

5-Amino-1-naphthol: two-dimensional sheets built up from $R_4^4(18)$ rings formed by O—H...N, N—H...O and π – π interactions

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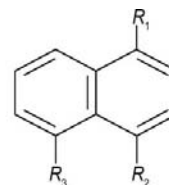
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The crystal structure of the title compound, $C_{10}H_9NO$, (I), contains intermolecular O—H...N and N—H...O hydrogen bonds which together form sheets parallel to the (001) plane containing rings with an unusual $R_4^4(18)$ motif. These rings are additionally stabilized by an intermolecular π – π stacking interaction. The significance of this study lies in the comparison drawn between the molecular structure of (I) and those of related compounds (1,5-diaminonaphthalene, 8-amino-2-naphthol, 3-amino-2-naphthol and aniline), which shows a close similarity in the noncoplanar orientation of the amine group and the aromatic moiety. Comparison of the crystal structures of (I) and several of its simple analogues (1-naphthol, naphthalene-1,4-diol, naphthalene-1,5-diol and 4-chloro-1-naphthol) shows a close similarity in the packing of the molecules, which form π -stacks along the shortest crystallographic axes with a substantial spatial overlap between adjacent molecules.

Comment

5-Amino-1-naphthol, (I), is a bifunctional monomer containing two functional groups, *i.e.* OH and NH_2 , and is thus a suitable candidate for polymerization which, depending on the electrolytic medium, can lead to different interesting materials (Ohsaka *et al.*, 1991). In a basic medium, polymerization occurs *via* the hydroxy groups, leading to the formation of a poly(naphthalene oxide) structure, while in either organic or aqueous acidic media polymerization takes place *via* the oxidation of the amine group, leading to the formation of poly(5-amino-1-naphthol) (PAN) (Cintra *et al.*, 2003; Rubinger *et al.*, 2006). This polymerization product belongs to the important class of conducting polymers, which are used as functional materials for applications in electrodes, sensors, *etc.*, and which have attracted much attention as an immobilization matrix for biomaterials such as enzymes and proteins (Takahashi & Córdoba de Torresi, 2008). Moreover, PAN has

been used as the active layer in an electronic pulse generator (Toniolo *et al.*, 2004).



- (I) $R_1=OH$, $R_2=H$, $R_3=NH_2$
 (II) $R_1=R_2=R_3=H$ (CSD refcode NAPHTA15)
 (III) $R_1=OH$, $R_2=R_3=H$ (CSD refcode NAPHOL01)
 (IV) $R_1=R_3=OH$, $R_2=H$ (CSD refcode VOGRUE)
 (V) $R_1=R_3=NH_2$, $R_2=H$ (CSD refcode ZZZKNU01)
 (VI) $R_1=R_2=OH$, $R_3=H$ (CSD refcode NPHHQU10)
 (VII) $R_1=OH$, $R_2=Cl$, $R_3=H$ (CSD refcode BOTSOT*)

A search of the Cambridge Structural Database (CSD, Version 5.30 of November 2008; Allen, 2002) for aminonaphthols revealed only two reports of two isomers of aminonaphthol, namely 8-amino-2-naphthol (CSD refcode MATCEQ; Dey *et al.*, 2005) and 3-amino-2-naphthol (CSD refcode QEPGAU; Dey *et al.*, 2006), and no prior reports of structures of amino-substituted 1-naphthols. We present here the structure of 5-amino-1-naphthol, (I) (Fig. 1 and Table 1), and compare it with those of its simple analogues, naphthalene, (II), 1-naphthol, (III), naphthalene-1,5-diol, (IV), 1,5-diaminonaphthalene, (V), naphthalene-1,4-diol, (VI), and 4-chloro-1-naphthol, (VII) [CSD refcodes NAPHTA15 (Oddershede & Larsen, 2004), NAPHOL01 (Rozycka-Sokolowska *et al.*, 2004), VOGRUE (Belskii *et al.*, 1990), ZZZKNU01 (Bernès *et al.*, 2004), NPHHQU10 (Gaultier & Hauw, 1967) and BOTSOT (Rozycka-Sokolowska & Marciniak, 2009), respectively].

In (I), the two substituents at positions 1 and 5 of the naphthalene ring system exert an influence on the geometric parameters in the aromatic rings, and especially on the lengths of the C3—C4, C8—C9, C4—C5 and C9—C10 bonds. Thus, the C3—C4 and C8—C9 bonds are shorter by *ca* 0.05 Å than the corresponding distances in (II) (1.374 Å), while the C4—C5 and C9—C10 bonds are longer by *ca* 0.05 Å than those in (II) (1.417 Å). The other C—C bond distances in (I),

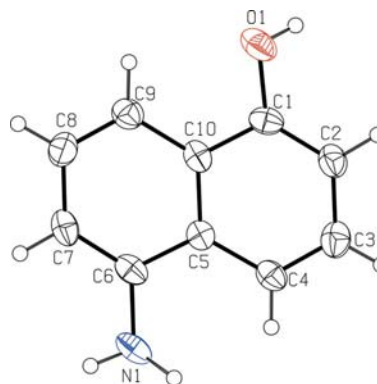


Figure 1

A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

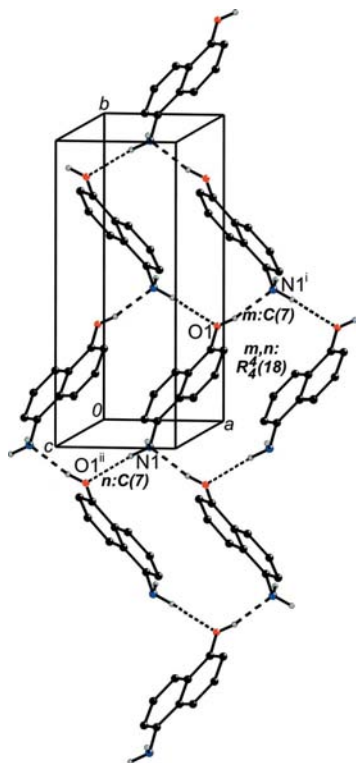


Figure 2

Part of the crystal structure of (I), showing the intermolecular O—H...N (*m*) and N—H...O (*n*) hydrogen bonds (dashed lines) running vertically, which can be described by the graph-set notation *C*(7) and together produce a sheet parallel to the (001) plane and built up from the $R_4^i(18)$ rings. All aromatic H atoms have been omitted for clarity. [Symmetry codes: (i) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $1 - x, -\frac{1}{2} + y$.]

in the range 1.390 (4)–1.419 (5) Å (Table 1), are similar to those found in (II) and to the typical aromatic bond length of 1.384 (13) Å (Allen *et al.*, 1987). The valence angles within the rings lie in the range 114.2 (3)–124.0 (3)°.

Despite the variations in bond lengths and angles, the naphthalene ring system remains planar, with the largest out-of-plane deviation being -0.011 (3) Å for atom C9. Atoms O1 and N1 attached to this ring are coplanar with it, deviating from the ring plane by only 0.038 (2) and -0.080 (3) Å, respectively. The dihedral angle between this plane and the plane formed by the atoms of the amine group is 44 (2)°. This angle, significantly different from 0°, is in close agreement with those observed for MATCEQ [48 (2)°], QEPGAU [42 (1)°] and ZZZKNU01 [29 (2), 44 (2) and 33 (2)°], and also with the values of the dihedral angles between the amino and ring planes observed in the two independent molecules of aniline [37 (4) and 38 (4)°; CSD refcode BAZGOY (Fukuyo *et al.*, 1982)]. It is noteworthy that this noncoplanar orientation of the amine group and the naphthalene ring, and the sum of the C6—N1—H1A, C6—N1—H1B and H1A—N1—H1B valence angles [334 (7)°], indicate that the geometry around atom N1 of molecule (I) is pyramidal, as previously found for aniline (Fukuyo *et al.*, 1982). This pyramidalization of the NH₂ group is associated with a lengthening of the C6—N1 bond [1.424 (4) Å], which compares well with the bonds observed in related compounds such as MATCEQ and QEPGAU

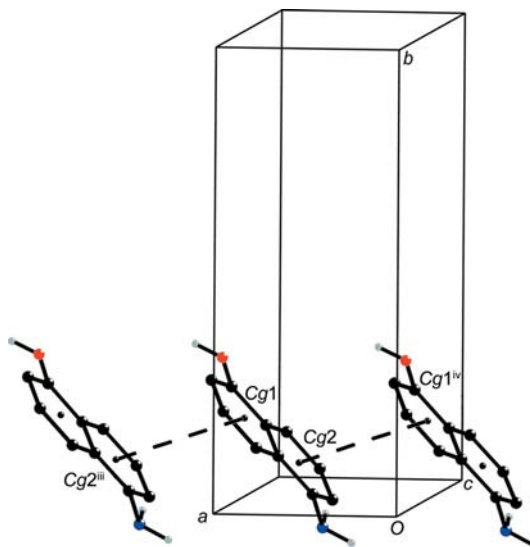
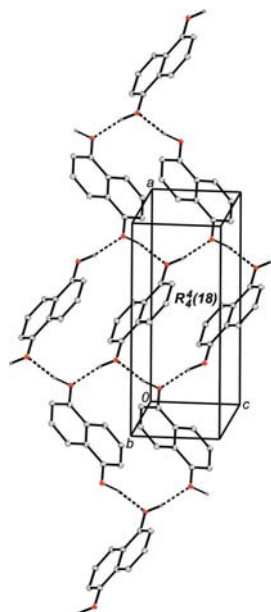


Figure 3

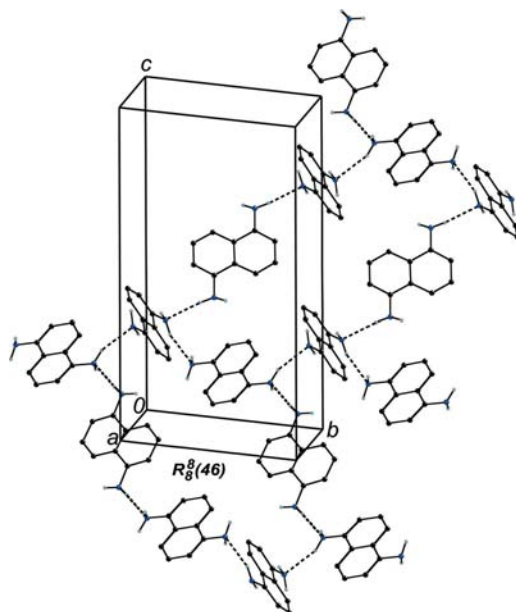
Part of the crystal structure of (I), showing the intermolecular π – π interactions (dashed lines) linking the molecules into stacks parallel to the crystallographic *a* axis. All aromatic H atoms have been omitted for clarity. Cg1 and Cg2 are the centroids of the C1–C5/C10 and C5–C10 benzene rings, respectively, and are denoted by small spheres. [Symmetry codes: (iii) $1 + x, y, z$; (iv) $-1 + x, y, z$.]

[1.416 (2) and 1.415 (2) Å, respectively], but is somewhat elongated in comparison with the C—N distances observed in aniline [1.386 (6) and 1.398 (6) Å] and ZZZKNU01 [1.385 (3)–1.407 (3) Å] and with the value given by Allen *et al.* (1987) for a C_{ar}—NH₂ (Nsp³ pyramidal) bond [1.394 (11) Å]. The C1—O1 bond length [1.379 (4) Å] is in a close agreement with the corresponding distances in the simple analogues of (I), such as (III), (IV), (VI) and (VII) [1.376 (1), 1.385, 1.377 and 1.394 (3) Å, respectively].

The crystal structure of (I) contains two independent strong nearly linear O1—H1...N1 and N1—H1A...O1 hydrogen bonds (Table 2), which connect each molecule with four others. Hydroxy atom O1 in the molecule at (*x*, *y*, *z*) acts as a hydrogen-bond donor, *via* atom H1, to atom N1 in the molecule at $(2 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, so forming a zigzag *C*(7) chain (Bernstein *et al.*, 1995) (motif *m* in Fig. 2) running parallel to [010]. A zigzag chain with the same *C*(7) descriptor and parallel to the same direction is also formed by the N1—H1A...O1ⁱⁱ hydrogen bond [motif *n* in Fig. 2; symmetry code: (ii) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$]. Together, these two hydrogen bonds produce a sheet parallel to the (001) plane built up from the $R_4^i(18)$ rings (Fig. 2). The non-H atoms belonging to the (001) sheets lie in domains $(0.09 + z/2) < c < (0.41 + z/2)$, where *z* is zero or an integer, and there are no direction-specific interactions between the molecules of adjacent sheets. The $R_4^i(18)$ rings are additionally stabilized by intermolecular π – π interactions between the C1–C5/C10 (centroid Cg1) and C5–C10 (centroid Cg2) benzene rings which connect molecules related by translation along the [100] direction into stacks parallel to the shortest crystallographic axis, *i.e.* axis *a* (Fig. 3). The perpendicular distances of the ring centroids Cg1 and Cg2 from the planes containing the symmetry-related centroids Cg2 at $(1 + x, y, z)$ and Cg1 at $(-1 + x, y, z)$, respectively, are

**Figure 4**

Part of the crystal structure of (IV) (Belskii *et al.*, 1990), showing a sheet of $R_4^4(18)$ rings lying parallel to the (110) plane. O—H...O hydrogen bonds are shown as dashed lines. All aromatic H atoms have been omitted for clarity.

**Figure 5**

Part of the crystal structure of (V) (Bernès *et al.*, 2004), showing the formation of a sheet parallel to the (102) plane and built up from the $R_8^8(46)$ rings formed by the N—H...N hydrogen bonds (dashed lines). All aromatic H atoms have been omitted for clarity.

3.4526 (14) and 3.4647 (14) Å, and the centroid–centroid separation is 3.690 (2) Å. The planes of the C1–C5/C10 and C5–C10 rings are nearly parallel, making an angle of only 0.55 (17)°.

The formation of molecular stacks parallel to the shortest crystallographic axis and the presence of strong interstack interactions are common characteristics of the crystal packing in (I) and its two simple analogues, (III) [see Fig. 3(a) in Rozycka-Sokolowska & Marciniak (2009)] and (IV) (Fig. 4), as well as in the 4-substituted derivatives of 1-naphthol, (VII) and (VI) [see Figs. 2 and 3(d), respectively, in Rozycka-Sokolowska & Marciniak (2009)]. It is also worth noting that in the crystal packing in (I), and in 1,4- and 1,5-naphthalenediol, which crystallize with $Z' = 0.5$ in the space groups $Pnma$ and $P2_1/n$, respectively, there is an additional common feature, namely the formation of a continuous two-dimensional framework containing rings based upon an unusual $R_4^4(18)$ structural motif. Such sheets are also found in the structure of 1,5-diaminonaphthalene, (V) (space group $P2_1/c$, $Z' = 1.5$), although they were not discussed in the original report (Bernès *et al.*, 2004). The sheets in (V) lie parallel to (102) and are built up from $R_8^8(46)$ rings formed by two N—H...N hydrogen bonds (Fig. 5). Moreover, the supramolecular aggregation in (I) differs significantly from the pattern found in (III) and (VII), where single O—H...O hydrogen bonds connect molecules of each of these compounds into simple one-dimensional $C(2)$ chains [see Figs. 2 and 3(a) in Rozycka-Sokolowska & Marciniak (2009)].

Analysis of the values of the ‘pitch’ and ‘roll’ parameters [pitch (P) and roll (R) angles and pitch (dp) and roll (dr) distances], estimated according to Curtis *et al.* (2004), and of the extent of the area overlap of adjacent π -stacked molecules

(AO), calculated according to a model proposed by Janzen *et al.* (2004), indicates that the solid-state packing of (I) provides a spatial overlap between molecules in the π -stack ($P = 44.71^\circ > R = 15.98^\circ$, $dp = 3.42 \text{ \AA} > dr = 0.99 \text{ \AA}$, AO = 19.4%), similar to what was found previously for (III), (VI) and (VII) (Rozycka-Sokolowska & Marciniak, 2009). Moreover, a comparison of these values with the parameters estimated for (IV) ($P = 43.85^\circ > R = 10.77^\circ$, $dp = 3.28 \text{ \AA} > dr = 0.65 \text{ \AA}$, AO = 24.7%) and (V) [$P_1 = 25.38^\circ < R_1 = 48.01^\circ$, $dp_1 = 1.64 \text{ \AA} < dr_1 = 3.84 \text{ \AA}$, $P_2 = 22.84^\circ < R_2 = 47.82^\circ$, $dp_2 = 1.46 \text{ \AA} < dr_2 = 3.81 \text{ \AA}$ (1 and 2 denote two independent columns of molecules running along the crystallographic a axis; no π -overlap between adjacent molecules)] leads to the conclusion that the modification of the molecular structure of (V) by the replacement of one or two NH_2 groups at the 1 or 1 and 5 positions, respectively, by one or two hydroxy groups results in the appearance of π - π stacking interactions and in a transformation of the arrangement of the aromatic rings of the naphthalene moiety, from the typical herring-bone arrangement in (V) ($dp < dr$) to practically parallel π -stacking with a spatial overlap between adjacent molecules in (I) and (IV) ($dp > dr$). Taking this into account, we can additionally conclude that the parallel arrangement of 5-amino-1-naphthol molecules in the solid state is caused by the presence of a hydroxy substituent at position 1.

In summary, we note that (I), as a material yielding π -stacking with substantial spatial overlap in the solid state [similar to (VI); Rozycka-Sokolowska & Marciniak, 2009], is an attractive candidate for electronic applications, including 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).

Experimental

Crystals of (I) were obtained from commercially available 5-amino-1-naphthol (Aldrich, purity 97%) by slow evaporation from a methanol solution at a constant temperature of 279 K.

Crystal data

C ₁₀ H ₉ NO	V = 794.2 (3) Å ³
M _r = 159.18	Z = 4
Orthorhombic, P2 ₁ 2 ₁ 2 ₁	Mo Kα radiation
a = 4.8894 (10) Å	μ = 0.09 mm ⁻¹
b = 12.404 (3) Å	T = 290 K
c = 13.096 (3) Å	0.23 × 0.06 × 0.02 mm

Data collection

Oxford Xcalibur3 CCD diffractometer	5049 measured reflections
Absorption correction: multi-scan (CrysAlis RED; Oxford Diffraction, 2008)	978 independent reflections
T _{min} = 0.966, T _{max} = 1.000	516 reflections with I > 2σ(I)
	R _{int} = 0.092

Refinement

R[F ² > 2σ(F ²)] = 0.051	H atoms treated by a mixture of independent and constrained refinement
wR(F ²) = 0.059	Δρ _{max} = 0.13 e Å ⁻³
S = 0.89	Δρ _{min} = -0.13 e Å ⁻³
978 reflections	
119 parameters	

Table 1

Selected bond lengths (Å).

O1—C1	1.379 (4)	C5—C6	1.389 (4)
N1—C6	1.424 (4)	C5—C10	1.419 (4)
C1—C10	1.390 (4)	C6—C7	1.408 (5)
C1—C2	1.393 (4)	C7—C8	1.410 (4)
C2—C3	1.415 (5)	C8—C9	1.327 (4)
C3—C4	1.322 (4)	C9—C10	1.469 (5)
C4—C5	1.466 (4)		

Table 2

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1...N1 ⁱ	0.80 (4)	1.94 (4)	2.725 (4)	166 (4)
N1—H1A...O1 ⁱⁱ	0.88 (3)	2.16 (3)	3.042 (3)	172 (3)

Symmetry codes: (i) -x + 2, y + 1/2, -z + 1/2; (ii) -x + 1, y - 1/2, -z + 1/2.

All aromatic H atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C). The H atoms of the hydroxy and amine groups were located in a difference Fourier map and refined with U_{iso}(H) = 1.5U_{eq}(O,N). In the absence of significant resonant scattering, the Flack (1983) parameter was indeterminate and the Friedel equivalent reflections were merged using MERG4 in SHELXL97 (Sheldrick, 2008).

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).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3309). Services for accessing these data are described at the back of the journal.

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