

## 4-Chloro-1-naphthol

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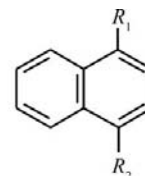
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Molecules of the title compound,  $C_{10}H_7ClO$ , (I), are connected by a single strong  $O-H\cdots O$  hydrogen bond into a simple  $C(2)$  chain, which runs parallel to the  $c$  axis and is additionally stabilized by intermolecular  $\pi-\pi$  stacking interactions. The significance of this study lies in the comparison drawn between the crystal structure of (I) and those of several of its simple analogues. This comparison shows a close similarity in the packing of the molecules that form  $\pi$ -stacks along the shortest crystallographic axes. A substantial spatial overlap is observed between adjacent molecules in such a  $\pi$ -stack, depending mainly on the kind of substituent.

## Comment

Naphthalene derivatives are used in various scientific fields, such as metal complexation, materials chemistry, medicinal chemistry, structural chemistry, molecular recognition, macromolecular chemistry, supramolecular chemistry, fluorescence chemistry and asymmetric synthesis, as backbones, platforms or functional devices (Ohta *et al.*, 2005, and references 8–16 therein). Halo-substituted hydroxyaromatic compounds (among them the title compound) are a class of starting materials for the preparation of bis(hydroxyaromatic) compounds, which find many uses in chemical applications such as dyes, plastics, pharmaceuticals and agrochemicals, and in forming polymers such as polycarbonates, polyester carbonates, polyesters, polyethers, polyetherimides and polyether ketones (Patel *et al.*, 2005). A search of the Cambridge Structural Database (CSD, Version 5.30 of November 2008; Allen, 2002) for chloro-substituted hydroxy-derivatives of naphthalene revealed only five reports of four chloro-substituted naphthalenediols, namely 1,5-dichloro-2,6-dihydroxynaphthalene [CSD refcodes JIMFAM (Nakasuji *et al.*, 1991) and JIMFAM01 (Ahn *et al.*, 1995)], 1,5-dichloro-2,6-naphthoquinone 1,5-dichloro-2,6-dihydroxynaphthalene (JIMDUE; Nakasuji *et al.*, 1991), 1,5-dichloronaphthalene-2,6-diol dioxane solvate (RAYPOW; Ahn *et al.*, 1995) and bis(1,4-dichloronaphthalene-2,3-diol) dioxane (ZIPYEC; Ahn *et al.*, 1994), and no prior reports of the structures of chloro-substituted naphthols. Thus, this paper concerning the results

of structural studies of the title compound, (I), would appear to be the first example involving a chloronaphthol. The crystal structure of (I) is presented here and is also compared with those of five of its simple analogues, namely 1-hydroxynaphthalene, (II), 1,4-dihydroxynaphthalene, (III), 1,4-dichloronaphthalene, (IV), 1,4-dibromonaphthalene, (V), and naphthalene, (VI) [NAPHOL01 (Rozycka-Sokolowska *et al.*, 2004), NPHHQU10 (Gaultier & Hauw, 1967), DCLNAQ (Bellows *et al.*, 1978), DBRNAQ01 (Trotter, 1986) and NAPHTA15 (Oddershede & Larsen, 2004), respectively].



- (I)  $R_1 = OH, R_2 = Cl$   
 (II)  $R_1 = OH, R_2 = H$   
 (III)  $R_1 = R_2 = OH$   
 (IV)  $R_1 = R_2 = Cl$   
 (V)  $R_1 = R_2 = Br$   
 (VI)  $R_1 = R_2 = H$

Although the presence of a hydroxyl group and a Cl atom in (I) at positions 1 and 4, respectively, modifies the geometric parameters within the aromatic rings [the C–C bond distances and C–C–C bond angles lie in the ranges 1.355 (4)–1.431 (3) Å and 117.6 (3)–124.0 (2)°, respectively; Table 1], the naphthalene ring remains planar (Fig. 1); the largest out-of-plane deviation is 0.017 (3) Å for atom C1. Atoms O1 and Cl1 deviate from the plane of this ring by only 0.003 (2) and 0.053 (1) Å, respectively. The C4–Cl1 bond length is close to those observed in several chloro derivatives of naphthalene, such as 1,2,3,4,6,7-, 1,2,3,5,6,7-, 1,2,4,5,6,8- and 1,2,4,5,7,8-hexachloronaphthalene [YAFHUI and YAFYEU (Jakobsson *et al.*, 1992) and YILROA and YILRUG (Jakobsson *et al.*, 1994), respectively] and (IV), as well as in compounds such as JIMFAM and JIMFAM01, JIMDUE, RAYPOW and ZIPYEC.

In the crystal structure of (I), there is a single strong and practically linear  $O-H\cdots O$  hydrogen bond (Table 2) that links hydroxy atom O1 at  $(x, y, z)$ , via atom H1, to hydroxy atom O1 belonging to the molecule at  $(2 - x, 2 - y, -\frac{1}{2} + z)$ , so

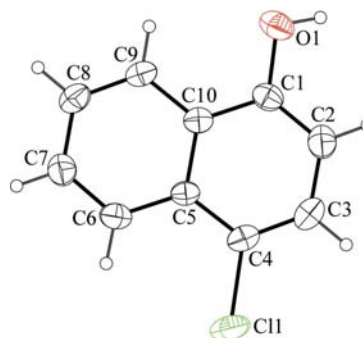
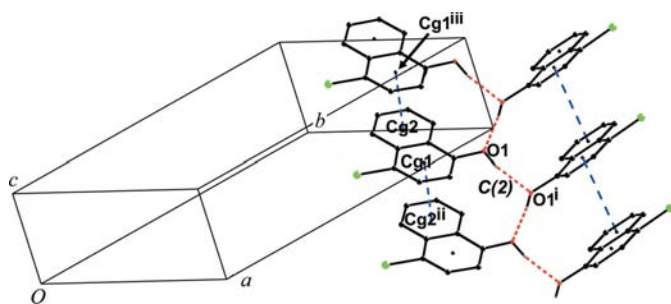


Figure 1

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.



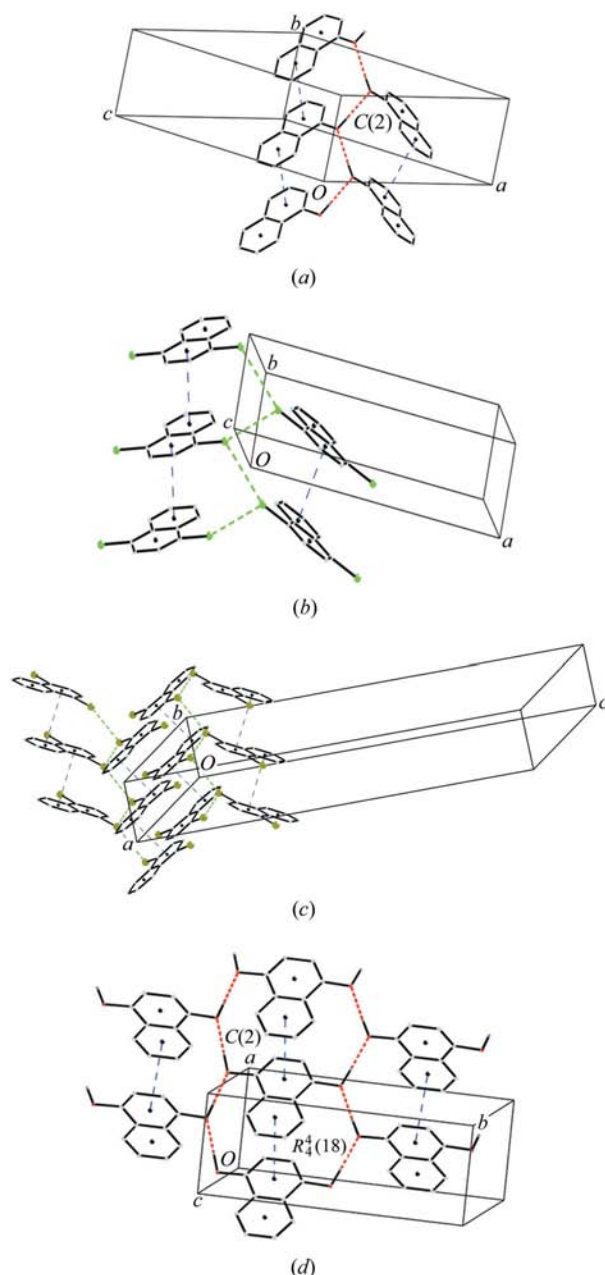
**Figure 2**

Part of the crystal structure of (I), showing the interstack O—H...O hydrogen bond forming a  $C(2)$  chain along the [001] direction, and the intrastack  $\pi$ – $\pi$  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)  $2 - x, 2 - y, -\frac{1}{2} + z$ ; (ii)  $x, y, -1 + z$ ; (iii)  $x, y, 1 + z$ .]

generating a simple  $C(2)$  chain (Fig. 2) which runs parallel to the shortest crystallographic  $c$  axis and is built from molecules related by the  $2_1$  screw axis. This chain is additionally stabilized by intermolecular  $\pi$ – $\pi$  stacking interactions involving 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 symmetry-related centroids  $Cg2$  at  $(x, y, -1 + z)$  and  $Cg1$  at  $(x, y, 1 + z)$ , respectively, are 3.590 (1) and 3.576 (1) Å, and the centroid-to-centroid separation is 3.714 (2) Å. The planes of rings C1–C5/C10 and C5–C10 make an angle of only 1.02°. Two  $C(2)$  chains run through each unit cell and there are no direction-specific interactions between them. In the crystal structure of (I), there are no close contacts between Cl atoms, the shortest Cl...Cl distance being 4.189 (2) Å.

It is worth mentioning that the presence of the  $2_1$  screw axis along the shortest crystallographic axis and the formation of molecular stacks along this axis are common characteristics of the crystal packing in (I) and four of its simple analogues, *viz.* (II)–(V). In the case of (II) and (III), adjacent stacks are held together mainly by a strong interstack O—H...O hydrogen bond. In the case of (IV) and (V), adjacent stacks are held together by weak halogen–halogen interactions of types Cl...Cl and Br...Br, with distances of 3.621 and 3.613–3.701 Å, respectively. Similar to (I), the O—H...O hydrogen bond in (II) and the halogen–halogen interactions in (IV) and (V) link molecules related by the  $2_1$  screw axis into simple infinite chains parallel to the shortest axes [ $b = 4.7980$  (10), 3.9394 (6) and 4.063 (3) Å, respectively; Fig. 3(a)–(c)]. Although the O—H...O hydrogen bond in the crystal structure of (III) can be described by the same  $C(2)$  graph-set motif as those in (I) and (II), in contrast with the supramolecular aggregation in these two compounds the single hydrogen bond connects molecules of (III) into a two-dimensional sheet parallel to (100) and built up from  $R_4^4(18)$  rings (Fig. 3d).

The application of the phenomenological approach proposed by Curtis *et al.* (2004) for the description of distortions from an 'ideal' cofacial  $\pi$ -stack based on 'pitch' and 'roll' parameters, such as the pitch ( $P$ ) and roll ( $R$ ) angles and the pitch ( $dp$ ) and roll ( $dr$ ) distances, in combination with a simple



**Figure 3**

Part of the crystal structures of (a) (II), (b) (IV), (c) (V) and (d) (III), showing the intermolecular  $\pi$ – $\pi$  interactions (thin dashed lines) linking the molecules of each of these compounds into stacks parallel to the shortest crystallographic axes, as well as the interstack O—H...O and halogen–halogen interactions (thick dashed lines). All H atoms not involved in these interactions have been omitted for clarity. The centroids of the benzene rings ( $Cg$ ) are denoted by small spheres.

model introduced by Janzen *et al.* (2004) for the approximation of the area overlap ( $AO$ ) of adjacent  $\pi$ -stacking molecules, reveals that the solid-state packing of (I) provides substantial spatial overlap between molecules in the  $\pi$ -stack ( $P > R$ ,  $dp > dr$ ,  $AO = 40.7\%$ ; Table 3). Analysis of the parameters given in Table 3 indicates that  $\pi$ -stacking with substantial spatial overlap between molecules is also observed for (II)–(V). Thus, it may be concluded that a modification of the molecular structure of (VI) by the replacement of one H atom at position 1 by a hydroxy group, or two H atoms at

positions 1 and 4 by (i) one hydroxy group and one halogen (Cl or Br) atom, (ii) two hydroxy groups, or (iii) two halogen atoms, results not only in the elimination of intermolecular C—H... $\pi$ (arene) interactions and the appearance of O—H...O hydrogen bonds [in (I)–(III)] or halogen–halogen interactions [in (IV) and (V)], but primarily in a transformation of the arrangement of the aromatic rings, from typical herring-bone in (VI) with no  $\pi$ -overlap between adjacent molecules ( $P < R$ ,  $dp < dr$ ; Table 3) to practically parallel  $\pi$ -stacking in (I)–(V) ( $P > R$ ,  $dp > dr$ ). It is also worth stressing that hydroxy and halogen substitution at positions 1 and 4 of the molecule of (VI) not only promote  $\pi$ -stacking but also influence the overlap between adjacent molecules in the  $\pi$ -stack. The area of overlap depends mainly on the kind of substituent; among the five naphthalene derivatives considered here, three with one or two halogen substituents [(I), (IV) and (V)] distinguish themselves with larger (average ca 11%) area overlap than those that possess only hydroxy groups as substituents [(II) and (III)] (Table 3).

Bearing in mind that materials yielding  $\pi$ -stacking with substantial spatial overlap in the solid state are particularly attractive because they often lead to devices with high charge-carrier mobilities (Anthony *et al.*, 2002; Li *et al.*, 1998; Horowitz *et al.*, 1996; Laquindanum *et al.*, 1997), and taking into account the fact that in the crystal structure of (I) such  $\pi$ -stacking is predominant, we can suppose that this derivative of (VI) will turn out to be a promising material for device applications, particularly in the area of functional devices such as organic field-effect transistors (OFETs).

## Experimental

4-Chloro-1-naphthol was obtained from Sigma and used without further purification. Crystals of (I) suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution in ethyl acetate at a constant temperature of 279 K.

### Crystal data

$C_{10}H_7ClO$	$V = 829.64$ (9) $\text{\AA}^3$
$M_r = 178.61$	$Z = 4$
Orthorhombic, $Pna2_1$	Mo $K\alpha$ radiation
$a = 11.7106$ (8) $\text{\AA}$	$\mu = 0.40$ $\text{mm}^{-1}$
$b = 16.9105$ (8) $\text{\AA}$	$T = 290$ K
$c = 4.1894$ (3) $\text{\AA}$	$0.49 \times 0.13 \times 0.08$ mm

### Data collection

Oxford Xcalibur3 CCD area-detector diffractometer	4455 measured reflections
Absorption correction: multi-scan ( <i>CrysAlis RED</i> ; Oxford Diffraction, 2008)	1116 independent reflections
$T_{\min} = 0.945$ , $T_{\max} = 0.973$	854 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.024$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.027$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.079$	$\Delta\rho_{\text{max}} = 0.13$ $e \text{\AA}^{-3}$
$S = 1.13$	$\Delta\rho_{\text{min}} = -0.15$ $e \text{\AA}^{-3}$
1116 reflections	Absolute structure: Flack (1983), with 289 Friedel pairs
114 parameters	Flack parameter: 0.07 (13)
1 restraint	

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

C11—C4	1.748 (3)	C5—C6	1.413 (4)
O1—C1	1.394 (3)	C5—C10	1.431 (3)
C1—C2	1.355 (4)	C6—C7	1.367 (4)
C1—C10	1.415 (3)	C7—C8	1.401 (4)
C2—C3	1.410 (4)	C8—C9	1.364 (4)
C3—C4	1.356 (4)	C9—C10	1.417 (3)
C4—C5	1.417 (3)		
C1—C2—C3	119.5 (3)	C6—C7—C8	120.6 (3)
C4—C3—C2	120.5 (2)	C9—C8—C7	120.5 (2)
C3—C4—C5	121.8 (2)	C8—C9—C10	120.6 (2)
C6—C5—C4	124.0 (2)	C1—C10—C9	122.4 (2)
C6—C5—C10	118.4 (2)	C1—C10—C5	118.6 (2)
C4—C5—C10	117.6 (3)	C9—C10—C5	119.0 (2)
C7—C6—C5	120.9 (2)		

**Table 2**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1-H1\cdots O1^i$	0.88 (4)	1.87 (4)	2.720 (3)	160 (3)

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

**Table 3**

$\pi$ -Stacking distances ( $d$ ; the shortest distance between the planes of two adjacent molecules in the  $\pi$ -stack), pitch ( $P$ ,  $dp$ ) and roll ( $R$ ,  $dr$ ) parameters and area overlaps ( $AO$ ) for compounds (I)–(VI).

Parameter	(I)	(II)	(III)	(IV)	(V) <sup>†</sup>	(VI)
Substituents	One Cl + one OH	One OH	Two OH	Two Cl	Two Br	None
$d$ ( $\text{\AA}$ )	3.566	3.529	3.485	3.518	3.533, 3.531	2.540
$P$ ( $^\circ$ )	28.7	42.29	43.4	22.03	26.32, 25.77	25.94
$R$ ( $^\circ$ )	13.83	8.62	0.07	17.29	16.69, 17.06	64.14
$dp$ ( $\text{\AA}$ )	1.95	3.21	3.30	1.42	1.75, 1.70	1.24
$dr$ ( $\text{\AA}$ )	0.88	0.53	0.00	1.10	1.06, 1.08	5.24
$AO$ (%)	40.7	27.0	31.5	42.6	38.9, 39.5	

<sup>†</sup> The values for (V) are given for two independent stacks of molecules.

All aromatic H atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H = 0.93  $\text{\AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The hydroxyl H atom was located in a Fourier difference map and refined isotropically, with O—H = 0.88 (4)  $\text{\AA}$ .

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: SK3305). Services for accessing these data are described at the back of the journal.

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