

For both compounds, data collection: *P3/P4-PC Diffractometer Program* (Siemens, 1991a); cell refinement: *P3/P4-PC Diffractometer Program*; data reduction: *XDISK* (Siemens, 1991b); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990a); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990b); software used to prepare material for publication: *SHELXTL/PC* and *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1166). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Fluorene-9-carboxylic Acid

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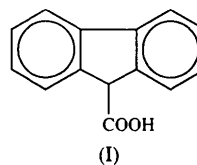
Abstract

In fluorene-9-carboxylic acid, C₁₄H₁₀O₂, there are two crystallographically independent sets of molecules each of which exhibits hydrogen bonding of the cyclic dimer

type about a center of symmetry. Additionally, one of the sets shows disordering of the carboxyl O atoms. Within the carboxyl groups, however, the carboxyl H atoms were found to be, or modelled as, ordered.

Comment

This study of fluorene-9-carboxylic acid, (I), is the third in a series on hydrogen bonding in fluorene monocarboxylic acids, studies of fluorene-1-carboxylic acid (F1CA) and fluorene-4-carboxylic acid (F4CA) having been reported previously (Blackburn, Dobson & Gerkin, 1996a,b).



The hydrogen bonding is of the cyclic dimer type about a center of symmetry, as shown in Fig 1. The C—O and O—H distances found in the *B* molecule carboxyl group (Table 2) are entirely consistent with an ordered carboxylic H atom; in the disordered carboxyl group of the *A* molecule, the C—O distances and the Fourier difference map, from which the H-atom positions were assigned, strongly suggest the interpretation that these H atoms are also ordered. The dihedral angle between the planes of the disordered carboxyl groups (O1A—C14—O2A and O1A*—C14—O2A*) is 55.8°. The donor-acceptor distances are (as in F1CA and F4CA) below average for organic O···O hydrogen bonds (2.77 Å; Ceccarelli, Jeffrey & Taylor, 1981).

With respect to interatomic distances in the fluorene core, the two independent molecules reported here exhibit pseudo-mirror symmetry to within smaller deviations than in the cases of F1CA and F4CA: the r.m.s. deviations within the seven pairs of core distances which would be identical under mirror symmetry are 0.004 (3) and 0.005 (3) Å, respectively, for the *A* and *B* molecules. The one unique core interatomic distance, C11—C12, has values of 1.463 (3) and 1.470 (3) Å for *A* and *B*, respectively; in our report on F4CA we surmised that further measurements of this distance would very probably fall in the range from 1.471–1.492 Å.

As in describing F1CA and F4CA, we have chosen best-fit planes for atoms C1–C4, C10 and C11 and atoms C5–C8, C12 and C13 to define the molecular dihedral angle. The maximum distance of any of these atoms from the best-fit plane including that atom is 0.004 (3) Å for the *A* molecule, 0.006 (3) Å for the *B* molecule; these distances are less than those for F1CA or F4CA. The resulting molecular dihedral angle is 0.2 (1)° for *A* and 1.2 (1)° for the *B* molecule, values closest to those for fluorene itself at room temperature (Belsky, Zavodnik &

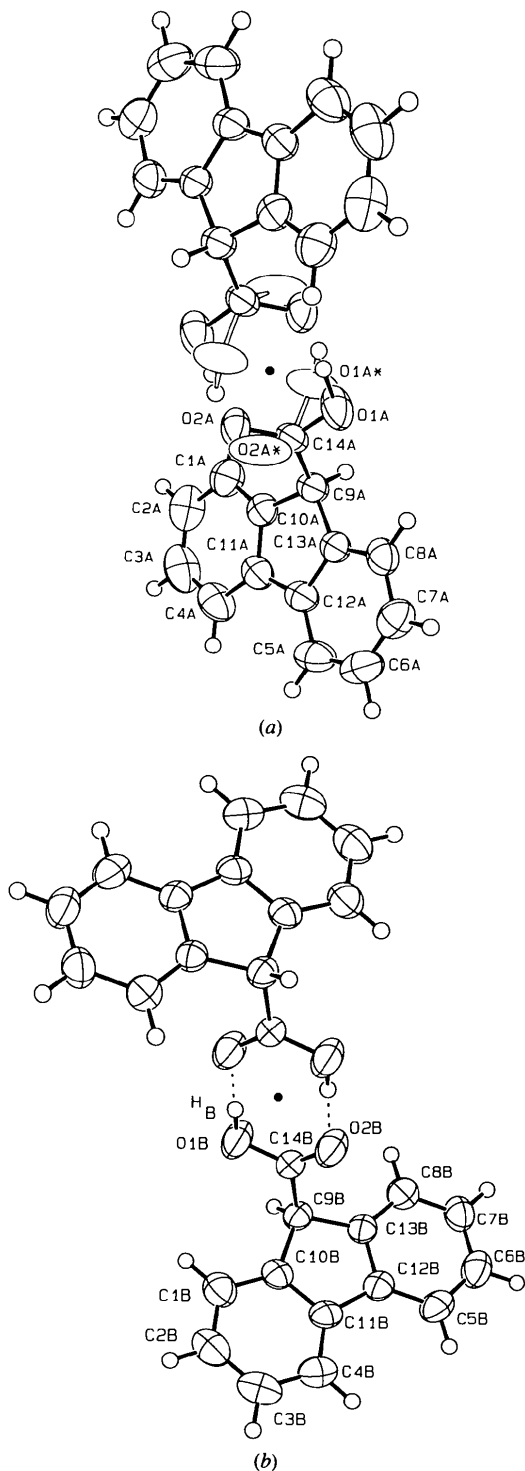


Fig. 1. ORTEP (Johnson, 1976) drawing of (a) *A* and (b) *B* fluorene-9-carboxylic acid hydrogen-bonded cyclic dimers showing our numbering scheme. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H atoms, for which they have been set artificially small. The centers of symmetry are shown as solid circles, hydrogen bonds as dashed lines. For clarity, depiction of the hydrogen bonding of the two (disordered) *A*-molecule carboxyl groups has been omitted.

Vozzhennikov, 1984) and at low temperature (Gerkin, Lundstedt & Reppart, 1984), and to the β -phase *B* molecule in F4CA.

The five-membered ring, to which the carboxyl group is attached in the title molecule, is by far the least planar in both the *A* and *B* molecules, the maximum atomic deviations being 0.011 (2) and 0.015 (2) Å, respectively. The dihedral angle between the best-fit plane describing this ring and the plane of the attached carboxyl group is 65 (1)° for *A*, 76 (1)° for *A** and 74 (1)° for *B*.

Excluding atoms involved in hydrogen bonding, the closest calculated intermolecular approaches involve O1A* of a given molecule with O1A* and H_A of another, and with O2A* of a third. These distances fall short of the corresponding van der Waals radius sums (Bondi, 1964) by distances from 0.36 to 0.60 Å. However, purely statistically, the combined probability of either of these occupations occurring is only ~0.2 and if there is a significant unfavorable energetic effect, the disordering will simply not involve these two particular site combinations. Apart from these unlikely approaches, the closest approaches involve C5*B* and H5*A* and are ~0.14 Å less than the corresponding radius sum.

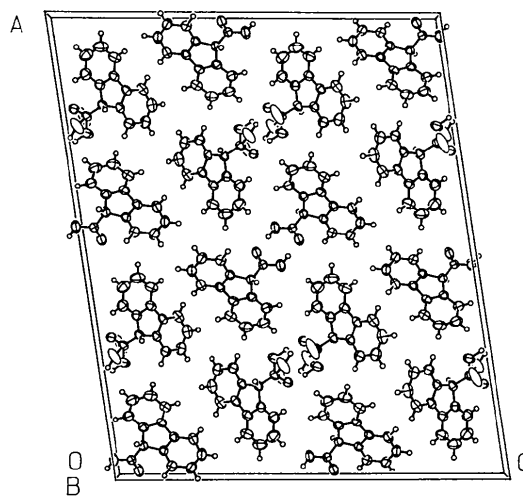


Fig. 2. ORTEP (Johnson, 1976) drawing of the packing of fluorene-9-carboxylic acid. Displacement ellipsoids are drawn at the 50% probability level for all atoms except H atoms, for which they have been set artificially small.

Experimental

Fluorene-9-carboxylic acid from Aldrich Chemical Company was dissolved in ether and the solution was filtered. Slow evaporation of solvent from the filtrate at room temperature produced clear crystals, one of which was cut to provide the experimental sample.

Crystal data

C₁₄H₁₀O₂ $M_r = 210.23$

Monoclinic

C2/c

 $a = 33.749 (4) \text{ \AA}$ $b = 4.459 (3) \text{ \AA}$ $c = 28.151 (3) \text{ \AA}$ $\beta = 98.59 (1)^\circ$ $V = 4189 (3) \text{ \AA}^3$ $Z = 16$ $D_x = 1.333 \text{ Mg m}^{-3}$ D_m not measured

Data collection

AFC-5S diffractometer

 ω scansAbsorption correction:
none

5523 measured reflections

5430 independent reflections

2473 observed reflections

 $[I > 3\sigma(I)]$ $R_{\text{int}} = 0.014$ $\theta_{\text{max}} = 27.50^\circ$

Refinement

Refinement on F^2 $R = 0.040$ $wR = 0.050$ $S = 1.64$

2473 reflections

321 parameters

 $w = 1/[\sigma(F)]^2$ $(\Delta/\sigma)_{\text{max}} < 0.01$ $\Delta\rho_{\text{max}} = 0.17 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$ Mo $K\alpha$ radiation $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25

reflections

 $\theta = 11.8\text{--}15.2^\circ$ $\mu = 0.083 \text{ mm}^{-1}$ $T = 296 \text{ K}$

Cut rod

 $0.39 \times 0.39 \times 0.27 \text{ mm}$

Colorless

C3B	0.17418 (8)	0.2910 (7)	0.1127 (1)	0.0770 (10)
C4B	0.15072 (7)	0.3701 (6)	0.14706 (9)	0.0649 (8)
C5B	0.08318 (7)	0.6377 (6)	0.20903 (8)	0.0597 (8)
C6B	0.05185 (8)	0.7827 (7)	0.22569 (8)	0.0665 (9)
C7B	0.02556 (7)	0.9617 (6)	0.19564 (9)	0.0636 (8)
C8B	0.02974 (7)	0.9973 (6)	0.14779 (8)	0.0566 (7)
C9B	0.07140 (6)	0.8472 (6)	0.08057 (8)	0.0458 (7)
C10B	0.10895 (6)	0.6537 (5)	0.08622 (8)	0.0469 (6)
C11B	0.11778 (6)	0.5524 (5)	0.13354 (8)	0.0485 (7)
C12B	0.08788 (6)	0.6752 (5)	0.16123 (7)	0.0471 (7)
C13B	0.06096 (6)	0.8526 (5)	0.13099 (7)	0.0453 (6)
C14B	0.03923 (6)	0.7033 (6)	0.04465 (8)	0.0466 (7)

† Site occupancy = 0.66(2). ‡ Site occupancy = 0.34(2).

Table 2. Selected geometric parameters (\AA , $^\circ$)

C1A—C2A	1.386 (4)	C3B—C4B	1.384 (4)
C1A—C10A	1.377 (3)	C4B—C11B	1.384 (3)
C2A—C3A	1.375 (4)	C5B—C6B	1.380 (3)
C3A—C4A	1.378 (4)	C5B—C12B	1.388 (3)
C4A—C11A	1.388 (3)	C6B—C7B	1.384 (4)
C5A—C6A	1.380 (4)	C7B—C8B	1.385 (3)
C5A—C12A	1.383 (3)	C8B—C13B	1.378 (3)
C6A—C7A	1.371 (4)	C9B—C10B	1.522 (3)
C7A—C8A	1.386 (3)	C9B—C13B	1.513 (3)
C8A—C13A	1.383 (3)	C9B—C14B	1.512 (3)
C9A—C10A	1.519 (3)	C10B—C11B	1.396 (3)
C9A—C13A	1.517 (3)	C11B—C12B	1.470 (3)
C9A—C14A	1.510 (3)	C12B—C13B	1.395 (3)
C10A—C11A	1.390 (3)	C14A—O1A	1.252 (4)
C11A—C12A	1.463 (3)	C14A—O2A	1.233 (4)
C12A—C13A	1.395 (3)	C14A—O1A*	1.250 (7)
C1B—C2B	1.385 (4)	C14A—O2A*	1.202 (8)
C1B—C10B	1.382 (3)	C14B—O1B	1.295 (2)
C2B—C3B	1.377 (4)	C14B—O2B	1.214 (2)
C2A—C1A—C10A	118.8 (3)	C7B—C8B—C13B	128.3 (2)
C1A—C2A—C3A	120.4 (3)	C10B—C9B—C13B	102.6 (2)
C2A—C3A—C4A	121.2 (3)	C1B—C10B—C9B	128.9 (2)
C3A—C4A—C11A	118.7 (3)	C1B—C10B—C11B	121.3 (2)
C6A—C5A—C12A	119.4 (2)	C9B—C10B—C11B	109.8 (2)
C5A—C6A—C7A	121.0 (3)	C4B—C11B—C10B	120.0 (2)
C6A—C7A—C8A	120.4 (3)	C4B—C11B—C12B	131.3 (2)
C7A—C8A—C13A	118.9 (2)	C10B—C11B—C12B	108.7 (2)
C10A—C9A—C13A	102.7 (2)	C5B—C12B—C11B	131.0 (2)
C1A—C10A—C9A	129.4 (2)	C5B—C12B—C13B	120.1 (2)
C1A—C10A—C11A	120.9 (2)	C11B—C12B—C13B	108.9 (2)
C9A—C10A—C11A	109.7 (2)	C8B—C13B—C9B	128.8 (2)
C4A—C11A—C10A	120.0 (3)	C8B—C13B—C12B	121.2 (2)
C4A—C11A—C12A	130.9 (2)	C9B—C13B—C12B	110.0 (2)
C10A—C11A—C12A	109.1 (2)	C10A—C9A—C14A	114.6 (2)
C5A—C12A—C11A	131.5 (2)	C13A—C9A—C14A	112.3 (2)
C5A—C12A—C13A	119.5 (2)	C9A—C14A—O1A	114.6 (3)
C11A—C12A—C13A	108.9 (2)	C9A—C14A—O2A	122.9 (2)
C8A—C13A—C9A	129.7 (2)	O1A—C14A—O2A	122.6 (3)
C8A—C13A—C12A	120.7 (2)	C9A—C14A—O1A*	117.4 (4)
C9A—C13A—C12A	109.6 (2)	C9A—C14A—O2A*	121.4 (4)
C2B—C1B—C10B	117.8 (2)	O1A*—C14A—O2A*	121.0 (5)
C1B—C2B—C3B	121.2 (2)	C10B—C9B—C14B	109.5 (2)
C2B—C3B—C4B	121.1 (3)	C13B—C9B—C14B	112.9 (2)
C3B—C4B—C11B	118.5 (2)	C9B—C14B—O1B	114.2 (2)
C6B—C5B—C12B	118.5 (2)	C9B—C14B—O2B	122.5 (2)
C5B—C6B—C7B	121.1 (2)	O1B—C14B—O2B	123.3 (2)
C6B—C7B—C8B	120.8 (2)		

Table 3. Hydrogen-bonding geometry (\AA , $^\circ$)†

D—H...A	D—H	H...A	D...A	D—H...A
O1A—H _A ...O2A ⁱ	1.11	1.55	2.663 (5)	178
O1A*—H _A *...O2A* ⁱ	1.02	1.77	2.650 (11)	142
O1B—H _B ...O2B ⁱⁱ	1.03 (3)	1.63 (3)	2.652 (2)	172 (3)

Symmetry codes: (i) $\frac{1}{2} - x, -\frac{1}{2} - y, -z$; (ii) $-x, 1 - y, -z$.† Since the positions of H_A and H_A* are fixed, no uncertainties are given for distances or angles involving them.Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
O1A†	0.2436 (1)	-0.058 (2)	0.0532 (3)	0.091 (2)
O1A*‡	0.2582 (6)	0.078 (2)	0.0328 (5)	0.093 (4)
O2A†	0.29729 (9)	-0.231 (2)	0.0282 (2)	0.071 (2)
O2A*‡	0.2818 (7)	-0.362 (2)	0.0481 (5)	0.115 (5)
C1A	0.36933 (8)	0.2045 (7)	0.07627 (9)	0.0677 (9)
C2A	0.41083 (9)	0.1993 (8)	0.0853 (1)	0.081 (1)
C3A	0.43043 (8)	0.0383 (8)	0.1233 (1)	0.087 (1)
C4A	0.40956 (8)	-0.1209 (7)	0.15346 (10)	0.0728 (9)
C5A	0.34255 (8)	-0.4460 (7)	0.21000 (9)	0.0689 (9)
C6A	0.30879 (10)	-0.5541 (7)	0.22652 (9)	0.0754 (10)
C7A	0.27117 (8)	-0.4824 (7)	0.20385 (9)	0.0697 (9)
C8A	0.26631 (7)	-0.2971 (6)	0.16387 (9)	0.0595 (8)
C9A	0.30322 (7)	0.0184 (6)	0.10500 (8)	0.0498 (7)
C10A	0.34822 (7)	0.0446 (5)	0.10603 (8)	0.0510 (7)
C11A	0.36799 (7)	-0.1178 (6)	0.14460 (8)	0.0539 (7)
C12A	0.33831 (7)	-0.2626 (5)	0.16993 (8)	0.0517 (7)
C13A	0.30000 (7)	-0.1878 (5)	0.14711 (7)	0.0475 (7)
C14A	0.28067 (7)	-0.1007 (6)	0.05846 (8)	0.0490 (8)
O1B	0.04085 (5)	0.7750 (5)	0.00041 (6)	0.0728 (6)
O2B	0.01473 (5)	0.5301 (5)	0.05647 (5)	0.0722 (6)
C1B	0.13245 (7)	0.5746 (6)	0.05198 (8)	0.0613 (8)
C2B	0.16532 (8)	0.3925 (7)	0.0662 (1)	0.0741 (10)

Scan widths were $(1.20 + 0.35 \tan\theta)^\circ$ 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. Full-matrix least-squares refinement was performed. In later stages of the refinement, aromatic-ring-H atoms were made canonical: C—H distance = 0.98 Å; $U_{iso} = 1.2U_{eq}$ of the attached atom. Atoms H9A and H9B (on C9A and C9B) and carboxyl-H atom H_B were refined isotropically.

The A molecule carboxyl-O atoms were found to be disordered over two sites, labelled A and A*, with (refined and final) occupancies of 0.66 (2) and 0.34 (2), respectively. Following refinement with all but the two partially occupied carboxylic-H atoms, H_A and H_A^{*}, included in the model, they were assigned fixed coordinates from the resulting Fourier difference map and were assigned a fixed U_{iso} very slightly larger than that of the refined B molecule carboxylic-H atom, H_B.

The maximum effect of extinction was 4.7% of F_o for 004. The maximum peak in the final difference map occurred ~ 1.2 Å from O1A* and O2A, but was not suitably oriented to be assigned as a potential partial-occupancy carboxylic-H atom; the minimum peak occurred near the center of one of the benzenoid rings of the B molecule.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC 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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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1245). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A New Conformationally Restricted Aspartic Acid Analogue with a Cyclohexanone Skeleton

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Abstract

In the compound (1*R*,2*S*)-2-benzamido-2-methoxy-carbonyl-5-oxocyclohexane-1-carboxylic acid, C₁₆H₁₇NO₆, the cyclohexanone ring adopts a distorted chair conformation. The carboxylic acid and the methyl ester groups occupy the axial positions, while the benzamido group is equatorial. The values determined for the torsion angles about the N—C^α(φ) and C^α—CO(ψ) bonds correspond to a semi-extended conformation for the amino acid residue. The crystal structure is stabilized by two intermolecular hydrogen bonds (O—H \cdots O and N—H \cdots O) involving the carboxylic acid, the benzamido and the methyl ester groups.

Comment

The use of uncommon amino acid residues in the synthesis of peptides with restricted conformational flexibility has acquired increasing importance in the design of specifically folded analogues of biologically active