

1189 reflections
112 parameters
H-atom positional
parameters refined

$$w = 1/[\sigma^2(F) + (0.039F)^2]$$

Scattering factors as coded in
SDP/PDP User's Guide
(Enraf-Nonius, 1985)

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

O1—C1	1.242 (2)	N3—C1	1.325 (2)
N1—C2	1.332 (2)	C2—C3	1.400 (2)
N1—C6	1.347 (2)	C3—C4	1.367 (2)
N2—C1	1.379 (1)	C4—C5	1.381 (2)
N2—C2	1.389 (2)	C5—C6	1.374 (2)
C2—N1—C6	117.3 (1)	N1—C2—C3	122.4 (1)
C1—N2—C2	130.4 (1)	N2—C2—C3	117.7 (1)
O1—C1—N2	118.2 (1)	C2—C3—C4	118.8 (1)
O1—C1—N3	123.4 (1)	C3—C4—C5	119.6 (1)
N2—C1—N3	118.4 (1)	C4—C5—C6	118.0 (1)
N1—C2—N2	119.9 (1)	N1—C6—C5	123.8 (1)

H atoms were initially located from difference Fourier maps; their coordinates were refined but they were assigned a common $U_{\text{iso}} = 0.0506 \text{\AA}^2$.

Data collection: *CAD-4 Manual* (Enraf-Nonius, 1988). Data reduction: *SDP/PDP User's Guide* (Enraf-Nonius, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SDP/PDP User's Guide*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *KAPPA* (Macíček, unpublished).

This work has been supported by the Bulgarian National Foundation, research grants Ch-402 and Ch-588. We thank Mrs Rosica Petrova for collecting the diffraction data and Dr Jan Fábry for providing facilities under projects 203/93/0154 and 202/93/1154 from the Grant Agency of the Czech Republic.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1272). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). **C53**, 1275–1278

4-(3-Phenanthryl)butanoic Acid

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(Received 19 February 1997; accepted 24 April 1997)

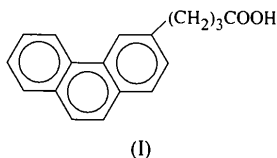
Abstract

The title compound, $\text{C}_{18}\text{H}_{16}\text{O}_2$, crystallized in the centrosymmetric space group $P2_1/a$. The single type of carboxylic hydrogen bond forms cyclic dimers about centers of symmetry. The carboxylic H atom is ordered as are the carboxylic O atoms. This structure comprises double layers of aromatic rings in a herring-bone array separated by double layers of hydrogen-bonded aliphatic strings and is a very close analog of the structures of 4-(2-naphthyl)butanoic acid and other terminally aryl-substituted *n*-aliphatic carboxylic acids.

Comment

This study of 4-(3-phenanthryl)butanoic acid, (I), is one of a series of studies of hydrogen bonding in carboxylic acids. It follows a recent report on the related acid,

4-(2-naphthyl)butanoic acid (Dobson & Gerkin, 1996), and earlier reports on (2-naphthyl)ethanoic acid (Barrett & Gellman, 1993), 4-(2-anthryl)butanoic acid (Durfee, Gruszecka, Olszak, Storck, Bradaczek & Willig, 1989) and 4-(1-pyrenyl)butanoic acid (Olszak, Willig, Durfee, Dreissig & Bradaczek, 1989). Of particular further interest is the packing of the rings (aromatic portion), the strings (aliphatic portion) and the carboxyl groups in such solids.



In 4-(3-phenanthryl)butanoic acid (Fig. 1), there is a single type of hydrogen bond which forms cyclic dimers about centers of symmetry, as shown in Fig. 2. Geometric details of the hydrogen bond are given in Table 2. The carboxylic H atom is found to be

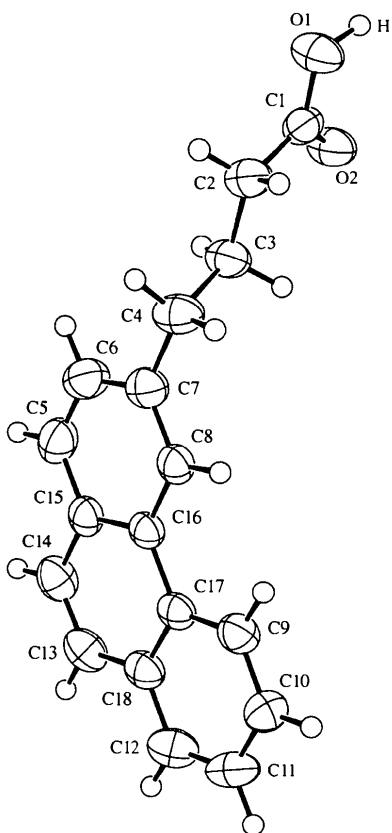


Fig. 1. ORTEPII (Johnson, 1976) drawing of the 4-(3-phenanthryl)butanoic acid molecule showing the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H, for which they have been set artificially small.

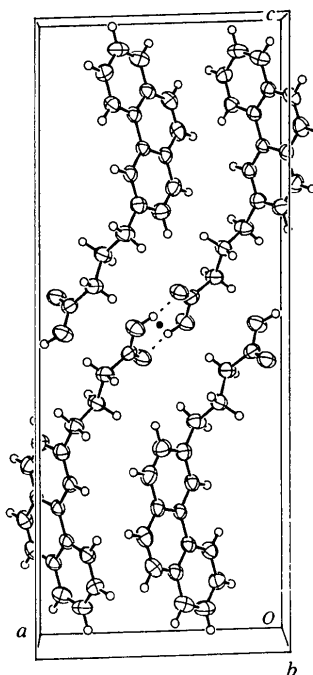


Fig. 2. ORTEPII (Johnson, 1976) packing diagram of 4-(3-phenanthryl)butanoic acid. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H, for which they have been set artificially small. Hydrogen bonds are shown as dashed lines and the center of symmetry as a filled sphere.

ordered, as are the carboxylic O atoms O1 and O2, whose distances from the carboxylic C atom, C1, are 1.318 (3) and 1.214 (4) Å, respectively. As expected for ordered carboxylic O atoms, the principal axes of their displacement tensors are almost normal to the carboxyl group plane as is apparent in Figs. 1 and 2.

The leading aspect of the molecular geometry, as in the related molecules cited above, are the relations between the best-fit planes describing the ring, the string and the carboxyl group. The average deviation of the ring C atoms from the best-fit plane describing the phenanthrene core is 0.011 Å and the maximum deviation is 0.020 Å, while the typical e.s.d. of a single distance is 0.003 Å. Thus, the phenanthrene core in this structure is not quite so nearly planar as the naphthalene core in the 2-naphthyl analog. The best plane through the C1–C4 aliphatic string is such that the average deviation of these atoms from it is 0.038 (3) Å, very slightly less than for the string in the 2-naphthyl analog. The dihedral angle between the ring plane and the string plane here is 78.2 (2)°, while it is 75.9 (2)° in the 2-naphthyl analog. The dihedral angle between the carboxyl group plane and the string plane is 5.1 (4)°, and between the carboxyl group plane and the ring plane, 83.2 (3)°. The corresponding angles in the 2-naphthyl analog are 4.5 (3) and 80.5 (2)°. Thus, the two structures are very similar on an intramolecular basis.

Also, as with the structures cited above, the overall structure (Fig. 2) can be viewed as composed of double layers of aromatic rings separated by double layers of aliphatic chains connected to each other by cyclic dimer hydrogen bonds at the chain termini. In the title structure, adjacent phenanthryl groups adopt a herringbone angle of $84.52(6)^\circ$, a value substantially different from that in phenanthrene itself (58.25° , calculated from Kay, Okaya & Cox, 1971) and in the 2-naphthyl analog [$51.6(4)^\circ$]. However, as is apparent from Olszak, Willig, Durfee, Dreissig & Bradaczek (1989), in 4-(1-pyrenyl)butanoic acid, the difference in packing is more striking since in pyrene itself, face-to-face pyrene dimers are the basic structural entities.

All intramolecular distances and angles fall within normal ranges. The closest intermolecular approaches, excluding pairs of atoms within directly hydrogen-bonded groups, are between a ring C atom, C9, and a ring H atom on C14, H14ⁱⁱ, which falls short of the Bondi (1964) radius sum by 0.13 \AA , and between C9 and ring carbon C13ⁱⁱⁱ which falls short by 0.04 \AA [symmetry codes: (ii) $\frac{1}{2} + x, \frac{1}{2} - y, z$; (iii) $x, 1 + y, z$]. No other intermolecular approach is significantly less than the corresponding Bondi sum.

Experimental

4-(3-Phenanthryl)butanoic acid was obtained as colorless small flakes from a sample in Dr M. S. Newman's chemical collection. This solid was dissolved in ether and the solution was evaporated at room temperature to produce colorless thin hexagonal plates, one of which was cut to provide the experimental sample.

Crystal data

$C_{18}H_{16}O_2$
 $M_r = 264.32$
 Monoclinic
 $P2_1/a$
 $a = 10.580(2) \text{ \AA}$
 $b = 5.034(2) \text{ \AA}$
 $c = 25.762(2) \text{ \AA}$
 $\beta = 91.56(1)^\circ$
 $V = 1371.7(6) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.280 \text{ Mg m}^{-3}$
 D_m not measured

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 11.2\text{--}17.4^\circ$
 $\mu = 0.077 \text{ mm}^{-1}$
 $T = 296 \text{ K}$
 Cut plate
 $0.38 \times 0.35 \times 0.08 \text{ mm}$
 Colorless

Data collection

Rigaku AFC-5S diffractometer
 ω scans
 Absorption correction: none
 3715 measured reflections
 3531 independent reflections
 1916 reflections with
 $I > 0.4\sigma(I)$
 $R_{int} = 0.057$

$\theta_{max} = 27.5^\circ$
 $h = 0 \rightarrow 13$
 $k = 0 \rightarrow 6$
 $l = -33 \rightarrow 33$
 6 standard reflections every 150 reflections
 intensity variation: $\pm 2.6\%$ (average maximum relative intensity)

Refinement

Refinement on F^2
 $R = 0.062$
 $wR = 0.115$
 $S = 1.24$
 1916 reflections
 186 parameters
 H atoms: see below
 $w = 1/\sigma^2(F^2)$
 $(\Delta/\sigma)_{max} < 0.01$
 $\Delta\rho_{max} = 0.39 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.33 \text{ e \AA}^{-3}$

Extinction correction:
 Zachariasen (1963, 1968)
 Extinction coefficient:
 $6(2) \times 10^{-7}$
 Scattering factors from
 Stewart, Davidson &
 Simpson (1965) (H) and
 Cromer & Waber (1974)
 (C, O)

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

O1—C1	1.318 (3)	O2—C1	1.214 (4)
O1—C1—O2	122.8 (3)	O2—C1—C2	124.8 (3)
O1—C1—C2	112.5 (3)		

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H \cdots O2 ⁱ	0.96 (4)	1.73 (4)	2.682 (3)	172 (3)

Symmetry codes: (i) $2 - x, 1 - y, 1 - z$.

Scan widths were $(1.50 + 0.35 \tan \theta)^\circ$ in ω , with 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 were consistent with centrosymmetry indicated space group $P2_1/a$ (No. 14) and since refinement proceeded well it was adopted. Fourier difference methods were used to locate the initial H-atom positions. In later stages of refinement, all H atoms except the carboxylic H atom were made canonical with $C-H = 0.98 \text{ \AA}$ and $U_{iso} = 1.2U_{eq}$ of the attached C atom. The carboxylic H atom was refined isotropically. The maximum effect of extinction was 2.2% of F_o for 204. The maximum positive residual peak was located $\sim 1.2 \text{ \AA}$ from C5 and the maximum negative peak $\sim 1.4 \text{ \AA}$ from C1 and C2.

Data collection: *MSCI/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCI/AFD 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*.

I thank Dr J. C. Gallucci for help of various sorts. The diffractometer was purchased with funds provided in part by an NIH grant.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1335). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C53, 1278–1280

2-Bromo-3-methyl-2-butenoic Acid (2-Bromosenecioic Acid)

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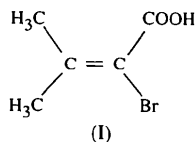
(Received 30 January 1997; accepted 11 April 1997)

Abstract

The title compound, C₅H₇BrO₂, crystallized in space group *P* $\bar{1}$. Molecules are linked to form normal centrosymmetric hydrogen-bonded dimers with O \cdots O 2.625 (4) Å. The carboxyl H and O atoms are ordered, but the H atoms of both methyl groups are disordered. The Br and C atoms lie very nearly in a plane which makes a dihedral angle of 30.0 (1)° with the carboxyl group plane.

Comment

This study is one of a continuing series on hydrogen bonding in carboxylic acids. In 2-bromo-3-methyl-2-butenoic acid, (I), the hydrogen bonding is of the cyclic dimer type about a center of symmetry as shown in Fig. 1, which also shows our numbering scheme.



The five C atoms and the Br atom of the title acid lie very nearly in a plane, the maximum deviation of an atom from the best-fit plane through them being 0.018 (4) Å, the average deviation being 0.007 (4) Å. The dihedral angle between this plane and the carboxyl group plane is 30.0 (1)°.

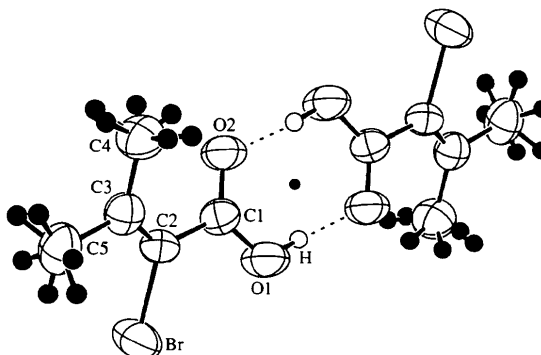


Fig. 1. *ORTEPII* (Johnson, 1976) diagram of the hydrogen-bonded cyclic dimer of 2-bromo-3-methyl-2-butenoic acid showing the molecular numbering scheme and the center of symmetry about which the dimer is formed. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H, for which they have been set arbitrarily small. The half-occupancy H atoms of the disordered methyl groups are shown as filled spheres. The center of symmetry is shown as a filled sphere and the hydrogen bonds as dashed lines.

The best available comparison of molecular geometry is perhaps afforded by trichloroacrylic acid, Cl₂C=CClCOOH (Fleck, Göckel & Weiss, 1987), which was found to be slightly less planar: the maximum deviation of an atom from the best-fit plane through the three C atoms and the three Cl atoms (the analog of the plane described above for the title acid) is reported to be 0.05 Å. Using our numbering scheme, with values for trichloroacrylic acid in brackets, distances are: C1—O1 1.277 (4) [1.285 (3)], C1—O2 1.239 (4) [1.207 (3)], C1—C2 1.475 (5) [1.502 (3)] and C2—C3 1.315 (4) Å [1.319 (3) Å], and angles are: O1—C1—O2 122.3 (3) [124.9 (2)], C2—C1—O1 116.9 (3) [112.7 (2)] and C2—C1—O2 120.8 (3)° [122.4 (2)°]. In the cyclic dimer hydrogen bond of trichloroacrylic acid, O_d—H is reported as 0.69 (3) Å, O_d⋯O_a as 2.677 (3) Å and O_d—H⋯O_a as 165°, the latter two values agreeing well with those for the title compound (Table 2).

It should be noted that in the Fourier difference map used to assign the coordinates of the carboxyl H atom near O1 there was no peak near O2 assignable as a (fractional occupancy) H atom. Thus, the H atom on O1 was assigned as ordered. The presence of the Br atom, however, makes this assessment less definitive than would be expected, for example, for the unsubstituted analog, (CH₃)₂C=CHCOOH.