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Anthracene-9-carboxylic Acid

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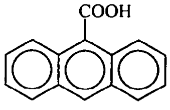
Abstract

Anthracene-9-carboxylic acid, $C_{15}H_{10}O_2$, was found to crystallize in the centrosymmetric space group $P2_1/n$. The hydrogen bonding is of the cyclic-dimer type about a center of symmetry. The carboxyl O atoms are ordered, as is the carboxyl H atom. The anthracene core is almost planar and shows good agreement with the anthracene core of anthracene-1,8-dicarboxylic acid. The carboxyl group plane makes a dihedral angle of 54.87 (6)° with the best-fit anthracene core plane.

Comment

This study of anthracene-9-carboxylic acid, (I), was conducted as one of a series of studies on hydrogen bonding in aromatic carboxylic acids. It follows a study of the non-centrosymmetric structure of anthracene-1,8-dicarboxylic acid (Fitzgerald & Gerkin, 1996). In an earlier study of anthracene-9-carboxylic acid, (I), Heller & Schmidt (1971) reported a triclinic cell but gave no atomic coordinates. The sample reported here was found to be monoclinic.



(I)

In the present $P2_1/n$ structure, there is a single type of hydrogen bond which forms a cyclic dimer about a center of symmetry, as shown in Fig. 1. Geometric details of the hydrogen bond are given in Table 2.

The carboxyl H atom is ordered, as are the carboxyl O atoms, for which the C—O distances are 1.240 (2) and 1.292 (2) Å (Table 2). As in previous studies (Fitzgerald & Gerkin, 1993, 1996) and as is apparent from Fig. 1, the principal displacement tensor axes of the O atoms are almost perpendicular to the carboxyl group plane.

The anthracene core exhibits close conformity to mirror symmetry with respect to a mirror through the C9 and C10 atoms; for the eight pairs of distances which would be identical under this symmetry, the r.m.s. deviation within pairs is 0.002_4 Å, while the e.s.d. of individual distances is 0.002–0.003 Å. For the pseudo-mirror at right angles to this, the r.m.s. deviation within the analogous six pairs of distances is 0.014 Å. The average difference between corresponding distances in the cores of the 1,8-diacid and this acid is 0.009 Å, while the individual e.s.d.'s are 0.007–0.009 and 0.002–0.003 Å, respectively.

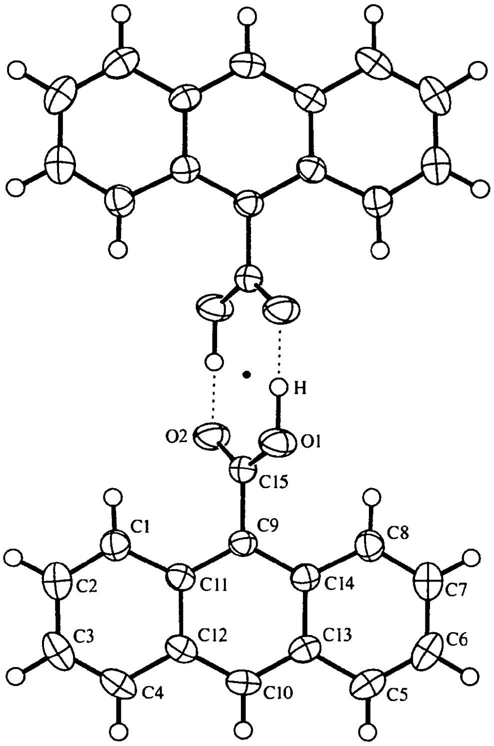


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the anthracene-9-carboxylic acid hydrogen-bonded cyclic dimers showing the atomic numbering scheme. Displacement ellipsoids are drawn at 50% probability for all atoms, except H atoms for which they have been set artificially small. The center of symmetry is shown as a filled circle.

The molecular core is almost planar. The average distance of the core atoms from the best-fit core plane is 0.020 Å, which may be compared with 0.018 Å for the 1,8-diacid. The dihedral angle between the plane of the carboxyl group and the best-fit core plane is 54.87 (6)°, substantially larger than the analogous angles in the 1,8-diacid of 13.9 (2) and 21.6 (2)°.

The molecular packing is shown in Fig. 2. The dihedral angle between the two orientations of the best-fit anthracene core planes is 23.29 (3)°. Excepting pairs of atoms involved directly in hydrogen bonding, the closest intermolecular approaches are between the O2 and H6^i atoms [symmetry code: (i) x, $1+y$, z]. These closest approaches are not significantly less than the corresponding sum of the Bondi (1964) radii.

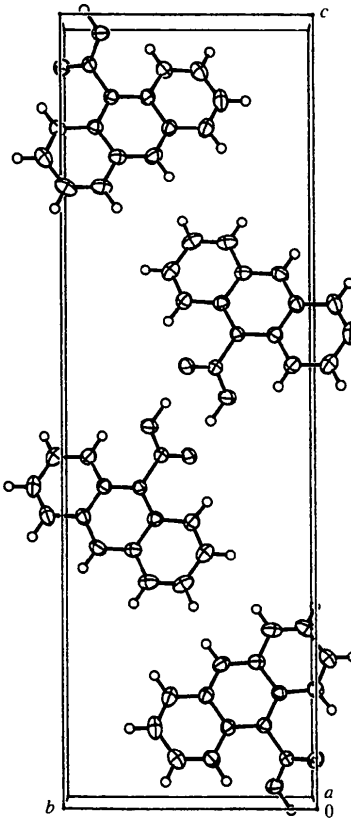


Fig. 2. *ORTEP*II (Johnson, 1976) packing diagram of anthracene-9-carboxylic acid. Displacement ellipsoids are drawn at 50% probability for all atoms, except H atoms for which they have been set artificially small.

Experimental

Anthracene-9-carboxylic acid, obtained from the Aldrich Chemical Company, was dissolved with slight heating in ethyl acetate and the resulting solution slightly acidified with dilute nitric acid and filtered. Slow evaporation of the filtrate at room temperature produced plates, one of which was cut to provide the experimental sample.

Crystal data

$C_{15}H_{10}O_2$
$M_r = 222.24$
Monoclinic
$P2_1/n$
$a = 3.897\,(3)$ Å
$b = 9.355\,(2)$ Å
$c = 28.980\,(3)$ Å
$\beta = 90.79\,(4)°$
$V = 1056.4\,(8)$ Å^3
$Z = 4$
$D_x = 1.397$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13.5$–$14.9°$
$\mu = 0.086$ mm^{-1}
$T = 296$ K
Cut plate
$0.46 \times 0.31 \times 0.16$ mm
Yellow

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: empirical *via* ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.957$, $T_{\max} = 1.000$
2934 measured reflections
2562 independent reflections
1638 observed reflections [$I > \sigma(I)$]

$R_{\rm int} = 0.017$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 5$
$k = 0 \rightarrow 12$
$l = -37 \rightarrow 37$
6 standard reflections monitored every 150 reflections intensity variation: ±2.2% (average maximum relative intensity)

Refinement

Refinement on F
$R = 0.044$
$wR = 0.049$
$S = 1.60$
1638 reflections
159 parameters
H atoms: see below
$w = 1/[\sigma^2(F)]$
$(\Delta/\sigma)_{\max} = < 0.01$
$\Delta\rho_{\max} = 0.25$ e Å^{-3}
$\Delta\rho_{\min} = -0.17$ e Å^{-3}

Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: $10\,(3) \times 10^{-7}$
Atomic scattering factors from Stewart, Davidson & Simpson (1965) for H atoms and Cromer & Waber (1974) for C and O atoms

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.2132 (4)	0.3430 (1)	0.51848 (4)	0.0471 (4)
O2	−0.0917 (4)	0.5035 (1)	0.55668 (4)	0.0473 (4)
C1	0.3610 (5)	0.5129 (2)	0.64160 (6)	0.0388 (5)
C2	0.5048 (5)	0.5663 (2)	0.68067 (7)	0.0456 (6)
C3	0.5753 (6)	0.4782 (3)	0.71908 (7)	0.0494 (6)
C4	0.4987 (5)	0.3379 (2)	0.71734 (6)	0.0455 (6)
C5	0.0278 (6)	−0.0797 (2)	0.63513 (7)	0.0456 (6)
C6	−0.1253 (6)	−0.1385 (2)	0.59770 (8)	0.0489 (6)
C7	−0.2068 (5)	−0.0532 (2)	0.55894 (7)	0.0459 (6)
C8	−0.1290 (5)	0.0882 (2)	0.55821 (6)	0.0388 (5)
C9	0.1271 (4)	0.3018 (2)	0.59804 (6)	0.0305 (5)
C10	0.2691 (5)	0.1306 (2)	0.67483 (6)	0.0390 (6)
C11	0.2723 (5)	0.3648 (2)	0.63798 (6)	0.0314 (5)
C12	0.3459 (5)	0.2753 (2)	0.67704 (6)	0.0351 (5)
C13	0.1144 (5)	0.0686 (2)	0.63623 (6)	0.0343 (5)
C14	0.0411 (5)	0.1552 (2)	0.59659 (6)	0.0318 (5)
C15	0.0742 (5)	0.3904 (2)	0.55569 (6)	0.0329 (5)

Table 2. *Geometric parameters and hydrogen-bonding geometry (Å, °)*

C1—C2	1.352 (2)	C9—C11	1.411 (2)
C1—C11	1.431 (2)	C9—C14	1.412 (2)
C2—C3	1.409 (3)	C10—C12	1.388 (3)
C3—C4	1.347 (3)	C10—C13	1.390 (3)
C4—C12	1.429 (2)	C11—C12	1.434 (2)
C5—C6	1.348 (3)	C13—C14	1.431 (2)
C5—C13	1.428 (3)	C9—C15	1.493 (2)
C6—C7	1.411 (3)	C15—O1	1.292 (2)
C7—C8	1.357 (3)	C15—O2	1.240 (2)
C8—C14	1.432 (2)		
C2—C1—C11	121.0 (2)	C9—C11—C12	118.5 (2)
C1—C2—C3	121.3 (2)	C4—C12—C10	121.7 (2)
C2—C3—C4	120.0 (2)	C4—C12—C11	118.8 (2)
C3—C4—C12	121.3 (2)	C10—C12—C11	119.5 (2)
C6—C5—C13	121.1 (2)	C5—C13—C10	121.5 (2)

C5—C6—C7	120.2 (2)	C5—C13—C14	119.2 (2)
C6—C7—C8	121.0 (2)	C10—C13—C14	119.3 (2)
C7—C8—C14	121.1 (2)	C8—C14—C9	123.8 (2)
C11—C9—C14	121.5 (2)	C8—C14—C13	117.4 (2)
C11—C9—C15	119.5 (2)	C9—C14—C13	118.8 (2)
C14—C9—C15	119.0 (2)	C9—C15—O1	116.2 (2)
C12—C10—C13	122.3 (2)	C9—C15—O2	121.4 (2)
C1—C11—C9	123.9 (2)	O1—C15—O2	122.4 (2)
C1—C11—C12	117.5 (2)		

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H···O2^{i}	1.11 (3)	1.54 (3)	2.646 (2)	176 (3)

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

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 were consistent with centrosymmetry-indicated space group $P2_1/n$ (No. 14) and since refinement proceeded well, it was adopted. Fourier difference methods were used to locate the H-atom positions. In the later stages of refinement, ring H atoms H1–H8 and H10 were made canonical, with a C—H distance of 0.98 Å and $U_{\rm iso} = 1.2 \times U_{\rm eq}$ of the associated C atom. The carboxylic H atom was refined isotropically. The maximum effect of extinction was 7.3% of F_o for $10\bar{5}$. The maximum positive residual peak was located near the midpoint of the C13—C14 bond, with the maximum negative peak located near the center of the central ring.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). 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*.

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Lists of structure factors, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1282). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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N-Acetyl-L-glutamic Acid

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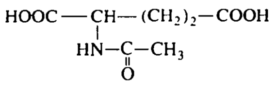
Abstract

In the structure of *N*-acetyl-L-glutamic acid, $C_7H_{11}NO_5$, each molecule is directly hydrogen bonded to four others by a total of six hydrogen bonds. Two carboxylic O atoms and the N atom are donors, while all three acceptors are O atoms. There is also an intramolecular hydrogen bond with the N atom as donor and a carboxylic O atom as acceptor. The carboxyl O and H atoms are ordered. The conformation of the carbon chain with respect to the C3—C4 bond is *trans* as in L-glutamic acid hydrochloride, rather than *gauche* as in the β form of L-glutamic acid.

Comment

This structural study of *N*-acetyl-L-glutamic acid, (I), is one of a continuing series on hydrogen bonding in carboxylic acids. In addition to its two carboxyl groups, this acid has further potential hydrogen-bonding groups, namely the NH group and the carbonyl O atom.



$\mathrm{HOOC{-}CH(NH{-}C({=}O){-}CH_3){-}(CH_2)_2{-}COOH}$

(I)

In the title acid (Figs. 1 and 2), all of the groups mentioned above are indeed involved in hydrogen bonding. Each H atom bonded to a potential hydrogen-bond donor atom (H1, H5 and H6) participates in a single intermolecular hydrogen bond. (In addition, H6 participates in an intramolecular hydrogen bond.) Moreover, each potential acceptor atom that is not already bonded to an H atom (O21, O25 and O5) participates in one

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