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Network of C—H···O interactions in dimethyl anthracene-1,8-dicarboxylate

Wade D. Aumiller and Roger E. Gerkin

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA. E-mail: gerkin@chemistry.ohio-state.edu

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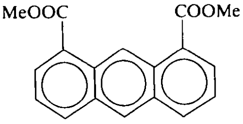
Abstract

The title compound, $C_{18}H_{14}O_4$, crystallized in the centrosymmetric space group *Pbca* with one molecule as the asymmetric unit. Six leading C—H···O interactions are present, with H···O distances ranging from 2.65 to 2.80 Å and C···O distances ranging from 3.518 (4) to 3.659 (4) Å. Both ring and chain patterns of interactions occur, and the chains form a three-dimensional network. The dihedral angles between the best-fit planes of the non-H atoms of the ester groups and the best-fit planes of the rings to which they are attached are 35.0 (2) and 44.0 (2)°. The molecules occur in layers along the **b** axis.

Comment

This report is one of a series on hydrogen bonding and C—H···O interactions in aromatic compounds, and follows reports on two other 1,8-disubstituted anthracenes, namely anthracene-1,8-dicarboxylic acid (hereafter ADCA; Fitzgerald & Gerkin, 1996) and 1,8-bis(hydroxymethyl)anthracene (hereafter BHMA; Aumiller & Gerkin, 1997). In the title ester, (I), substantial C—H···O interaction is expected, since there are no conventional hydrogen-bond donors, but there are four potential acceptors, *i.e.* O1–O4.



(I)

Compound (I) crystallized in the centrosymmetric space group *Pbca* with one molecule as the asymmetric unit. The refined molecule and the labeling scheme are given in Fig. 1. As expected, a number of C—H···O interactions occur with parameters falling well within the limits suggested by Taylor & Kennard (1982) for significant attractive interactions; geometrical details for the six leading interactions are given in Table 2. These interactions link a given molecule to seven neighbors. The results of basic first- and second-level graph-set analysis (Bernstein *et al.*, 1995) involving these interactions, labeled *a–f* for this purpose in the order of their appearance in Table 2, are given in Table 3. (The second-level descriptors involving interaction *a* are given in non-extended form.) The 21 entries comprise seven rings and 14 chains. The chains propagate variously along [100] (five instances), [001] (eight instances) and [010] (a single instance) to form a three-dimensional network of interactions.

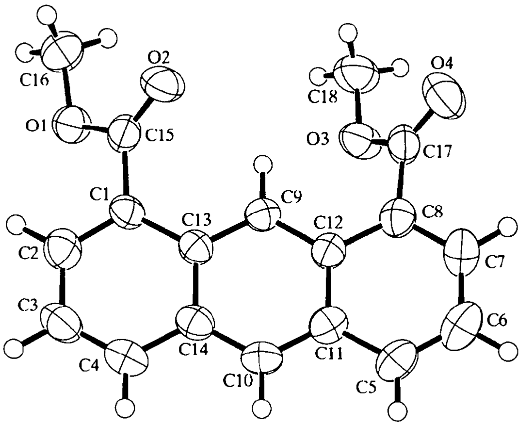


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (I), showing the atomic labeling scheme. Displacement ellipsoids are drawn for 50% probability for all non-H atoms and spheres of arbitrary small radius depict H atoms.

The individual rings of the anthracene core of (I) are nearly planar, the maximum deviations of any of their atoms from the best-fit planes describing them being 0.016 (3), 0.010 (3) and 0.024 (3) Å, while the average deviations are 0.009 (6), 0.006 (3) and 0.014 (8) Å for the rings composed of atoms C1–C4/C13/C14, C9–C14 and C5–C8/C11/C12, respectively. The dihedral angles between the best-fit planes of the central ring and the outer rings are 2.7 (2) and 4.0 (2)°, and between the outer rings is 1.6 (2)°. Thus, the core as a whole is roughly planar, the maximum deviation of any of its atoms from the best-fit plane being 0.060 (3) Å. In comparison, the maximum deviations from the anthracene cores in ADCA and BHMA are 0.046 (6) and 0.030 (4) Å, respectively. In (I), the non-H atoms of the ester groups (O1/O2/C15/C16 and O3/O4/C17/C18) also lie approximately in planes, their maximum deviations from the best-fit planes describing them being 0.004 (3) and 0.032 (3) Å. The dihedral angles between the best-fit planes of the ester groups and the best-fit planes of the rings to which they are attached are 35.0 (2) and 44.0 (2)°. The packing diagram (Fig. 2) illustrates these features and shows the layering of molecules along the **b** axis.

The anthracene core of (I) displays moderate conformity to mirror symmetry with respect to a mirror through C9 and C10; for the eight pairs of distances which would be identical under this symmetry, the r.m.s. deviation within pairs is 0.005 Å, while the s.u.'s of the

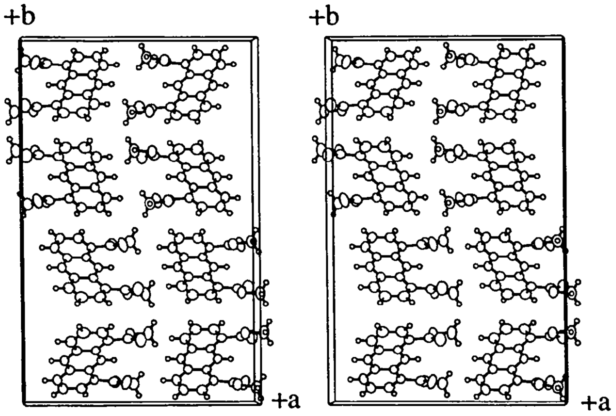


Fig. 2. *ORTEP*II (Johnson, 1976) packing diagram of (I) viewed down the **c** axis. Displacement ellipsoids are drawn for 50% probability for all non-H atoms and spheres of arbitrary small radius depict H atoms.

individual distances are 0.004 Å. In comparison, these values for ADCA and BHMA are 0.008 and 0.007–0.009 Å, and 0.006 and 0.004–0.005 Å.

Selected bond distances and angles of (I) are given in Table 1. All distances and angles fall within normal limits. The closest intermolecular approaches, excluding pairs of atoms involved in the tabulated C—H···O interactions, are between H5 and H18$A^{\rm iii}$ [symmetry code: (iii) $-\frac{1}{2}+x$, y, $-\frac{3}{2}-z$] and fall short of the corresponding Bondi (1964) van der Waals radius sum by 0.04 Å.

Experimental

Compound (I) was synthesized from 1,8-dichloroanthraquinone following the procedures of Vance (1993), which were adapted from those of Akiyama *et al.* (1960, 1962*a*,*b*) and Akiyama & Nakagawa (1971). Recrystallization of (I) by slow cooling of a hot methanol solution produced crystals suitable for analysis.

Crystal data

$C_{18}H_{14}O_4$
$M_r = 294.31$
Orthorhombic
Pbca
$a = 17.400\,(3)$ Å
$b = 27.085\,(2)$ Å
$c = 6.119\,(2)$ Å
$V = 2884\,(1)$ Å^3
$Z = 8$
$D_x = 1.356$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.2$–$17.2°$
$\mu = 0.096$ mm^{-1}
$T = 296$ K
Irregular hexagonal plate
$0.50 \times 0.31 \times 0.11$ mm
Amber

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: none
3314 measured reflections
3314 independent reflections
1259 reflections with $I > 2\sigma_I$
$\theta_{\rm max} = 27.55°$

$h = 0 \rightarrow 22$
$k = 0 \rightarrow 35$
$l = 0 \rightarrow 7$
6 standard reflections every 150 reflections intensity decay: ±2.2% (average maximum relative intensity)

Refinement

Refinement on F^2
$R(F) = 0.063$
$wR(F^2) = 0.076$
$S = 1.29$
3314 reflections
199 parameters
H-atom parameters not refined
$w = 1/[\sigma_{\rm cs}^2 + (0.003I)^2]$

$(\Delta/\sigma)_{\rm max} = 0.0002$
$\Delta\rho_{\rm max} = 0.63$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.64$ e Å^{-3}
Extinction correction: none
Scattering factors from Stewart *et al.* (1965) (H) and Creagh & McAuley (1992) (C, O)

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

O1—C15	1.334 (3)	O3—C17	1.340 (4)
O1—C16	1.440 (3)	O3—C18	1.444 (3)
O2—C15	1.195 (3)	O4—C17	1.192 (3)
C15—O1—C16	115.9 (3)	O1—C15—O2	123.3 (3)
C17—O3—C18	117.7 (3)	O1—C15—C1	110.9 (3)
C2—C1—C15	119.2 (3)	O2—C15—C1	125.8 (3)
C13—C1—C15	120.3 (3)	O3—C17—O4	123.1 (3)
C7—C8—C17	116.9 (3)	O3—C17—C8	111.1 (3)
C12—C8—C17	121.8 (3)	O4—C17—C8	125.8 (3)

Table 2. *Leading C—H···O interactions (Å, °)*

Note that no s.u.'s are given for quantities involving H atoms since they were fixed.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C16—H16*C*···O2$^{\rm i}$	0.98	2.65	3.615 (4)	169
C16—H16*B*···O2$^{\rm ii}$	0.98	2.70	3.642 (4)	162
C18—H18*C*···O4$^{\rm ii}$	0.98	2.72	3.659 (4)	160
C5—H5···O4$^{\rm iii}$	0.98	2.73	3.656 (4)	158
C16—H16*A*···O4$^{\rm ii}$	0.98	2.78	3.518 (4)	133
C7—H7···O3$^{\rm iv}$	0.98	2.80	3.542 (4)	133

Symmetry codes: (i) $2-x, -y, -z$; (ii) $x, y, 1+z$; (iii) $x-\frac{1}{2}, y, -\frac{3}{2}-z$; (iv) $x, \frac{1}{2}-y, z-\frac{1}{2}$.

Table 3. *Basic first- and second-level graph-set descriptors involving C—H···O interactions designated a–f in order as given in Table 2*

	a	*b*	*c*	*d*	*e*	*f*
a	$R_2^2(10)$	$R_4^2(8)$	$R_4^4(44)$	$C_2^2(20)$	$R_2^2(24)$	$C_2^2(20)$
b		$C(5)$	$R_2^2(22)$	$C_2^2(20)$	$R_2^2(12)$	$C_2^2(20)$
c			$C(5)$	$C_2^1(10)$	$R_2^1(14)$	$C_2^2(8)$
d				$C(7)$	$C_2^1(12)$	$C_2^2(8)$
e					$C(11)$	$C_2^2(14)$
f						$C(5)$

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1226). Services for accessing these data are described at the back of the journal.

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3-(2-Methylphenyl)propanoic acid

Roger E. Gerkin

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA. E-mail: gerkin@chemistry.ohio-state.edu

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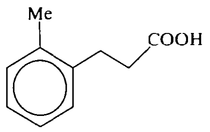
Abstract

The title acid, $C_{10}H_{12}O_2$, crystallized in the centrosymmetric space group $P2_1/c$ with one molecule in the asymmetric unit. There is a single hydrogen bond with $O_D\cdots O_A$ = 2.639 (2) Å and O_D—H$\cdots O_A$ = 175 (3)°. This bond forms an $R_2^2(8)$ cyclic dimer about a center of symmetry. The non-H atoms of the molecule lie nearly in a plane. The molecules in this structure are oriented such that their best-fit planes are either strictly parallel or make dihedral angles of 88.9 (1)°. The structure comprises double layers of aromatic rings separated by double layers of hydrogen-bonded aliphatic strings and is analogous to the structures of other terminally aryl-substituted *n*-aliphatic carboxylic acids.

Comment

This report on the title acid, (I), is one of a series on hydrogen bonding in carboxylic acids. It follows reports on the analogous 'terminal aromatic ring–*n*-aliphatic string–carboxyl group' acids 4-(2-naphthyl)-butanoic acid [(II); Dobson & Gerkin, 1996] and 4-(3-phenanthryl)butanoic acid [(III); Gerkin, 1997], as well as 4-(1-pyrenyl)butanoic acid [(IV); Olszak *et al.*, 1989], 4-(2-anthryl)butanoic acid [(V); Durfee *et al.*, 1989] and (2-naphthyl)ethanoic acid [(VI); Barrett & Gellman, 1993]. Of particular interest is the packing of the rings, the strings and the carboxyl groups in such solids.



(I)

Compound (I) crystallized in the centrosymmetric space group $P2_1/c$ with one molecule in the asymmetric unit. The refined molecule and the labeling scheme are shown in Fig. 1. There is a single hydrogen bond in this structure involving O1, H1 and O2$^{\rm i}$ [symmetry code: (i) $1-x$, $1-y$, $1-z$], in which the O_D—H distance is 0.97 (3), H$\cdots O_A$ is 1.67 (3), $O_D\cdots O_A$ = 2.639 (2) Å and O_D—H$\cdots O_A$ is 175 (3)°. The H atom and O atoms are ordered. This bond forms a first-level (Bernstein *et al.*, 1995) cyclic dimer with descriptor $R_2^2(8)$ about a center of symmetry; there are of course no higher-level graphs. Three of the cyclic dimers are shown in the packing diagram, Fig. 2. As is apparent there, this structure can be viewed as consisting of double layers of aromatic rings separated by double layers of hydrogen-bonded aliphatic strings. In this respect, it is similar to the other 'ring–string–carboxyl group' structures cited above. Further, in (I) and (II)–(IV) cited above, there is a small dihedral angle between the best-fit string plane and the carboxyl-group plane [(V) and (VI) are not compared since (V) has reported O-atom disorder, and (VI) has too short a string to define a string plane]. However, (I) is unlike (II)–(IV) in having its carboxyl group coplanar with its ring, as described below, rather than almost perpendicular to it [in (II) and (III), for example, the relevant dihedral angles are 80.5 (2) and 83.2 (3)°].