22 912 measured reflections
2791 independent reflections (plus 1930 Friedel-related reflections)
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.060$
$wR(F^2) = 0.141$
$S = 1.010$
4721 reflections
191 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 3.5783P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.39$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.34$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0001 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.003 (8)

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

Br1—C5	1.892 (4)	S1—O1	1.427 (4)
N1—C1	1.461 (6)	S1—O2	1.432 (4)
N1—C2	1.465 (6)	S1—C6	1.763 (5)
N1—S1	1.623 (4)		
O1—S1—O2	120.4 (3)	O2—S1—N1	106.4 (2)
O1—S1—N1	106.6 (3)	C8—C9—C12	121.6 (5)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2B···O2$^{\rm i}$	1.01 (6)	2.56 (5)	3.367 (6)	136 (4)
C10—H10···O1$^{\rm ii}$	0.93 (1)	2.57 (6)	3.382 (7)	147 (5)

Symmetry codes: (i) $-\frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{4} + z$; (ii) $y - 1, x, -z$.

Though data were collected to a 2θ maximum of 66.4°, only reflections having 2θ less than 55° were used for structure solution and refinement. The crystal structure in the tetragonal system can be solved in either of the enantiomorphous space groups $P4_32_12$ or $P4_12_12$. The crystal was initially solved in $P4_32_12$, but the R values and the Flack (1983) parameter indicated $P4_12_12$. These results led us to use $P4_12_12$. Only methyl-group H atoms were located geometrically; the other H atoms were located from a difference Fourier map and refined isotropically. The C—H bond lengths range from 0.87 (6) to 1.02 (4) Å, while $U_{\rm iso}$ values range from 0.03 (1) to 0.09 (2) Å^2.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL* (Sheldrick, 1995). Software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1214). Services for accessing these data are described at the back of the journal.

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C—H···O interactions in acenaphthene-5,6-dicarboxylic anhydride

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Abstract

The title substance, $C_{14}H_8O_3$, crystallized in the centrosymmetric space group $C2/c$ with a half-molecule in the asymmetric unit (the molecule lies on a twofold axis). The three leading C—H···O interactions have H···O distances 2.47 (2), 2.84 (2) and 2.91 (2) Å, and C···O distances 3.338 (2), 3.445 (2) and 3.606 (2) Å, respectively. These interactions link each molecule directly to six neighbors, leading to a three-dimensional network of C—H···O interactions. Structural comparisons are made with naphthalene-1,2-dicarboxylic anhydride and naphthalene-1,4,5,8-tetracarboxylic 1,8:4,5-dianhydride.

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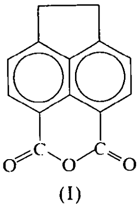
Comment

Although conventional hydrogen bonds are not possible in acenaphthene-5,6-dicarboxylic anhydride, (I), it is of structural interest in terms of potential C—H···O interactions since it possesses three potential O-atom acceptors and eight potential H-atom donors per molecule. We have previously reported on the three-dimensional network of C—H···O interactions that arises in naphthalene-1,2-dicarboxylic anhydride (hereafter, NDA; Fitzgerald & Gerkin, 1999), which also has three potential O-atom acceptors, but only six potential H-atom donors.



(I)

Compound (I) crystallized in the centrosymmetric space group *C*2/*c* with a half-molecule in the asymmetric unit (the molecule lies on a twofold axis). The refined molecule, with our numbering scheme, is shown in Fig. 1. In this structure there are three leading intermolecular C—H···O interactions, one of which has an H···O distance considerably less than the corresponding Bondi (1964) van der Waals radius sum, 2.70 Å. The geometric parameters of these interactions are given in Table 2; all fall well within the Taylor & Kennard (1982) limits for significantly attractive C—H···O interactions. These interactions link a central molecule directly to six neighboring molecules, as shown in Fig. 2. Graph-set descriptors for basic first- and second-level graphs (Bernstein *et al.*, 1995) are given in Table 3; for this analysis the interactions are denoted as *a*–*c* in the order of their appearance in Table 2. The basic first-level chains propagate along [010], [001] and [001] for *a*–*c*, respectively. In addition, complex first-level chains for *a* include those with descriptor $C(8)$, which propagate along [112] and $[1\bar{1}2]$, and $C_2^2(12)$, which propagates along [102]. Thus, a three-dimensional network of interactions is present. A number of the chains and rings, which include edge-sharing and vertex-sharing types, are readily apparent in Fig. 2. In comparison, NDA has four intermolecular C—H···O interactions with H···O distances less than the corresponding Bondi van der Waals radius sum. As in (I), these form numerous chains (and rings), which are also so disposed that a three-dimensional network arises.

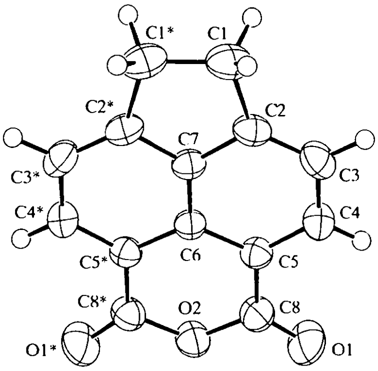


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (I), showing our numbering scheme. Displacement ellipsoids are drawn for 50% probability for all non-H atoms; circles of arbitrary small radius depict H atoms.

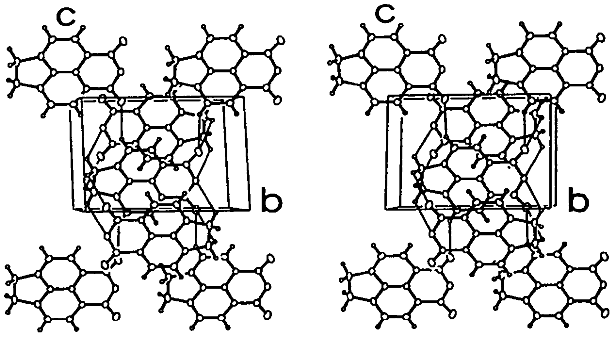


Fig. 2. An *ORTEP*II (Johnson, 1976) stereoview of (I) down the *a* axis showing a central molecule and the six neighbors to which it is linked by C—H···O interactions. Displacement ellipsoids are drawn for 20% probability for all non-H atoms; circles of arbitrary small radius depict H atoms. C—H···O interactions are depicted by the finer interatomic lines.

In (I), the 17 non-H atoms lie almost in a plane: the maximum deviation of any of these atoms from the best-fit plane describing them is 0.022 (1) Å, while the r.m.s. deviation is 0.012 Å. This degree of planarity is somewhat less than that of the 15 non-H atoms of NDA, for which the corresponding values are 0.014 (2) and 0.005 Å, but considerably greater than that of just the 16 non-H atoms comprising the four-ring core of naphthalene-1,4,5,8-tetracarboxylic 1,8:4,5-dianhydride (hereafter, NTD; Blackburn *et al.*, 1997), for which the maximum deviation from the best-fit plane is 0.045 (2) Å. In (I), all the molecular planes are parallel to one another; this parallelism is apparent for the portion of the structure depicted in Fig. 2.

For structural comparisons of the anhydride portion of (I), the corresponding portions of NDA and of NTD appear quite suitable. The mean values of the lengths of the three common pairs of chemically equivalent bonds in the anhydride groups of (I), NDA and NTD are, respectively: 1.459 (2), 1.474 (2), and 1.478 (2) Å; 1.193 (2), 1.190 (2), and 1.186 (2) Å; and 1.397 (2), 1.398 (2), and 1.390 (2) Å. Thus, there is very good agreement for the chemically equivalent bonds involving the O atoms, both within and among the anhydride groups of these three molecules.

Selected bond distances and angles are given in Table 1. All distances and angles fall within normal ranges. The closest intermolecular approaches, excluding pairs of atoms involved in the leading C—H···O interactions described above, are between C5 and C7^{iii} [symmetry code: (iii) $-x$, $1-y$, $-z$] and are 0.09 Å greater than the corresponding Bondi van der Waals radius sum.

Experimental

The title compound was obtained from Lancaster Synthesis Inc. as a gray-yellow powder. It was subjected to hydrolysis and the hydrolysis product was treated according to the procedure of Trost *et al.* (1971) to isolate the corresponding 5,6-dicarboxylic acid. The diacid was dissolved in ethylene glycol dimethyl ether/water (approximately 4:1) and the solution was filtered. Slow evaporation at room temperature produced (I) as a pale amber, clear, irregular polyhedron.

Crystal data

$C_{14}H_8O_3$
$M_r = 224.22$
Monoclinic
$C2/c$
$a = 15.140\,(2)$ Å
$b = 9.671\,(1)$ Å
$c = 7.621\,(2)$ Å
$\beta = 117.85\,(1)°$
$V = 986.6\,(2)$ Å^3
$Z = 4$
$D_x = 1.509$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 16.5–17.4°$
$\mu = 0.107$ mm^{-1}
$T = 296$ K
Uncut irregular polyhedron
0.38 × 0.31 × 0.23 mm
Pale amber

Data collection

AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1241 measured reflections
1129 independent reflections
785 reflections with $I > 2\sigma I$
$R_{\rm int} = 0.014$
$\theta_{\rm max} = 27.48°$

$h = 0 \rightarrow 19$
$k = 0 \rightarrow 12$
$l = -9 \rightarrow 8$
6 standard reflections every 150 reflections intensity variation: ±1.1% (average maximum relative intensity)

Refinement

Refinement on F^2
$R(F) = 0.041$
$wR(F^2) = 0.079$
$S = 1.85$
1129 reflections
96 parameters
All H-atom parameters refined
$w = 1/[\sigma^2_{\rm cs} + (0.014I)^2]$
$(\Delta/\sigma)_{\rm max} = 0.0002$

$\Delta\rho_{\rm max} = 0.25$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}
Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: $3.1\,(8) \times 10^{-7}$
Scattering factors from Stewart *et al.* (1965) (H) and Creagh & McAuley (1992) (C, O)

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

O1—C8	1.193 (2)	C1—C2	1.515 (2)
O2—C8	1.397 (2)	C5—C8	1.459 (2)
C1—C1*	1.550 (4)		
C8*—O2—C8	127.0 (2)	O1—C8—C5	127.5 (2)
O1—C8—O2	116.1 (1)	O2—C8—C5	116.4 (1)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O1^{i}	0.97 (1)	2.47 (2)	3.338 (2)	148 (1)
C1—H1*A*···O1^{ii}	0.99 (2)	2.84 (2)	3.445 (2)	120 (1)
C1—H1*B*···O2^{iii}	0.98 (2)	2.91 (2)	3.606 (2)	128 (1)

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

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

	a	*b*	*c*
a	$C(6)$	$R^2_4(12)$	$C^2_2(8)$
b		$C(8)$	$R^2_2(7)$
c			$C^1_2(5)[R^2_2(16)]$

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: FR1213). Services for accessing these data are described at the back of the journal.

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