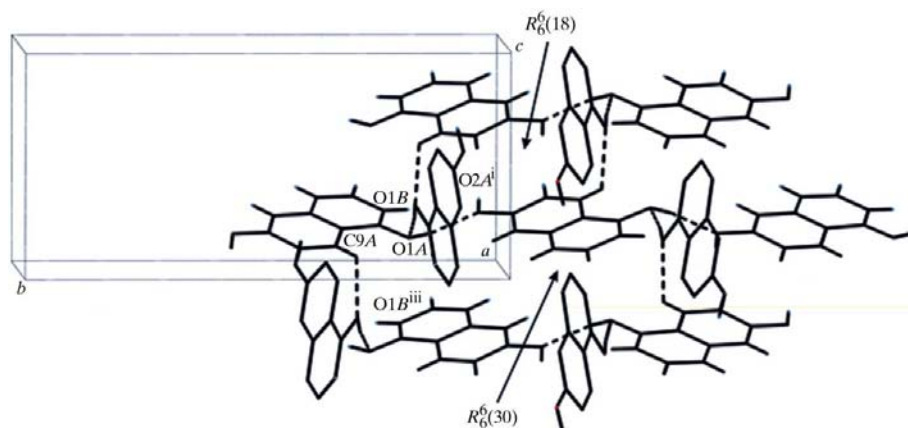


**Figure 1**  
Views of molecules *A* (left) and *B* (right), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The dashed line depicts the intermolecular hydrogen bond.

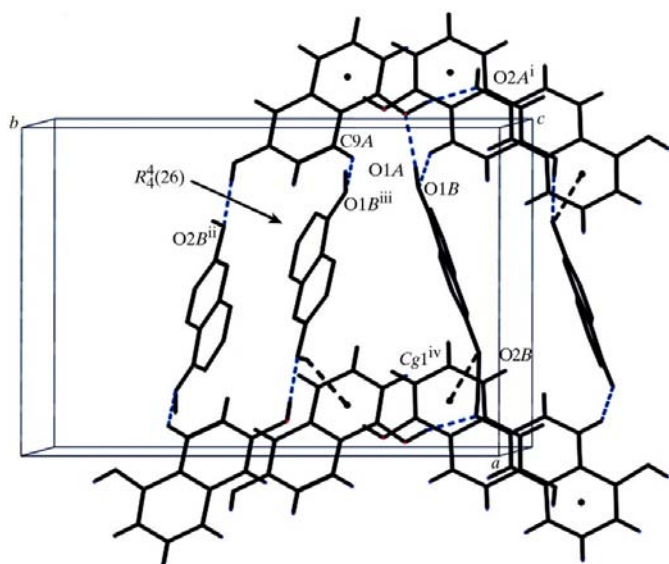


**Figure 2**

Part of the crystal structure of (I), showing the O—H···O hydrogen bonds (dashed lines, see Table 1 for details), as well as the C(8) chains (atoms belonging to this chain are represented by spheres) and the  $R_6^6(36)$  rings. All H atoms not involved in these hydrogen bonds have been omitted for clarity.


**Figure 3**

Part of the crystal structure of (I), showing the  $R_6^6(18)$  and  $R_6^6(30)$  rings formed by O—H...O and C—H...O hydrogen bonds (shown as dashed lines); symmetry codes are as given in Table 1. In order to differentiate molecules A and B, all H atoms of molecules A are included, while the H atoms of molecules B, except for atoms H11B and H12B, have been omitted.


**Figure 4**

Part of the crystal structure of (I), showing the  $R_3^3(26)$  rings formed by O—H...O and C—H...O hydrogen bonds (grey dashed lines), as well as the intermolecular O—H... $\pi$  interactions (black dashed lines). Symmetry codes are as given in Table 1; the centroid ( $Cg1$ ) of the C1A—C5A/C10A benzene ring is denoted by a small sphere. In order to differentiate molecules A and B, all H atoms of molecules A are included, while the H atoms of molecules B, except for atoms H11B and H12B, have been omitted.

C3A—C4A, C6A—C7A and C8A—C9A, and C1B—C2B, C3B—C4B, C6B—C7B and C8B—C9B, are shorter than the typical aromatic bond length of 1.384 (13) Å (Allen *et al.*, 1987), whereas all the other bonds are longer; the valence angles within the aromatic rings of these molecules lie in the ranges 118.4 (2)–122.6 (2) and 118.8 (2)–122.4 (2)°, respectively (Table 1). The naphthalene C1A—C10A and C1B—C10B ring systems are practically planar, with largest out-of-plane deviations of 0.049 (2) and  $-0.027$  (2) Å for atoms C1A and C1B, respectively. The O atoms attached to these rings at atoms C1A, C7A, C1B and C7B deviate from the planes of

these rings by only 0.130 (2), 0.029 (2),  $-0.062$  (2) and  $-0.056$  (2) Å, respectively. The angle between the mean planes formed by the C atoms of molecules A and B is 81.46 (7)°. This value is in close agreement with that observed for the other naphthalenediol isomer containing two independent molecules, *viz.* naphthalene-1,7-diol [the dihedral angle between the mean planes formed by the C atoms of the two independent molecules is 78.97° (Marciniak, 2007)], and it is about 25° less than the value of this parameter observed for naphthalene-2,3-diol (Belskii *et al.*, 1990). This noncoplanar orientation of two symmetry-independent molecules observed in (I) is in contrast to the nearly coplanar orientation of the independent molecules observed in naphthalene-2,6-diol [the dihedral angle between the mean planes formed by the C atoms of the two independent molecules is 4.6 (4)° (Belskii *et al.*, 1990)].

Apart from the above-mentioned O1B—H11B...O1A hydrogen bond, the crystal structure of (I) contains two intermolecular O—H...O hydrogen bonds and one intermolecular C—H...O hydrogen bond (Table 2 and Figs. 2–4). The O1A—H11A...O2A<sup>i</sup> interactions [symmetry code: (i)  $-x, y - \frac{1}{2}, -z + \frac{1}{2}$ ] link the A molecules into a C(8) chain (Bernstein *et al.*, 1995) running parallel to the [010] direction (Fig. 2). The A molecules belonging to the C(8) chains are connected to B molecules by two O—H...O hydrogen bonds, *viz.* O1B—H11B...O1A and O2A—H12A...O2B<sup>ii</sup> [symmetry code: (ii)  $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$ ], which are classified as *D* on the first-level graph set (Bernstein *et al.*, 1995). The combined effect of these three O—H...O hydrogen bonds is the formation of a puckered sheet parallel to the (001) plane containing  $R_6^6(36)$  rings (Fig. 2). The non-H atoms belonging to the (001) sheets lie in the domains  $(-0.05 + z/2) < c < (0.55 + z/2)$  (where  $z$  is zero or an integer). Moreover, each such sheet is linked to two neighbouring sheets by a classical O—H... $\pi$  hydrogen bond and a weak C—H...O hydrogen bond to form a continuous three-dimensional network (Fig. 4). Atom O2B in molecule B at  $(x, y, z)$ , belonging to the sheet in domain  $-0.05 < c < 0.55$ , acts as a hydrogen-bond donor, *via* atom H12B, to the C1A—

C5A/C10A benzene ring of molecule *A* at  $(x + 1, -y + \frac{1}{2}, z + \frac{1}{2})$ , which belongs to the adjacent sheet in domain  $0.45 < c < 1.05$ . As mentioned above, the structure of (I) also displays a C—H···O interaction, which links atom C9A of molecule *A* at  $(x, y, z)$ , via H9A, with atom O1B at  $(x, -y + \frac{1}{2}, z - \frac{1}{2})$ , and this can be described by the graph-set notation *D* (Fig. 2 and Table 1). A detailed analysis of the three-dimensional network indicates that, apart from the above-mentioned  $R_6^6(36)$  rings, this network contains  $R_6^6(18)$  and  $R_6^6(30)$  rings formed by the combined effect of the O1B—H11B···O1A, O1A—H11A···O2A<sup>i</sup> and C9A—H9A···O1B<sup>iii</sup> hydrogen bonds (Fig. 3), as well as  $R_4^4(26)$  rings by a combination of the C9A—H9A···O1B<sup>iii</sup> and O2A—H12A···O2B<sup>ii</sup> hydrogen bonds [symmetry code: (iii)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ] (Fig. 4).

## Experimental

The starting material was commercially available naphthalene-1,6-diol (Sigma Aldrich, purity 99%), which was purified by twofold crystallization from anhydrous ethanol (no impurities were detected by gas chromatography). Crystals of (I) were grown from solution in chloroform by slow evaporation of this solvent at a constant temperature of 293 K.

### Crystal data

C <sub>10</sub> H <sub>8</sub> O <sub>2</sub>	$V = 1540.1 (5) \text{ \AA}^3$
$M_r = 160.16$	$Z = 8$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 11.5109 (19) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$b = 16.882 (3) \text{ \AA}$	$T = 290 (2) \text{ K}$
$c = 7.9362 (19) \text{ \AA}$	$0.39 \times 0.33 \times 0.06 \text{ mm}$
$\beta = 93.034 (17)^\circ$	

### Data collection

Oxford Diffraction Xcalibur3 CCD diffractometer	8646 measured reflections
Absorption correction: analytical ( <i>CrysAlis RED</i> ; Oxford Diffraction, 2005)	2709 independent reflections
$T_{\min} = 0.996, T_{\max} = 0.999$	2034 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.045$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.058$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.140$	$\Delta\rho_{\text{max}} = 0.15 \text{ e \AA}^{-3}$
$S = 1.18$	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
2709 reflections	
238 parameters	
5 restraints	

H atoms involved in hydrogen-bond formation (attached to atoms O1A, O2A, O1B, O2B and C9A) were located in a difference Fourier map and refined with isotropic displacement parameters. All O—H distances and a C—H distance were restrained with DFIX 0.83 (3) Å and DFIX 0.93 (3) Å commands (Sheldrick, 1997), respectively. All other H atoms were included in the refinement at geometrically calculated positions and refined using a riding model, with C—H distances of 0.93 Å and with  $U_{\text{iso}}(\text{H})$  values set at  $1.2U_{\text{eq}}(\text{C})$ .

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*.

**Table 1**  
Selected geometric parameters (Å, °).

O1A—C1A	1.363 (3)	O1B—C1B	1.357 (3)
O2A—C7A	1.368 (3)	O2B—C7B	1.371 (3)
C1A—C2A	1.359 (3)	C1B—C2B	1.345 (3)
C1A—C10A	1.425 (3)	C1B—C10B	1.409 (3)
C2A—C3A	1.397 (3)	C2B—C3B	1.398 (4)
C3A—C4A	1.351 (3)	C3B—C4B	1.346 (3)
C4A—C5A	1.415 (3)	C4B—C5B	1.400 (3)
C5A—C6A	1.406 (3)	C5B—C6B	1.405 (3)
C5A—C10A	1.412 (3)	C5B—C10B	1.413 (3)
C6A—C7A	1.365 (3)	C6B—C7B	1.337 (3)
C7A—C8A	1.401 (3)	C7B—C8B	1.400 (3)
C8A—C9A	1.352 (3)	C8B—C9B	1.350 (3)
C9A—C10A	1.402 (3)	C9B—C10B	1.394 (3)
C2A—C1A—O1A	123.6 (2)	C2B—C1B—O1B	123.3 (2)
C2A—C1A—C10A	120.5 (2)	C2B—C1B—C10B	121.0 (2)
O1A—C1A—C10A	115.9 (2)	O1B—C1B—C10B	115.7 (2)
C1A—C2A—C3A	120.4 (2)	C1B—C2B—C3B	119.4 (2)
C4A—C3A—C2A	120.8 (2)	C4B—C3B—C2B	122.0 (2)
C3A—C4A—C5A	120.8 (2)	C3B—C4B—C5B	119.9 (2)
C6A—C5A—C10A	118.5 (2)	C4B—C5B—C6B	122.1 (2)
C6A—C5A—C4A	122.6 (2)	C4B—C5B—C10B	119.0 (2)
C10A—C5A—C4A	118.9 (2)	C6B—C5B—C10B	118.9 (2)
C7A—C6A—C5A	120.5 (2)	C7B—C6B—C5B	120.4 (2)
C6A—C7A—O2A	119.1 (2)	C6B—C7B—O2B	117.9 (2)
C6A—C7A—C8A	120.4 (2)	C6B—C7B—C8B	121.0 (2)
O2A—C7A—C8A	120.5 (2)	O2B—C7B—C8B	121.2 (2)
C9A—C8A—C7A	120.3 (2)	C9B—C8B—C7B	120.1 (2)
C8A—C9A—C10A	120.7 (2)	C8B—C9B—C10B	120.8 (2)
C9A—C10A—C5A	119.5 (2)	C9B—C10B—C1B	122.4 (2)
C9A—C10A—C1A	122.1 (2)	C9B—C10B—C5B	118.8 (2)
C5A—C10A—C1A	118.4 (2)	C1B—C10B—C5B	118.8 (2)

**Table 2**  
Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the C1A—C5A/C10A benzene ring.

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O1A—H11A···O2A <sup>i</sup>	0.86 (3)	1.89 (3)	2.726 (3)	165 (3)
O1B—H11B···O1A	0.84 (2)	1.96 (2)	2.783 (3)	169 (3)
O2A—H12A···O2B <sup>ii</sup>	0.83 (2)	1.91 (2)	2.737 (3)	176 (2)
C9A—H9A···O1B <sup>iii</sup>	0.95 (2)	2.54 (2)	3.191 (3)	126 (2)
O2B—H12B···Cg1 <sup>iv</sup>	0.84 (2)	2.55 (3)	3.243 (2)	140 (3)

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3120). Services for accessing these data are described at the back of the journal.

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