

C3—C2—C7	116.59 (17)	C3A—C2A—C7A	116.72 (18)
C2—C3—C4	117.34 (17)	C2A—C3A—C4A	117.40 (17)
N5—C4—C3	125.22 (18)	N5A—C4A—C3A	125.11 (19)
N5—C4—C14	114.58 (14)	N5A—C4A—C14A	114.99 (15)
C3—C4—C14	120.19 (15)	C3A—C4A—C14A	119.88 (15)
C4—N5—N6	117.85 (16)	C4A—N5A—N6A	117.65 (17)
C7—N6—N5	120.41 (16)	C7A—N6A—N5A	120.60 (16)
N6—C7—C2	122.54 (18)	N6A—C7A—C2A	122.49 (18)
C11—C1—C2—C3	12.6 (3)		
C11—C1—C2—C7	-168.00 (19)		
C2—C1—C11—C16	-99.7 (2)		
C2—C1—C11—C12	80.4 (2)		
C11A—C1A—C2A—C3A	6.9 (3)		
C11A—C1A—C2A—C7A	-173.37 (18)		
C2A—C1A—C11A—C16A	-105.2 (2)		
C2A—C1A—C11A—C12A	74.9 (2)		

The data collection nominally covered over a sphere of reciprocal space, by a combination of three sets of exposures; each set had a different  $\varphi$  angle for the crystal and each exposure covered  $0.3^\circ$  in  $\omega$ . The crystal-to-detector distance was 5.95 cm. Coverage of the unique set was over 88% complete to at least  $26^\circ$  in  $\theta$ . Crystal decay was monitored by repeating the initial frames at the end of data collection and analysing the duplicate reflections. H atoms were located by difference Fourier synthesis and refined with fixed individual displacement parameters  $\{U(\text{H}) = 1.5U_{\text{eq}}[\text{C}(\text{methyl})]\}$  or  $U(\text{H}) = 1.2U_{\text{eq}}(\text{C})\}$  using a riding model with C—H(secondary) = 0.99, C—H(methyl) = 0.98 or C—H(aromatic) = 0.95 Å. The methyl groups were allowed to rotate about their local three-fold axis.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SMART*. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *XP* (Sheldrick, 1991).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1176). Services for accessing these data are described at the back of the journal.

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## Phenanthrene-4-carboxylic Acid and 1,2-Dihydrophenanthrene-4-carboxylic Acid

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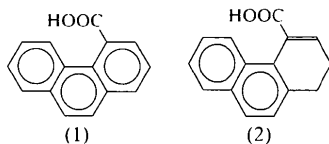
(Received 9 June 1997; accepted 6 January 1998)

### Abstract

Phenanthrene-4-carboxylic acid, C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>, crystallized in the centrosymmetric space group *P2<sub>1</sub>/n*, while 1,2-dihydrophenanthrene-4-carboxylic acid, C<sub>15</sub>H<sub>12</sub>O<sub>2</sub>, crystallized in the centrosymmetric space group *Pbca*. In each structure, there is a single type of hydrogen bond: it is of the cyclic dimer type about a center of symmetry. The O<sub>donor</sub>···O<sub>acceptor</sub> distances are 2.634 (2) and 2.651 (2) Å, and the O—H···O angles are 176 (3) and 173 (2)°, respectively, for the two structures. In each structure, the carboxy H and O atoms are ordered. The phenanthrene core of the fully aromatic acid is roughly planar; the dihedral angle between the best-fit core plane and the carboxy group plane is 63.7 (1)°. As expected, the hydrogenated ring of the second acid is much less nearly planar; the remaining naphthalenoid core is, however, roughly planar and the dihedral angle between this best-fit plane and the carboxy group plane is 60.4 (1)°.

### Comment

This is one of a series of reports on hydrogen bonding in polyaromatic carboxylic acids, and follows a report on phenanthrene-9-carboxylic acid (Fitzgerald & Gerkin, 1997). In phenanthrene-4-carboxylic acid, (1), and in 1,2-dihydrophenanthrene-4-carboxylic acid, (2), the hydrogen bonding is of the cyclic dimer type about a center of symmetry, as shown in Figs. 1(a) and 1(b), which also present the numbering schemes. The geometric parameters of the hydrogen bonds are given in Table 3. In terms of graph-set analysis (Bernstein *et al.*, 1995), for both (1) and (2), the first-level graph set is R<sub>2</sub><sup>2</sup>(8) and there are no higher-level graphs. As expected for ordered carboxy O atoms, the principal axes of the displacement tensors of O1 and O2 in both structures are almost normal to the carboxy group plane, as evident in Figs. 1(a) and 1(b). The carboxylic H atom, H4, is also ordered in both structures; although in (1), its distance from O1 is greater than customary (Table 3), there is no evidence for a H atom at this or a lesser distance from O2, and refinement is complicated by the occurrence of a small amount of carboxy group disorder as described below.



Excepting the carboxy group, (1) exhibits a pseudo-mirror plane normal to the C9—C10 bond direction: the r.m.s. difference within the seven pairs of distances which would be identical under such symmetry is 0.008 Å, and thus is only approximately twice the variance of the individual distances. This result is quantitatively superior to the corresponding result found for phenanthrene-9-carboxylic acid cited above.

The individual rings of the phenanthrene core of (1) are nearly planar: for the C1—C4,C11,C12 ring (plane 1), the C5—C8,C13,C14 ring (plane 2) and the C9—C14 ring (plane 3), respectively, the maximum deviation of one of the ring atoms from the best-fit plane describing the ring is 0.016 (2), 0.020 (2) and 0.042 (2) Å, while the average deviation is 0.010 (2), 0.013 (2) and 0.027 (2) Å. The dihedral angles between planes 1 and 2, 2 and 3, and 1 and 3 are, respectively, 10.4 (1), 6.7 (1) and 3.8 (1)°. Consequently, the phenanthrene core as a whole is roughly planar; the maximum deviation of a core atom from the best-fit plane describing the core is 0.146 (2) Å, while the average deviation is 0.078 (2) Å. The carboxy group plane makes a dihedral angle of 63.7 (1)° with the best-fit core plane. For comparison, in phenanthrene-9-carboxylic acid, the dihedral angle between the best-fit core plane and the carboxy group plane is 1.8 (1)°. The larger dihedral angle in (1) is readily rationalized in terms of the otherwise great overcrowding of atoms in the bay region of the molecule.

In (1), the near planarity of the phenanthrene core and the location of the carboxy group in the bay region of the molecule permit a small amount (4.5%; see *Experimental*) of disorder to occur such that the 4-position of the disordered molecule coincides with the 5-position of the ordered molecule [*i.e.*, the disordered molecule is related to the ordered molecule by a rotation by  $\pi$  about an axis normal to and bisecting the C9—C10 bond]. It appears most likely that, in order to avoid undue steric hindrance of carboxy groups, such disorder involves pairs of molecules. If the disordered O-atom positions as refined were to be adjusted to bring the C15B—O carboxy group distances into agreement with those for the ordered molecule, the O1B··O2B' [symmetry code: (i)  $-x, -y, 1-z$ ] distance in the disordered centrosymmetric cyclic dimer would become  $\sim 3.3$  Å, still consistent with weak hydrogen bonding.

In (2), the non-aromatic ring (C1—C4,C11,C12) departs noticeably, as expected, from near planarity; the maximum deviation of one of these atoms from the best-fit plane describing them is 0.384 (2) Å, while the average deviation is 0.176 (2) Å. The remaining naphthalenoid core is, however, roughly planar; the maxi-

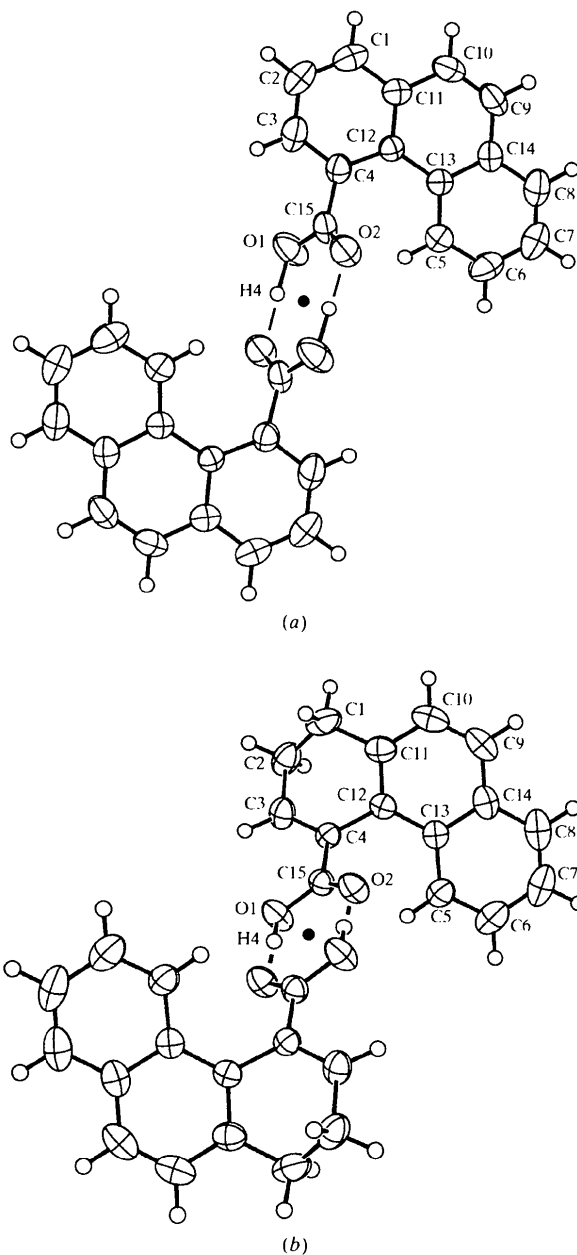


Fig. 1. ORTEP (Johnson, 1976) drawings of (a) the phenanthrene-4-carboxylic acid cyclic hydrogen-bonded dimer and (b) the 1,2-dihydrophenanthrene-4-carboxylic acid cyclic hydrogen-bonded dimer, showing the adopted numbering schemes. Displacement ellipsoids are drawn for 50% probability for all atoms except H atoms, for which they have been set artificially small. In (a), for clarity, the disordered component atoms (C15B, O1B and O2B) have been omitted. In each drawing, the hydrogen bonds are drawn as dashes and a solid sphere depicts a center of symmetry.

imum deviation of one of these atoms from the best-fit plane describing them is 0.090 (2) Å, while the average deviation is 0.051 (2) Å. The dihedral angle between this latter plane and the plane of the carboxy group is 60.4 (1)°, a value quite similar to that for the fully aro-

matic acid and for the same reason. However, the dihedral angle between the carboxy group plane and the plane defined by the three ring atoms nearest the carboxy group (C3, C4 and C12) is only 30.3 (1)° due to the lack of planarity of the non-aromatic ring.

Intramolecular distances and angles of special interest are given in Table 2. The closest intermolecular approaches (excluding disordered atoms O1B, O2B and C15B, and pairs of atoms within directly hydrogen-bonded groups) are, in (1), between C11 and H6<sup>iii</sup> [symmetry code: (iii)  $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$ ] and fall short of the corresponding Bondi (1964) van der Waals radius sum by 0.16 Å; in (2), the two closest approaches fall short of the corresponding radius sums by less than their standard uncertainties, 0.02 Å.

The differences in molecular geometries not withstanding, the packing efficiencies of the two compounds are very similar, the crystal volume per molecule being 278.6 (1) and 286.6 (1) Å<sup>3</sup>, respectively. [The slightly larger value for (2) is consistent with the data on closest approaches given above.]

## Experimental

Phenanthrene-4-carboxylic acid was obtained as a faintly yellow crystalline powder and 1,2-dihydrophenanthrene-4-carboxylic acid as a pale-ecru crystalline powder from samples in the chemical collection of Dr M. S. Newman. Each solid was dissolved in ethylene glycol-dimethyl ether at room temperature and the solutions were filtered. Solvent was then slowly evaporated at room temperature. For (1), this yielded poorly formed crystals, so the sample was refiltered, further evaporated and then seeded with one of these crystals. From the resulting growth a plate-like crystal was cut several times to produce the experimental sample. For (2), evaporation produced clumps of square colorless columns in a viscous red liquid; the cut end of one of these columns served as the experimental sample.

### Compound (1)

#### Crystal data

C<sub>15</sub>H<sub>10</sub>O<sub>2</sub>

$M_r = 222.24$

Monoclinic

$P2_1/n$

$a = 10.010 (2) \text{ \AA}$

$b = 10.737 (2) \text{ \AA}$

$c = 10.512 (2) \text{ \AA}$

$\beta = 99.41 (1)^\circ$

$V = 1114.6 (3) \text{ \AA}^3$

$Z = 4$

$D_x = 1.324 \text{ Mg m}^{-3}$

$D_m$  not measured

#### Data collection

AFC-5S diffractometer

$\omega/2\theta$  scans

Absorption correction: none

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 13.6\text{--}14.8^\circ$

$\mu = 0.082 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Cut plate

$0.42 \times 0.34 \times 0.14 \text{ mm}$

Colorless

$h = 0 \rightarrow 13$

$k = 0 \rightarrow 13$

$l = -13 \rightarrow 13$

2840 measured reflections  
2552 independent reflections  
1220 reflections with  
 $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.013$   
 $\theta_{\text{max}} = 27.5^\circ$

#### Refinement

Refinement on  $F^2$

$R(F) = 0.049$

$wR(F^2) = 0.114$

$S = 1.19$

2551 reflections

166 parameters

H atoms: see below

$w = 1/\sigma^2(F^2)$

$(\Delta/\sigma)_{\text{max}} < 0.01$

6 standard reflections  
every 150 reflections  
intensity variation:  $\pm 2.2\%$   
(average maximum  
relative intensity)

$\Delta\rho_{\text{max}} = 0.36 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$

Extinction correction:

Zachariasen (1963, 1968)

Extinction coefficient:

$7 (3) \times 10^{-7}$

Scattering factors from

Stewart *et al.* (1965) (H)

and Cromer & Waber

(1974) (C, O)

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

O1—C15	1.277 (3)	C4—C15	1.500 (3)
O2—C15	1.252 (2)	C5—C15B	1.500 (2)
C3—C4—C15	113.7 (2)	O1—C15—C4	116.9 (2)
C12—C4—C15	125.1 (2)	O2—C15—C4	119.9 (2)
O1—C15—O2	123.0 (2)		

### Compound (2)

#### Crystal data

C<sub>15</sub>H<sub>12</sub>O<sub>2</sub>

$M_r = 224.26$

Orthorhombic

$Pbca$

$a = 16.065 (3) \text{ \AA}$

$b = 16.534 (2) \text{ \AA}$

$c = 8.632 (2) \text{ \AA}$

$V = 2292.8 (6) \text{ \AA}^3$

$Z = 8$

$D_x = 1.299 \text{ Mg m}^{-3}$

$D_m$  not measured

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25 reflections

$\theta = 14.2\text{--}17.5^\circ$

$\mu = 0.080 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Cut square column

$0.38 \times 0.38 \times 0.27 \text{ mm}$

Colorless

$h = 0 \rightarrow 20$

$k = 0 \rightarrow 21$

$l = 0 \rightarrow 11$

6 standard reflections

every 150 reflections

intensity variation:  $\pm 1.6\%$

(average maximum

relative intensity)

#### Data collection

AFC-5S diffractometer

$\omega/2\theta$  scans

Absorption correction: none

3002 measured reflections

2628 independent reflections

1594 reflections with

$I > 2\sigma(I)$

$\theta_{\text{max}} = 27.50^\circ$

#### Refinement

Refinement on  $F^2$

$R(F) = 0.043$

$wR(F^2) = 0.104$

$S = 1.25$

2627 reflections

178 parameters

H atoms: see below

$w = 1/\sigma^2(F^2)$

$(\Delta/\sigma)_{\text{max}} < 0.01$

$\Delta\rho_{\text{max}} = 0.27 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

Stewart *et al.* (1965) (H)

and Cromer & Waber

(1974) (C, O)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (2)

O1—C15	1.318 (2)	C2—C3	1.497 (2)
O2—C15	1.222 (2)	C3—C4	1.336 (2)
C1—C2	1.515 (3)	C4—C12	1.483 (2)
C1—C11	1.516 (3)	C4—C15	1.479 (2)
C2—C1—C11	110.4 (2)	C4—C12—C11	116.8 (1)
C1—C2—C3	108.1 (2)	O1—C15—O2	122.9 (1)
C2—C3—C4	119.6 (2)	O1—C15—C4	115.2 (1)
C3—C4—C12	120.0 (2)	O2—C15—C4	121.8 (1)
C1—C11—C12	118.3 (2)		

Table 3. Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
(1)				
O1—H4 $\cdots$ O2 <sup>i</sup>	1.22 (4)	1.42 (4)	2.634 (2)	176 (3)
(2)				
O1—H4 $\cdots$ O2 <sup>ii</sup>	0.99 (2)	1.66 (2)	2.651 (2)	173 (2)

Symmetry codes: (i)  $-x, -y, 1-z$ ; (ii)  $1-x, 1-y, -z$ .

Scan widths were  $(1.50 + 0.35\tan\theta)$  and  $(1.10 + 0.35\tan\theta)^\circ$  in  $\omega$  for (1) and (2), respectively. Background/scan time-ratios were 0.5. The data were corrected for Lorentz and polarization effects. The Laue group assignments, systematic absences and intensity statistics consistent with centrosymmetry indicated space group  $P2_1/n$  (No. 14) for (1), and space group  $Pbca$  (No. 61) for (2); since refinement proceeded well they were adopted. Difference Fourier methods were used to locate the initial H-atom positions. In later stages of refinement for (1), all H atoms except the carboxy H atom, H4, were made canonical, with C—H distances of 0.98  $\text{\AA}$  and with  $U_{\text{iso}} = 1.2U_{\text{eq}}$  of the attached C atom. The carboxy H atom was refined isotropically. In later stages of refinement for (2), atoms H5—H10 were made canonical as described above, while the remaining six H atoms were refined isotropically; the refined C—H distances ranged from 0.98 (2) to 1.03 (2)  $\text{\AA}$ , with a mean value of 1.00 (1)  $\text{\AA}$ . When molecule (1) was initially refined on  $F$ , the three leading residual peaks in a difference Fourier map had locations suggestive of a (somewhat distorted) carboxy group on ring atom C5. Atom names C15B, O1B and O2B were assigned to these peaks; C15B was moved toward C5 along the ray connecting them until their separation matched the C4—C15 distance, at which point the position of C15B was fixed. Also the isotropic displacement parameters for these atoms were fixed at the values found for the corresponding ordered atoms. The occupancies of the two sites were then refined along with the coordinates of O1B and O2B. Since the refined value of the disordered site occupancy is only 0.045 (2), the contribution of the disordered atoms to the overall fit is small. However, the model with disorder is statistically superior, on the basis of the Hamilton ratio test (Hamilton, 1965), to the alternative model without disorder at the  $\alpha = 0.005$  level of significance. Although the refined values of the C15B to O1B and O2B distances are somewhat larger than the corresponding values for the ordered molecule, further modeling was not pursued. For (1), the maximum effect of extinction was 2.2% of  $F_o$  for 022; for (2), an extinction coefficient was not refined since the predicted value was negative. The maximum positive residual peak was located 1.42  $\text{\AA}$  from C10 for (1) and 0.92  $\text{\AA}$  from C5 for (2); the maximum negative peak was located 1.76  $\text{\AA}$  from C8 for (1) and 1.14  $\text{\AA}$  from C2 for (2).

For both compounds, data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation,

1988); cell refinement: *MSCIAFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structures: *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: BK1359). Services for accessing these data are described at the back of the journal.

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## 8-Aminocaprylic Acid

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## Abstract

The title acid, 8-aminoctanoic acid,  $\text{C}_8\text{H}_{17}\text{NO}_2$ , crystallized in the centrosymmetric space group  $P2_1/n$  in the zwitterionic form. The three H atoms involved in