organic compounds

4-Methoxy-1-naphthol: chains formed by O—H···O hydrogen bonds and π–π stacking interactions

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The structure of 4-methoxy-1-naphthol, $C_{11}H_{10}O_2$, (I), contains an intermolecular O—H···O hydrogen bond which links the molecules into a simple $C(2)$ chain running parallel to the shortest crystallographic b axis. This chain is reinforced by intermolecular π–π stacking interactions. Comparisons are drawn between the crystal structure of (I) and those of several of its simple analogues, including 1-naphthol and some monosubstituted derivatives, and that of its isomer 7-methoxy-2-naphthol. This comparison shows a close similarity in the packing of the molecules of its simple analogues that form π-stacks along the shortest crystallographic axes. A substantial spatial overlap is observed between adjacent molecules in such stacks. In this group of monosubstituted naphthols, the overlap depends mainly on the position of the substituents carried by the naphthalene moiety, and the extent of the overlap depends on the substituent type. By contrast with (I), in the crystal structure of the isomeric 7-methoxy-2-naphthol there are no O—H···O hydrogen bonds or π–π stacking interactions, and sheets are formed by O—H···π and C—H···π interactions.

Comment

This paper is a continuation of our structural studies of 1-naphthol derivatives carrying different substituents at positions 4 or 5. In previous papers, the structures of 4-chloro-1-naphthol [CSD (Allen, 2002) refcode BOTSOT; Rozycka-Sokolowska & Marciniak, 2009a] and 5-amino-1-naphthol (Rozycka-Sokolowska & Marciniak, 2009b) have been reported, and it was found that these compounds and also several of their simple analogues, i.e. 1-naphthol (CSD refcode NAPHOL01; Rozycka-Sokolowska et al., 2004), 1,4- and 1,5-dihydroxynaphthalene [CSD refcodes NPHHQU10 (Gaultier & Hauw, 1967) and VOGRUE (Belskii et al., 1990), respectively], 1,4-dichloro- and 1,5-dibromonaphthalene [CSD refcodes DCLNAQ (Bellows et al., 1978) and DBRNAQ01 (Trotter, 1986), respectively], show π-stacking with substantial

spatial overlap in the solid state. Hence they can be regarded as particularly attractive materials for the development of devices with high charge-carrier mobilities (Anthony et al., 2002; Li et al., 1998; Horowitz et al., 1996; Laquindanum et al., 1997; Chen et al., 2006).
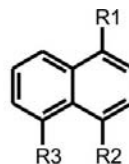

(I) R1=OH, R2=OCH₃, R3=H
(II) R1=OH, R2=R3=H (CSD refcode NAPHOL01)
(III) R1=R2=OH, R3=H (CSD refcode NPHHQU10)
(IV) R1=R3=OH, R2=H (CSD refcode VOGRUE)
(V) R1=OH, R2=Cl, R3=H (CSD refcode BOTSOT)
(VI) R1=OH, R2=H, R3=NH₂
 (Rozycka-Sokolowska & Marciniak, 2009a)
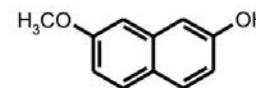
(VII) CSD refcode TEBFIP

We report here the structure of the title compound, (I) (Fig. 1), as a further example from the group of 4- or 5-substituted 1-naphthols. This work was undertaken to check whether (I), from the viewpoint of the crystal packing, will turn out to be a promising material for applications in electronic device fabrication. We also compare the crystal structure of (I) with those of five of its simple analogues (see scheme), i.e. 1-naphthol, (II), 1,4-dihydroxynaphthalene, (III), 1,5-dihydroxynaphthalene, (IV), 4-chloro-1-naphthol, (V), and 5-amino-1-naphthol, (VI), and also with that of the isomeric 7-methoxy-2-naphthol, (VII) (CSD refcode TEBFIP; Prince et al., 1991).

The values of bond distances (Table 1) and valence angles within the aromatic rings are in the ranges 1.353 (3)–1.424 (3) Å and 118.6 (2)–122.7 (2)°, respectively. From among 11 C_{ar}—C_{ar} bonds, four (C1—C2, C3—C4, C6—C7 and C8—C9) are shorter on average by 0.027 Å than the typical aromatic bond length [1.384 (13) Å] given by Allen et al. (1987), and all the other bonds are longer on average by 0.031 Å (Table 1). The C1—O1 bond length is in close
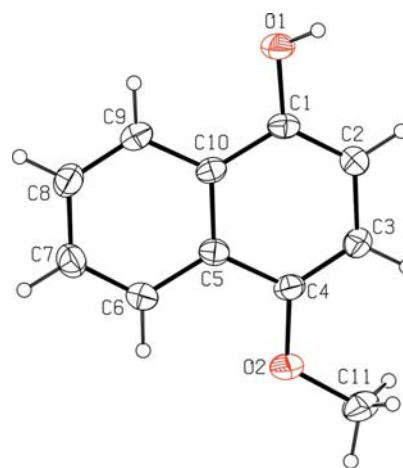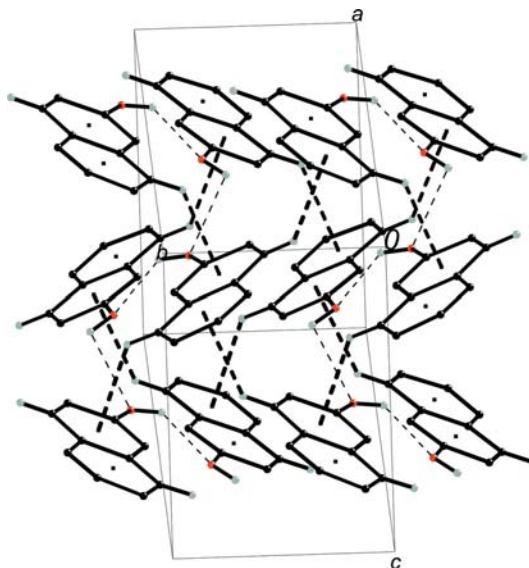

Figure 1
A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.
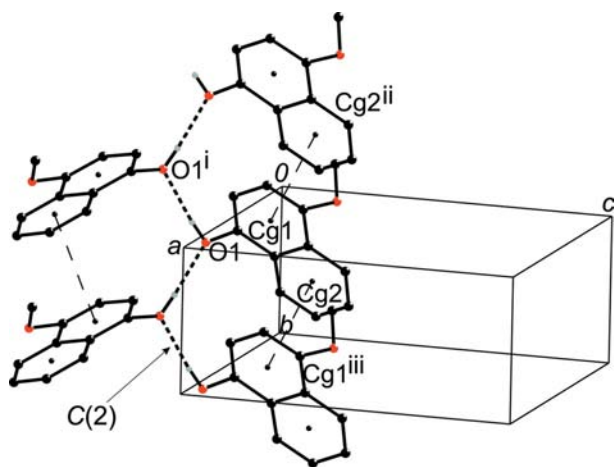
Figure 2
Part of the crystal structure of (I), showing the interstack O—H···O hydrogen bond forming a $C(2)$ chain along the [010] direction, and the intrastack π–π interactions. H atoms not involved in hydrogen bonding have been omitted for clarity. $Cg1$ and $Cg2$ are the centroids of the C1–C5/C10 and C5–C10 benzene rings, respectively, and are denoted by small spheres. [Symmetry codes: (i) $-x + 2, -\frac{1}{2} + y, -z$; (ii) $x, -1 + y, z$; (iii) $x, 1 + y, z$.]

agreement with the corresponding distances in the simple analogues of (I), such as (II), (III), (IV), (V) and (VI) [1.376 (1), 1.377, 1.385, 1.394 (3) and 1.379 (4) Å, respectively], and the lengths of the C4—O2 and O2—C11 bonds compare well with those found in (VII) and in the methoxy derivatives of naphthalene such as 2-methoxynaphthalene [C_{ar}—O = 1.3749 (11) Å and O—C_{methyl} = 1.4250 (14) Å; CSD refcode SAYRIT (Bolte & Bauch, 1998)], 1,4-dimethoxy-naphthalene [C_{ar}—O = 1.37 (1) and 1.39 (1) Å, and O—C_{methyl} = 1.46 (1) and 1.44 (1) Å; CSD refcode ALUJIA (Wiedenfeld *et al.*, 1999)] and 1,8-dimethoxynaphthalene [C_{ar}—O = 1.359 (2) and 1.362 (2) Å, and O—C_{methyl} = 1.425 (2) and 1.419 (2) Å; CSD refcode KEPKUL (Cosmo *et al.*, 1990)] and with the values given by Allen & Kirby (1984). The ten-membered aromatic ring formed by atoms C1–C10 is planar, with the largest out-of-plane deviation of −0.015 (2) Å for atom C9. The deviations of hydroxy atom O1 and methoxy atoms O2 and C11 from this plane are only 0.013 (2), −0.015 (2) and −0.117 (3) Å, respectively.

Each molecule of (I) is connected to two others by a strong, nearly linear, O—H···O hydrogen bond (Table 2). Hydroxy atoms O1 in the molecules at (x, y, z) and $(2 - x, \frac{1}{2} + y, -z)$ act as hydrogen-bond donors to atoms O1 at $(2 - x, -\frac{1}{2} + y, -z)$ and (x, y, z), respectively, so forming a simple $C(2)$ chain (Fig. 2). This chain runs parallel to the shortest crystallographic axis, *i.e.* axis b, and contains molecules related by the 2_1 screw axis. There are no interactions between adjacent $C(2)$ chains. However, in the crystal structure of (I), there is also an intermolecular π–π stacking interaction, which involves the C1–C5/C10 (centroid $Cg1$) and C5–C10 (centroid $Cg2$) benzene rings (Fig. 2). The perpendicular distances of the ring centroids $Cg1$ and $Cg2$ from the planes containing the translation-related centroids $Cg2$ at $(x, -1 + y, z)$ and $Cg1$ at $(x, 1 + y, z)$, respectively, are 3.514 (1) and 3.513 (1) Å, and the
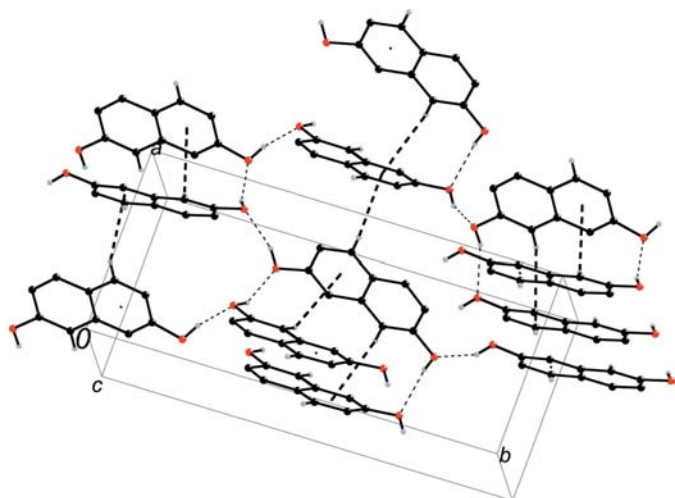

Figure 3
Part of the crystal structure of NAPHOB03 (Marciniak *et al.*, 2003), showing a sheet parallel to the (100) plane formed by O—H···O (thin dashed lines) and C—H···π (thick dashed lines) hydrogen bonds. All aromatic H atoms not involved in these interactions have been omitted for clarity. The centroids of benzene rings are denoted by small black squares.

Cg···Cg separation is 3.610 (1) Å. The planes of rings C1–C5/C10 and C5–C10 make an angle of only 0.43 (6)°. These aromatic π-stacking forces are an important factor in the stabilization of the one-dimensional chain in (I). Similarly, as in the cases of (II)–(VI), in order to estimate the area overlap (AO) of adjacent π-stacking molecules, the phenomenological approach proposed by Curtis *et al.* (2004), in combination with a simple model introduced by Janzen *et al.* (2004), was used. Analysis of the values of estimated parameters such as the pitch (P) and roll (R) angles, and the pitch (dp) and roll (dr) distances, and the value of AO, indicates that the solid-state packing of (I) provides a substantial overlap between molecules in the π-stack ($P = 42.07° > R = 8.95°$, $dp = 3.18$ Å $> dr = 0.55$ Å and AO = 27.4%). A comparison of the AO value estimated for (I) with the values given in our previous paper (Rozycka-Sokolowska & Marciniak, 2009*a*) for (II), (III) and (V) ($AO_{II} = 27.0\%$, $AO_{III} = 31.5\%$ and $AO_{V} = 40.7\%$) leads to the conclusion that modification of the molecular structure of (II) by replacement of one H atom at the 4-position by one hydroxy group or one Cl atom results in an increase of this overlap by 4.5 and 13.7%, respectively; in the case of methoxy substitution, the AO value is only 0.4% larger than that estimated for (II).

It is noteworthy that the presence of π-stacks with overlap between adjacent molecules is not a characteristic of the herringbone packing ($P < R$, $dp < dr$) in 1,3-, 1,6- and 1,7-dihydroxynaphthalene [CSD refcodes: HEGFAB (Marciniak *et al.*, 2006), RIGMOK (Marciniak, 2007*b*) and LICKEO (Marciniak, 2007*a*), respectively], in 2-naphthol [CSD refcode NAPHOB03 (Marciniak *et al.*, 2003)] and its simple derivatives such as (VII), 2,3-, 2,6- and 2,7-dihydroxynaphthalene [CSD refcodes: VOGSEP and VOGSAL (Belskii *et al.*, 1990),
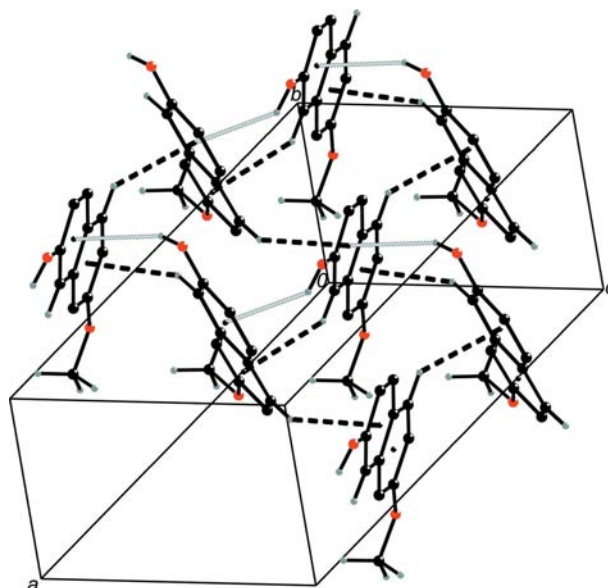
organic compounds
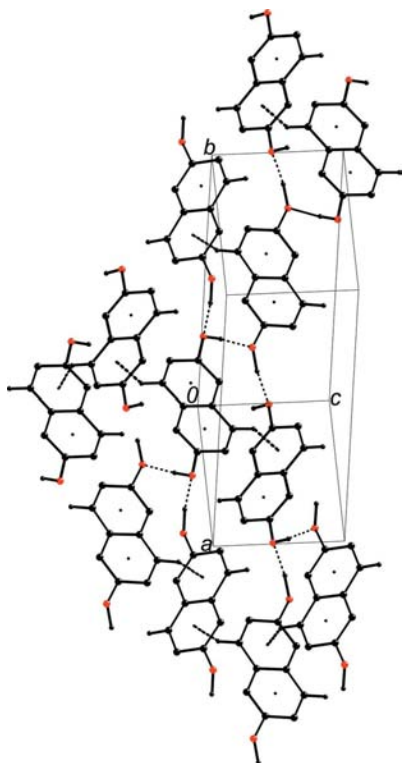
Figure 4
Part of the crystal structure of VOGSAL (Belskii *et al.*, 1990), showing a three-dimensional framework formed by O−H···O (thin dashed lines) and C−H···π (thick dashed lines) hydrogen bonds. All aromatic H atoms not involved in these interactions have been omitted for clarity. The centroids of benzene rings are denoted by small black spheres.

Figure 6
Part of the crystal structure of (VII) (Prince *et al.*, 1991), showing a sheet parallel to the (100) plane formed by O−H···π (thick grey solid lines) and C−H···π (thick dashed lines) hydrogen bonds. All aromatic H atoms not involved in these interactions have been omitted for clarity. The centroids of aromatic rings are denoted by small black spheres.

Figure 5
Part of the crystal structure of NPHLDL01 (Rozycka-Sokolowska *et al.*, 2005), showing a three-dimensional framework built up from O−H···O (thin dashed lines) and C−H···π (thick dashed lines) hydrogen bonds. All aromatic H atoms not involved in these interactions have been omitted for clarity. The centroids of benzene rings are denoted by small black spheres.
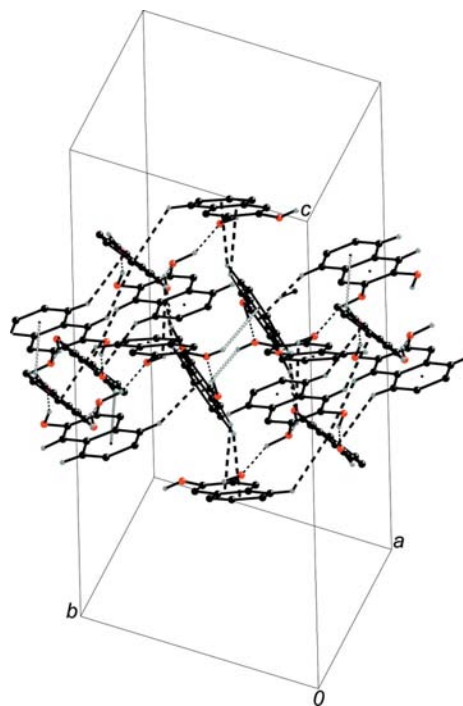

Figure 7
Part of the crystal structure of VOGSEP (Belskii *et al.*, 1990), showing a sheet parallel to the (001) plane formed by O−H···O (thin dashed lines), O−H···π (thick grey solid lines) and C−H···π (thick dashed lines) hydrogen bonds. All aromatic H atoms not involved in these interactions have been omitted for clarity. The centroids of aromatic rings are denoted by small black spheres.

and NPHLDL01 (Rozycka-Sokolowska *et al.*, 2005), respectively], where, apart from strong intermolecular O−H···O hydrogen bonds, there are also weak intermolecular hydrogen bonds of the X−H···π type. In the crystal structures of

HEGFAB and LICKEO, there are C−H···π hydrogen bonds [see Fig. 3 in Marciniak *et al.* (2006) and Fig. 4 in Marciniak (2007a), respectively], while in that of RIGMOK there is an interaction of the O−H···π type [see Fig. 4 in Marciniak

(2007*b*)]. C—H···π interactions also stabilize the crystal structures of NAPHOB03 (Fig. 3), VOGSAL (Fig. 4) and NPHLDL01 (Fig. 5), although this was not discussed in the original reports.

In the crystal structures of (VII) and VOGSEP, however, there are both C—H···π and O—H···π hydrogen bonds (Figs. 6 and 7, respectively), although not previously discussed. Taking into account these facts, and bearing in mind that (II) and its derivatives such as (I) and (III)–(VI) yield π-stacking with substantial overlap in the solid state, we may suppose that the parallel arrangement of molecules of these compounds is first of all a consequence of the presence of the substituents at position 1 of the naphthalene moiety and at positions 4 or 5. Moreover, a comparison of the AO values estimated for (II)–(VI) indicates that the overlap between adjacent molecules in the stacks is larger than that estimated for (II) when a substitution at the 4-position takes place [*i.e.* as in (I), (III) and (V)], while it is smaller when the substituent is at the 5-position [*i.e.* as in (IV) and (VI)]. Summing up, it is worth noting that in the case of monosubstituted naphthols, the parallel arrangement of the molecules depends on which positions in the naphthalene moiety carry the substituents, while the nature of the substituents, in both 4- and 5-substituted 1-naphthols, determines the extent of the area overlap.

The supramolecular aggregation in (I) is the same as that observed previously for two of its simple analogues, (V) and (II), crystallizing with $Z' = 1$ in the space groups $Pna2_1$ and $P2_1/c$, respectively [see Figs. 2 and 3*a*, respectively, in Rozycka-Sokolowska & Marciniak (2009*a*)] and it is simpler than that observed in the crystal structures of three further analogues, namely (III) ($Z' = \frac{1}{2}$, $Pnma$), (IV) ($Z' = \frac{1}{2}$, $P2_1/n$) and (VI) ($Z' = 1$, $P2_12_12_1$), where sheets containing $R_4^4(18)$ rings were identified [see Fig. 3*d* in Rozycka-Sokolowska & Marciniak (2009*a*) and Figs. 2 and 4 in Rozycka-Sokolowska & Marciniak (2009*b*), respectively]. By contrast with (I), in the structure of methoxynaphthol isomer (VII), crystallizing with $Z' = 1$ in the space group $P2_1/c$, there are no O—H···O hydrogen bonds or π–π stacking interactions. The herringbone packing of the molecules of (VII) is stabilized by three weak hydrogen bonds (Desiraju & Steiner, 1999), one O—H···π(arene) and two C—H···π(arene), although these were not discussed in the original report (Prince *et al.*, 1991). Together these interactions generate a sheet parallel to (100) (Fig. 6).

Experimental

Crystals of (I) were obtained from commercially available 4-methoxy-1-naphthol (Aldrich, purity ≥ 97%) by slow evaporation from a solution in toluene at a constant temperature of 293 K.

Crystal data

$C_{11}H_{10}O_2$	$V = 435.60\ (3)\ \text{Å}^3$
$M_r = 174.19$	$Z = 2$
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 8.5940\ (4)$ Å	$\mu = 0.09\ \text{mm}^{-1}$
$b = 4.7435\ (2)$ Å	$T = 290$ K
$c = 10.7293\ (5)$ Å	$0.46 \times 0.20 \times 0.13$ mm
$\beta = 95.183\ (4)°$	

Data collection

Oxford Diffraction Xcalibur3 CCD diffractometer	4893 measured reflections
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2008)	994 independent reflections
	865 reflections with $I > 2\sigma(I)$
$T_{min} = 0.966$, $T_{max} = 1.000$	$R_{int} = 0.024$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.036$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.084$	
$S = 1.03$	
994 reflections	$\Delta\rho_{max} = 0.12$ e Å^{-3}
122 parameters	$\Delta\rho_{min} = -0.17$ e Å^{-3}
1 restraint	

Table 1
Selected bond lengths (Å).

O1—C1	1.386 (2)	C4—C5	1.424 (3)
O2—C4	1.368 (2)	C5—C6	1.417 (3)
O2—C11	1.422 (3)	C5—C10	1.418 (2)
C1—C2	1.353 (3)	C6—C7	1.357 (3)
C1—C10	1.423 (3)	C7—C8	1.396 (3)
C2—C3	1.413 (3)	C8—C9	1.360 (3)
C3—C4	1.357 (3)	C9—C10	1.411 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O1^i	0.86 (4)	1.90 (4)	2.758 (2)	176 (3)

Symmetry code: (i) $-x + 2, y - \frac{1}{2}, -z$.

All C-bound H atoms were included in the refinement at geometrically idealized positions, with C—H distances of 0.93 (aromatic) and 0.96 Å (methyl), and with U_{iso}(H) = 1.2U_{eq}(aromatic C) or 1.5U_{eq}(methyl C). The H atom of the hydroxy group was located in a difference map and refined isotropically, giving an O—H distance of 0.86 (4) Å. In the absence of significant resonant scattering, the Flack (1983) parameter was indeterminate (Flack & Bernardinelli, 2000) and the Friedel equivalent reflections were merged prior to the final refinement.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2008); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2008); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009) and *DIAMOND* (Brandenburg, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2009).

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