Hydrogen bonding and C—H···O interactions in 4-phenanthrenemethanol at 150 K

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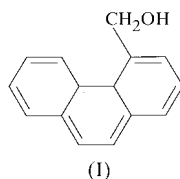Correspondence e-mail: gerkin@chemistry.ohio-state.edu

The title compound, $C_{15}H_{12}O$, crystallizes in the centrosymmetric space group $I4_1/a$ with one molecule in the asymmetric unit. In the single hydrogen bond, the H atom is ordered, the O_D···O_A distance is 2.788 (1) Å and the O—H···O angle is 176 (1)°. Each hydroxyl group forms hydrogen bonds with two other hydroxyl groups and the resulting chains of interactions, in four non-linked subsets of molecules, propagate along [001]. The single leading intermolecular C—H···O interaction has an H···O distance of 2.81 Å and a C—H···O angle of 140°; the single leading intramolecular C—H···O interaction has an H···O distance of 2.24 Å and a C—H···O angle of 152°. The phenanthrene core is less nearly planar in this structure than in the room temperature structure of phenanthrene-4-carboxylic acid.

Comment

This report on the title compound, (I), is one of a series on hydrogen bonding and C—H···O interactions in aromatic compounds.

Compound (I) crystallizes in the centrosymmetric space group $I4_1/a$ with one molecule in the asymmetric unit. The refined molecule and the labeling scheme are shown in Fig. 1. A single hydrogen bond and two leading C—H···O interactions (Taylor & Kennard, 1982; Steiner & Desiraju, 1998), one intramolecular, are present in this structure; geometric parameters are given in Table 2. These interactions link each molecule directly to four neighbours. The results of basic first- and second-level graph-set analysis (Bernstein *et al.*, 1995) involving these interactions, labelled *a–c* for this purpose in the order of their appearance in Table 2, are given in Table 3. All the tabulated chains propagate along [001]. The molecules

as a whole are divided into four sets, comprising those generated by space-group symmetry operators 1, 4, 5 and 8; 2, 3, 6 and 7; 9, 12, 14 and 15, and 10, 11, 13 and 16, which are 'chained' within, but not between, these sets by each of the chain patterns. One example of each of these sets is included in the packing stereodiagram (Fig. 2), in which portions of the first-level *a* hydrogen-bond chains within these four sets are apparent.

In (I), the maximum deviations from planarity for each of the six-membered rings and the core as a whole are from ~1.2 to ~2.1 times as large as the corresponding values for the comparison molecule, phenanthrene-4-carboxylic acid, (II), at room temperature (Fitzgerald & Gerkin, 1998).

Selected bond distances and angles for (I) are given in Table 1. All distances and angles fall within normal limits. Corresponding pairs of chemically equivalent bonds (ignoring the substituent at C4) in the core of (I) are in good agreement, the r.m.s. difference within the seven pairs of distances being 0.008 Å. This value may be compared with the corresponding
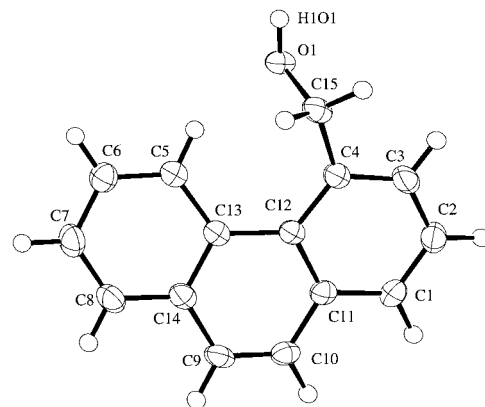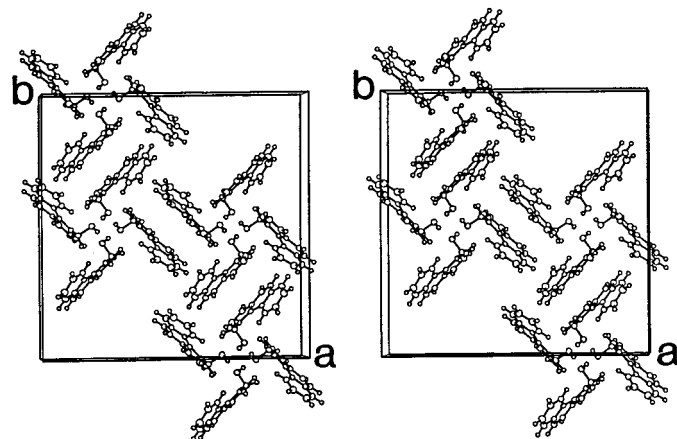

Figure 1
The refined molecule of (I) and the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

r.m.s. difference in (II) of 0.008 Å. Of the two remaining bonds in the core, C12—C13 is greater in both cases than C9—C10, by 0.124 (2) Å in (I) and by 0.132 (5) Å in (II). In (I), the closest intermolecular approaches, excluding pairs of atoms in hydrogen-bonded groups or the tabulated C—H···O interactions, are between C12 and H15A^{iii} [symmetry code: (iii) $y - \frac{1}{4}, \frac{3}{4} - x, z - \frac{1}{4}$] and fall short of the corresponding Bondi (1964) van der Waals radius sum by 0.06 Å. Two additional (smaller) shortfalls indicate a single noteworthy C—H···π interaction: C9—H9···(C5/C6/C7/C8/C14/C13)^{iv} [symmetry code: (iv) $\frac{1}{4} + y, \frac{3}{4} - x, -z - \frac{1}{4}$]. The (non-normalized) H9–centroid distance is 2.72 Å, while the H3–ring-atom distances range from 2.88 to 3.27 Å and the C9—H9···centroid angle is 161°. These values are consistent with those cited for significant C—H···π interactions, *e.g.* by Steiner *et al.* (1995).

It may be noted that, whereas in (II), approximately 4.5% of the molecules are found to be disordered (such that the substituted 4- and unsubstituted 5- positions are interchanged), in (I), there is no evidence for such disorder.

organic compounds

The preferential appearance of high symmetry in structures of monoalcohols has been discussed by Brock & Duncan (1994).

Figure 2
A stereodiagram of (I) viewed down the c axis toward the origin. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

Experimental

Compound (I) was obtained as a finely crystalline white powder from a sample in Dr M. S. Newman's chemical collection. Slow evaporation of an ethanolic solution of this powder at room temperature produced suitable crystals. A synthesis of (I) is described by Fierens *et al.* (1955).

Crystal data

$C_{15}H_{12}O$	Mo $K\alpha$ radiation
$M_r = 208.26$	Cell parameters from 29 288
Tetragonal, $I4_1/a$	reflections
$a = 22.5868$ (4) Å	$\theta = 2.61–27.48°$
$c = 8.3020$ (1) Å	$\mu = 0.080$ mm^{-1}
$V = 4235.4$ (1) Å^3	$T = 150$ K
$Z = 16$	Uncut capped column, colourless
$D_x = 1.306$ Mg m^{-3}	$0.38 \times 0.23 \times 0.23$ mm

Data collection

Nonius KappaCCD diffractometer	$R_{int} = 0.034$
ω scans with κ offsets	$\theta_{max} = 27.48°$
29 288 measured reflections	$h = -29 \rightarrow 29$
2431 independent reflections	$k = -29 \rightarrow 29$
2019 reflections with $I > 2\sigma(I)$	$l = -6 \rightarrow 10$

Refinement

Refinement on F^2	H atoms treated by a mixture of
$R(F) = 0.040$	independent and constrained
$wR(F^2) = 0.102$	refinement
$S = 1.92$	$w = 1/[\sigma_{cs}^2 + (0.034I)^2]$
2430 reflections	$(\Delta/\sigma)_{max} = 0.001$
149 parameters	$\Delta\rho_{max} = 0.25$ e Å^{-3}
	$\Delta\rho_{min} = -0.22$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C15	1.444 (1)	C4—C15	1.508 (1)
C2—C1—C11	120.92 (9)	C9—C10—C11	121.51 (9)
C1—C2—C3	118.96 (9)	C5—C13—C12	123.97 (9)
C12—C4—C15	125.38 (9)	O1—C15—C4	110.42 (8)

Table 2
Geometry of hydrogen-bonds and leading C—H···O interactions (Å, °)..

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O1···O1^i	0.96 (1)	1.83 (1)	2.788 (1)	176 (1)
C2—H2···O1^{ii}	0.98	2.81	3.619 (1)	140
C5—H5···O1	0.98	2.24	3.136 (1)	152

Symmetry codes: (i) $\frac{3}{4} - y, \frac{1}{4} + x, \frac{1}{4} + z$; (ii) $\frac{3}{4} - y, \frac{1}{4} + x, z - \frac{3}{4}$.

Table 3
Basic first- and second-level graph-set descriptors involving interactions designated *a–c* in the order given in Table 2.

	a	*b*	*c*
a	$C(2)$	$C_2^2(8)$	$C_2^1(8)[S(7)]$
b		$C(6)$	$C_2^1(9)[S(7)]$
c			$S(7)$

Difference Fourier methods were used to locate the initial H-atom positions, which were refined [C—H = 0.97 (1)–1.02 (1) Å, mean 0.99 (2) Å; $U_{iso}(H) = 1.0–1.3U_{eq}(C)$]. The H atoms, excepting the hydroxyl-H atom, were then made canonical, with C—H = 0.98 Å and $U_{iso}(H) = 1.2U_{eq}(C)$. In the later stages of refinement, the extinction coefficient was predicted to be negative, so it was not included in the model. The maximum peak in the final difference map occurs ~0.3 Å from C10 and the maximum negative peak occurs ~0.5 Å from C15.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation, 1995); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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