

ω - 2θ scans
Absorption correction:
 ψ scans (North, Phillips
& Mathews, 1968)
 $T_{\min} = 0.671$, $T_{\max} = 0.914$
4325 measured reflections
3930 independent reflections

$R_{\text{int}} = 0.065$
 $\theta_{\text{max}} = 77.52^\circ$
 $h = 0 \rightarrow 11$
 $k = 0 \rightarrow 22$
 $l = -15 \rightarrow 15$
3 standard reflections
every 200 reflections
intensity decay: 0.08%

Refinement

Refinement on F^2
 $R(F) = 0.043$
 $wR(F^2) = 0.119$
 $S = 1.78$
3930 reflections
249 parameters
H atoms: H on N1 refined,
others fixed
 $w = 1/[\sigma^2(F_o^2)$
 $+ 0.00031(F_o^2)^2]$

$(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.25 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.24 \text{ e } \text{\AA}^{-3}$
Extinction correction:
Zachariasen (1967)
Extinction coefficient:
 $0.53(6) \times 10^{-5}$
Scattering factors from
International Tables for
Crystallography (Vol. C)

Table 1. Hydrogen-bonding geometry (\AA , $^\circ$)

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1 \cdots O2^i$	0.90 (2)	2.03 (2)	2.910 (2)	166 (2)

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

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SIR92* (Altomare, Cascarano, Giacovazzo & Guagliardi, 1993). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1286). Services for accessing these data are described at the back of the journal.

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Phenanthrene-9-carboxylic Acid

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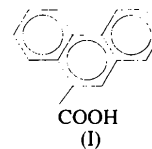
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Abstract

The title compound, $C_{15}H_{10}O_2$, crystallized in the centrosymmetric space group $C2/c$. Hydrogen bonding is of the cyclic dimer type about a center of symmetry. The carboxyl H and O atoms are ordered. The phenanthrene core is almost planar and the dihedral angle between the core plane and the carboxyl group plane is only $1.8(1)^\circ$. The bay H atoms, H4 and H5, lie close to the core plane and $2.02(2) \text{\AA}$ from each other; the refinement places them on opposite sides of the core plane, but this result has little statistical significance.

Comment

This is one of a series of reports on hydrogen bonding in polyaromatic carboxylic acids. Among earlier reports are those on anthracene-9-carboxylic acid and anthracene-1-carboxylic acid (Fitzgerald & Gerkin, 1997*a,b*). Phenanthrene-9-carboxylic acid, (I), crystallized in the centrosymmetric space group $C2/c$. The hydrogen bonding is of the cyclic dimer type about a center of symmetry. A diagram of the dimer showing our numbering scheme appears in Fig. 1. Geometric details of the hydrogen bond are given in Table 2. Those data and data from Table 1 make clear that both the carboxyl H atom and the carboxyl O atoms are ordered.



With respect to pseudo-mirror symmetry, the phenanthrene core in this acid shows an r.m.s. deviation of 0.014\AA within the seven pairs of distances which would be identical under mirror symmetry, the e.s.d.'s of the individual distances being 0.002 – 0.003\AA . For the five pairs of distances unique to the outer rings of the core, the corresponding r.m.s. deviation is 0.005\AA . Thus it appears that the presence of the carboxyl group on the central ring interferes substantially with the pseudo-symmetry of the core. Interestingly, however, in phenanthrene itself, as reported by Kay, Okaya & Cox (1971), pseudo-symmetry is not much better satisfied, the r.m.s.

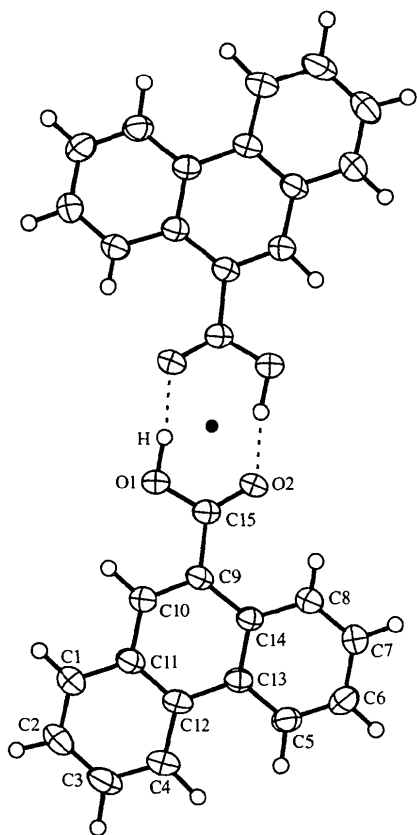


Fig. 1. ORTEP (Johnson, 1976) drawing of the phenanthrene-9-carboxylic acid hydrogen-bonded cyclic dimer showing our numbering scheme. Displacement ellipsoids are drawn for 50% probability for all atoms except H for which they have been set artificially small. The center of symmetry is shown as a filled sphere and the hydrogen bonds as dashed lines.

deviation of the seven corresponding pairs of distances being 0.012 Å, while the individual e.s.d.'s are 0.005–0.008 Å.

In the title acid, the phenanthrene core is almost planar. The average deviation of the core atoms from the best-fit plane through them is 0.012 Å, while the maximum deviation is 0.031 Å and the e.s.d.'s of the individual values are near 0.002 Å. For phenanthrene itself, Kay, Okaya & Cox (1971) gave the dihedral angles between the outer and central ring best-fit planes as 1.2 and 1.2°, and between the two outer ring best-fit planes as 2.4°. The corresponding values for the title acid are 1.37 (7), 0.38 (7) and 1.59 (7)°. Thus the carboxyl group has not affected the degree of planarity. Moreover, the dihedral angle between the best-fit core plane and the carboxyl group plane in the title acid is only 1.8 (1) Å, making the entire set of non-H atoms very nearly planar.

An additional point of interest in this phenanthrene derivative is the disposition of the bay H atoms, H4 and H5. The refined distances C4—H4 and C5—H5 are

0.99 (2) and 1.00 (2) Å, while the C3—C4—H4, C12—C4—H4, C6—C5—H5 and C13—C5—H5 angles are 119 (1), 119 (1), 117 (1) and 120 (1)°, respectively. The refinement places these H atoms on opposite sides of the best-fit core plane at distances of 0.01₁ and 0.01₇ Å from it; their location on opposite sides of the plane thus has little statistical significance. They lie at a distance 2.02 (2) Å from each other, 0.38 Å less than the Bondi (1964) radius sum; nonetheless, as evidenced by the data given above, their geometry with respect to the core is at most slightly affected. For comparison, in phenanthrene itself, Kay, Okaya & Cox (1971) determined the H-atom parameters by neutron diffraction and found distances for C4—H4 and C5—H5 of 1.06 (2) and 1.09 (2) Å, and angles C3—C4—H4, C12—C4—H4, C6—C5—H5 and C13—C5—H5 of 119.0 (10), 120.5 (9), 116.8 (9) and 123.5 (9)°, respectively, and a H4—H5 distance 2.04 (2) Å. Thus, given the expected difference in the C—H distances determined by the two methods, the two sets of results are highly concordant.

In the title acid, all other intramolecular distances and angles fall within normal ranges. The closest intermolecular approach, excluding pairs of atoms within hydrogen-bonded carboxyl groups, is between O2 and H2ⁱⁱ [symmetry code: (ii) $\frac{1}{2} + x, -\frac{1}{2} + y, z$] and falls short of the Bondi (1964) van der Waals radius sum by only 0.06 Å.

Experimental

Phenanthrene-9-carboxylic acid was produced in ~75% yield from phenanthrene-9-carboxaldehyde (Aldrich Chemical Company) by oxidation with Ag₂O. The general procedure was that of Burtner & Cusic (1943) for converting anthracene-9-carboxaldehyde to anthracene-9-carboxylic acid. Slow crystallization of the title acid from ethanol at room temperature produced multifaceted columns, one of which was cut to provide the experimental sample.

Crystal data

C₁₅H₁₀O₂

M_r = 222.24

Monoclinic

C2/c

a = 19.824 (2) Å

b = 5.373 (2) Å

c = 21.638 (1) Å

β = 113.308 (6)°

V = 2116.7 (7) Å³

Z = 8

D_x = 1.395 Mg m⁻³

D_m not measured

Mo Kα radiation

λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 14.4–14.8°

μ = 0.086 mm⁻¹

T = 296 K

Cut column

0.42 × 0.38 × 0.19 mm

Pale yellow

Data collection

Rigaku AFC-5S diffractometer

ω scans

Absorption correction: none

θ_{max} = 27.5°

h = 0 → 25

k = 0 → 6

l = -28 → 25

2766 measured reflections
 2684 independent reflections
 1680 reflections with
 $I > \sigma(I)$
 $R_{\text{int}} = 0.015$

Refinement

Refinement on F
 $R = 0.044$
 $wR = 0.048$
 $S = 1.64$
 1680 reflections
 167 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement
 $w = \sigma_F^{-2}$
 $(\Delta/\sigma)_{\text{max}} = < 0.01$

6 standard reflections
 every 150 reflections
 intensity variation: $\pm 3.0\%$
 (average maximum
 relative intensity)

$\Delta\rho_{\text{max}} = 0.18 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.18 \text{ e } \text{\AA}^{-3}$
 Extinction correction:
 Zachariasen (1963, 1968)
 Extinction coefficient:
 $5.8(8) \times 10^{-7}$
 Scattering factors from
 Stewart, Davidson &
 Simpson (1965) and
 Cromer & Waber (1974)

Table 1. Selected geometric parameters (\AA , $^\circ$)

O1—C15	1.322 (2)	C9—C15	1.491 (2)
O2—C15	1.219 (2)		
C10—C9—C15	117.3 (2)	C9—C15—O2	125.3 (2)
C14—C9—C15	122.8 (1)	C15—O1—H	109 (1)
C9—C15—O1	113.8 (1)	O1—C15—O2	120.9 (1)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O1—H...O2 ⁱ	1.02 (2)	1.66 (3)	2.675 (2)	173 (2)

Symmetry code: (i) $1 - x, -y, 1 - z$.

Scan widths were $(1.40 + 0.35 \tan \theta)^\circ$ in ω , with a background/scan time-ratio of 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignment, systematic absences and intensity statistics consistent with centrosymmetry indicated space group $C2/c$ (No. 15); since refinement proceeded well it was adopted. Fourier difference methods were used to locate the H-atom positions. In later stages of refinement, ring H atoms H1—H3, H6—H8 and H10 were made canonical with a C—H distance of 0.98 \AA and $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the associated C atom. Atoms H4, H5 and H were refined isotropically. The maximum effect of extinction was 10.0% of F_o for 114. The maximum positive residual peak was located near the midpoint of the C13—C14 bond; the maximum negative peak was located near the center of the central ring.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1046). Services for accessing these data are described at the back of the journal.

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Benzophenone-3,3',4,4'-tetracarboxylic Acid Dihydrate[†]

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Abstract

The title compound, $C_{17}H_{10}O_9 \cdot 2H_2O$, crystallizes in the centrosymmetric space group $P2_1/a$ but does not exhibit strong eight-membered cyclic dimer hydrogen bonds about centers of symmetry or otherwise. A richly three-dimensional hydrogen-bonding network is observed, however, which arises from 19 hydrogen bonds per asymmetric unit; it includes a 14-membered cyclic dimer about a center of symmetry and hydrogen-bonding rings of 18 and 30 members involving the acid molecule and a water molecule, both also about centers of symmetry. The carboxyl H and O atoms are ordered in each of the carboxyl groups. The configuration of the benzophenone core is quite similar to that in benzophenone itself and the configuration of the adjacent

[†] Alternative name: 4-(3,4-dicarboxybenzoyl)phthalic acid dihydrate.