N(2)—C(1)—C(14)—C(15)	−132.1 (4)
C(9)—C(1)—C(14)—C(15)	100.9 (5)
C(1)—C(14)—C(15)—C(16)	52.4 (6)
C(6)—C(7)—O(7)—C(13)	−67.2 (6)
C(7)—C(8)—O(8)—C(7′)	−30.4 (5)
C(17)—C(18)—O(18)—C(17′)	−69.2 (6)
C(9′)—C(1′)—N(2′)—C(3′)	25.0 (6)
C(1′)—N(2′)—C(3′)—C(4′)	−58.1 (7)
N(2′)—C(3′)—C(4′)—C(10′)	55.4 (7)
C(8)—O(8)—C(7′)—C(8′)	130.0 (4)
C(8)—O(8)—C(7′)—C(6′)	−56.1 (5)
N(2′)—C(1′)—C(9′)—C(10′)	7.7 (6)
C(1′)—C(9′)—C(10′)—C(4′)	−7.2 (6)
C(3′)—C(4′)—C(10′)—C(9′)	−22.5 (7)
N(2′)—C(1′)—C(14′)—C(15′)	−67.5 (6)
C(9′)—C(1′)—C(14′)—C(15′)	59.6 (6)
C(1′)—C(14′)—C(15′)—C(16′)	−79.6 (6)
C(18)—O(18)—C(17′)—C(16′)	−5.4 (6)
C(5′)—C(6′)—O(6′)—C(12′)	9.0 (6)

The methoxy group at C6 is disordered over two positions, denoted —O6—C12 and —O106—C112, with occupancy factors fixed at 0.6 and 0.4, respectively (based on heights in the $\Delta\rho$ map). The parameters for the H atoms found in the $\Delta\rho$ map were refined. The remainder were placed at calculated positions with the isotropic displacement factors set equal to $1.1 \times U_{eq}$ of the bonded atom.

Data collection: *Syntex P*2₁ *Software*. Cell refinement: *Syntex P*2₁ *Software*. Data reduction: *XP*21 (Pavelčík, 1987). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1971).

Lists of structure factors, least-squares-planes data, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1162). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Two $P2_1/n$ Monoclinic Phases of Fluorene-4-carboxylic Acid at 296 K

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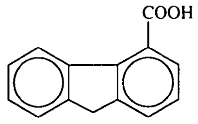
Abstract

The structures of two phases of fluorene-4-carboxylic acid, $C_{14}H_{10}O_2$, from room-temperature growths have been determined. In the α phase, O—H···O hydrogen bonding occurs *via* cyclic dimers about a center of symmetry; in the β phase, cyclic dimers with O—H···O hydrogen bonds are formed between two crystallographically inequivalent molecules and do not involve a center of symmetry, though centers of symmetry are present in the crystal. The present evidence strongly suggests that the β phase is metastable with respect to the α phase at room temperature, but the regions of stability have not been determined.

Comment

As one of a series of studies of hydrogen bonding in crystalline carboxylic acids, we have previously described the structure of fluorene-1-carboxylic acid (hereafter, F1CA) (Blackburn, Dobson & Gerkin, 1996). Here we report on another fluorene monocarboxylic acid, fluorene-4-carboxylic acid, (I). No previous structural report on this acid has appeared.



(I)

Growths of this acid produced two monoclinic phases, designated α and β, whose structures have been determined. In Fig. 1, an *ORTEP*II (Johnson, 1976) drawing of the α-phase dimer is presented together with our numbering scheme; the two β-phase molecules are shown in Fig. 2.

The hydrogen bonding in the α phase (Fig. 1) is of the cyclic dimer type about a center of inversion; in the β phase it is also of cyclic dimer type (Fig. 2) but is formed by two crystallographically inequivalent molecules, and does not involve a center of inversion. Geometric details of these hydrogen bonds are given in Table 5. All have donor–acceptor distances which are

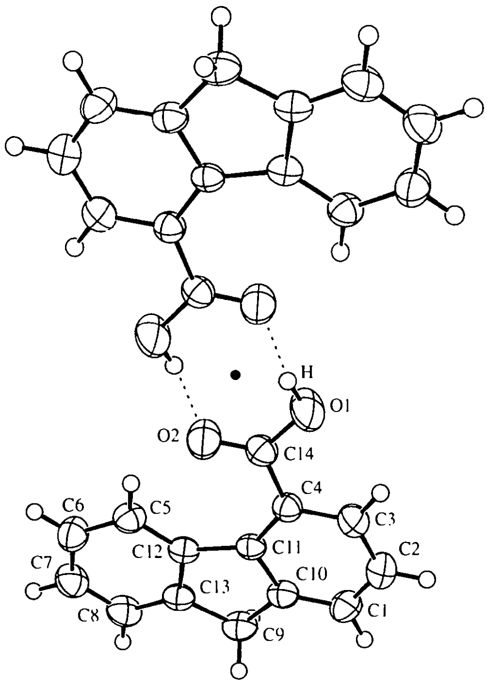


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of the α-phase fluorene-4-carboxylic acid dimer showing our numbering scheme, the center of symmetry and the hydrogen bonds. Displacement ellipsoids are drawn at the 50% probability level for all atoms except the H atoms for which they have been set artificially small.

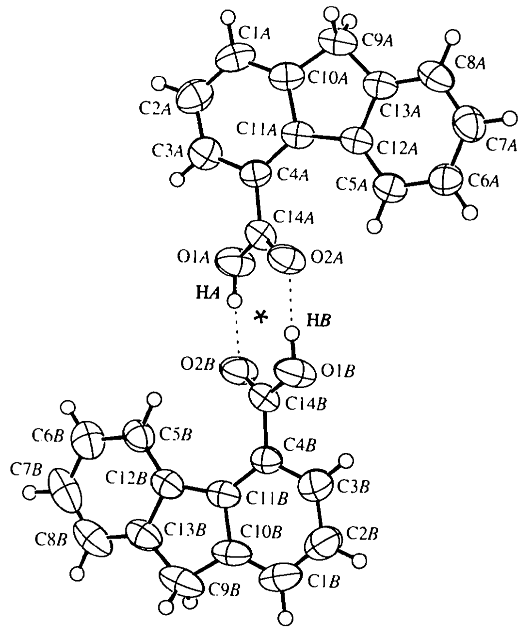


Fig. 2. *ORTEP*II (Johnson, 1976) drawing of the β-phase fluorene-4-carboxylic acid dimer showing our numbering scheme, the pseudo-center of symmetry and the hydrogen bonds. Displacement ellipsoids are drawn at the 50% probability level for all atoms except the H atoms for which they have been set artificially small.

below average for organic O—H···O hydrogen bonds (2.77 Å; Ceccarelli, Jeffrey & Taylor, 1981), indicating strong interactions. From the carboxyl group C—O and O—H distances (Tables 2, 4, 5) and the location of the carboxyl H atoms it is apparent that each of the three carboxyl H atoms is ordered.

With respect to interatomic distances in the fluorene core the three independent molecules reported here, as was the case in F1CA (Blackburn *et al.*, 1996), display pseudo-mirror symmetry: the r.m.s. deviations within the seven pairs of distances in the cores which would be identical under mirror symmetry are 0.007 (6), 0.011 (7) and 0.009 (9) Å, respectively, for the α, β-*A* and β-*B* molecules. The one unique core interatomic distance, C11—C12, was determined as 1.492 (3), 1.477 (5) and 1.487 (5) Å for α, β-*A* and β-*B*, respectively; these values may be compared with 1.471 (4) Å in F1CA, 1.472 (3) Å for fluorene at low temperature (Gerkin, Lundstedt & Reppart, 1984) and 1.491 (8) Å for fluorene at room temperature (Belsky, Zavodnik & Vozzhennikov, 1984). Since no clear trends are apparent in these data, it may be concluded only that further measurements of the C11—C12 distance will very probably fall within the range 1.471–1.492 Å.

As in describing F1CA, we have chosen best-fit planes for atoms C1–C4, C10 and C11, and for atoms C5–C8, C12 and C13 to define the molecular dihedral angle. Whereas in that previous case the maximum distance of an atom from either of the best-fit planes including that atom was 0.008 Å, here it is 0.016 (α), 0.016 (β-*A*) and 0.017 Å (β-*B*), all occurring in the first of these two planes. Thus, in contrast to the previous case, the presence of the carboxyl group is associated with rumpling of the first plane. The values of the dihedral angles are 5.1 (1) (α), 2.4 (1) (β-*A*) and 1.8 (2)° (β-*B*); the value for F1CA was 3.0 (1)°. The dihedral angles between the carboxyl group plane and the best-fit planes of the rings to which they are attached (the first planes described above) are 16.3 (2) (α), 36.8 (2) (β-*A*) and 30.7 (2)° (β-*B*), all considerably larger than the value found for F1CA, 4.4 (2)°.

Excluding atoms involved in hydrogen bonding, the closest intermolecular approaches are in good agreement with the van der Waals radius (Bondi, 1964) sums excepting one approach in the β phase, between C12*A* and H10*B*^{i} [symmetry code (i) $-x$, $1 - y$, $-z$], which is ~0.15 Å less.

After it was established that the rod and prism samples belonged to different phases, the growth of the β phase from purified material became of interest. Despite repeated and varied attempts to grow other samples of the β phase, only the α phase has subsequently been identified. The results to date show that while the presence of impurities may be a necessary condition for the appearance of the β phase, it is not a sufficient condition since the α phase has appeared in growths from impure starting material. The present evidence strongly suggests that the β phase is metastable with respect to the α phase at room temperature, but the regions of stability of the two phases have not yet been established.

Experimental

Fluorene-4-carboxylic acid was obtained from Aldrich Chemical Company. In one preparative method, the solid as received was dissolved in warm toluene and treated with Norit-A decolorizing carbon. This mixture was filtered and the filtrate solvent was allowed to evaporate at room temperature. From the resulting crystal growth a clear colorless rod was selected. In another preparative method, the solid as received was dissolved in toluene and the solution was filtered. The solvent was allowed to evaporate from the filtrate at room temperature. From the crystals so produced, a pale-golden prism was selected. As subsequent analysis demonstrated, these two crystals belonged to different phases. The rod was assigned as α phase, the prism as β phase.

α-Fluorene-4-carboxylic acid

Crystal data

$C_{14}H_{10}O_2$
$M_r = 210.23$
Monoclinic
$P2_1/n$
$a = 10.454\,(2)$ Å
$b = 5.507\,(2)$ Å
$c = 18.000\,(2)$ Å
$\beta = 99.90\,(1)^\circ$
$V = 1020.8\,(5)$ Å^3
$Z = 4$
$D_x = 1.368$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 12.9–14.6^\circ$
$\mu = 0.085$ mm^{-1}
$T = 296$ K
Cut rod
0.92 × 0.19 × 0.08 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: none
2746 measured reflections
2608 independent reflections
1166 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.056$

$\theta_{\rm max} = 27.50^\circ$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 7$
$l = -23 \rightarrow 23$
6 standard reflections monitored every 150 reflections
intensity variation: ±2.6% (average maximum relative intensity)

Refinement

Refinement on F
$R = 0.048$
$wR = 0.037$
$S = 1.90$
1166 reflections
150 parameters
H atoms: see below
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\rm max} = <0.01$
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}

Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: $6.8\,(16) \times 10^{-7}$
Atomic scattering factors from Stewart, Davidson & Simpson (1965) for H atoms and from Cromer & Waber (1974) for C and O atoms

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for α-fluorene-4-carboxylic acid*

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

	x	y	z	$U_{\rm eq}$
O1	0.3750 (3)	−0.2866 (5)	0.4664 (1)	0.0878 (10)
O2	0.4933 (2)	−0.3446 (4)	0.5767 (1)	0.0712 (8)
C1	0.1720 (3)	0.3455 (5)	0.5978 (2)	0.053 (1)
C2	0.1364 (3)	0.2131 (6)	0.5325 (2)	0.060 (1)
C3	0.2158 (3)	0.0270 (6)	0.5154 (2)	0.0506 (10)
C4	0.3304 (3)	−0.0365 (5)	0.5637 (1)	0.0387 (8)
C5	0.5758 (3)	−0.0832 (5)	0.7171 (2)	0.0448 (9)
C6	0.6593 (3)	−0.0551 (6)	0.7855 (2)	0.0522 (10)
C7	0.6416 (3)	0.1323 (6)	0.8342 (2)	0.055 (1)
C8	0.5410 (3)	0.2934 (5)	0.8154 (2)	0.0509 (10)
C9	0.3394 (3)	0.4130 (5)	0.7183 (2)	0.0461 (9)
C10	0.2849 (3)	0.2872 (5)	0.6458 (1)	0.0398 (8)
C11	0.3652 (2)	0.0935 (5)	0.6317 (1)	0.0342 (8)
C12	0.4734 (3)	0.0782 (5)	0.6974 (1)	0.0353 (8)
C13	0.4570 (3)	0.2655 (5)	0.7479 (1)	0.0391 (8)
C14	0.4071 (3)	−0.2351 (5)	0.5376 (2)	0.0420 (9)
H	0.413 (4)	−0.428 (8)	0.459 (2)	0.17 (2)

Table 2. *Selected geometric parameters (Å, °) for α-fluorene-4-carboxylic acid*

C1—C2	1.379 (4)	C8—C13	1.379 (3)
C1—C10	1.375 (4)	C9—C10	1.500 (3)
C2—C3	1.386 (4)	C9—C13	1.493 (4)
C3—C4	1.398 (4)	C10—C11	1.408 (3)
C4—C11	1.412 (3)	C11—C12	1.492 (3)
C5—C6	1.390 (4)	C12—C13	1.405 (3)
C5—C12	1.390 (4)	C4—C14	1.480 (4)
C6—C7	1.387 (4)	C14—O1	1.300 (3)
C7—C8	1.373 (4)	C14—O2	1.205 (3)
C10—C9—C13	103.1 (2)	C3—C4—C14	116.2 (2)
C9—C10—C11	110.9 (2)	C11—C4—C14	125.2 (2)
C10—C11—C12	107.1 (2)	C4—C14—O1	114.3 (3)
C11—C12—C13	108.2 (2)	C4—C14—O2	125.2 (3)
C9—C13—C12	110.6 (2)	O1—C14—O2	120.5 (3)

β-Fluorene-4-carboxylic acid

Crystal data

$C_{14}H_{10}O_2$
$M_r = 210.23$
Monoclinic
$P2_1/n$
$a = 9.308\,(2)$ Å
$b = 12.464\,(2)$ Å
$c = 17.833\,(2)$ Å
$\beta = 95.29\,(1)^\circ$
$V = 2060.3\,(6)$ Å^3
$Z = 8$
$D_x = 1.355$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.5–13.8^\circ$
$\mu = 0.119$ mm^{-1}
$T = 296$ K
Prism
0.31 × 0.31 × 0.19 mm
Pale golden

Data collection

Rigaku AFC-5*S* diffractometer
ω scans
Absorption correction: none
5274 measured reflections
4978 independent reflections
1629 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.045$

$\theta_{\rm max} = 27.50^\circ$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 16$
$l = -23 \rightarrow 23$
6 standard reflections monitored every 150 reflections
intensity variation: ±2.5% (average maximum relative intensity)

Refinement

Refinement on F
$R = 0.045$
$wR = 0.047$
$S = 1.50$
1629 reflections
297 parameters
H atoms: see below
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = <0.01$
$\Delta\rho_{\max} = 0.22$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from Stewart, Davidson & Simpson (1965) for H atoms and from Cromer & Waber (1974) for C and O atoms

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for β-fluorene-4-carboxylic acid*

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

	x	y	z	U_{eq}
O1*A*	0.1992 (3)	0.4982 (2)	0.5234 (2)	0.075 (1)
O1*B*	−0.5222 (3)	0.7679 (2)	0.0650 (2)	0.077 (1)
O2*A*	0.1715 (3)	0.4425 (2)	0.4052 (1)	0.0648 (9)
O2*B*	−0.5660 (3)	0.8195 (2)	−0.0531 (1)	0.0747 (10)
C1*A*	0.4883 (5)	0.7738 (3)	0.4074 (3)	0.066 (1)
C1*B*	−0.2665 (5)	0.4796 (3)	−0.0563 (3)	0.080 (2)
C2*A*	0.5106 (4)	0.7149 (3)	0.4733 (2)	0.071 (2)
C2*B*	−0.2404 (5)	0.5352 (4)	0.0107 (3)	0.080 (2)
C3*A*	0.4179 (4)	0.6322 (3)	0.4865 (2)	0.062 (1)
C3*B*	−0.3264 (4)	0.6215 (3)	0.0251 (2)	0.066 (1)
C4*A*	0.3045 (4)	0.6030 (3)	0.4338 (2)	0.049 (1)
C4*B*	−0.4354 (4)	0.6570 (3)	−0.0273 (2)	0.051 (1)
C5*A*	0.0569 (4)	0.5881 (3)	0.2812 (2)	0.057 (1)
C5*B*	−0.6793 (4)	0.6855 (3)	−0.1821 (2)	0.062 (1)
C6*A*	−0.0264 (4)	0.6040 (3)	0.2139 (2)	0.064 (1)
C6*B*	−0.7606 (5)	0.6749 (4)	−0.2506 (3)	0.078 (2)
C7*A*	0.0026 (4)	0.6883 (4)	0.1666 (2)	0.070 (1)
C7*B*	−0.7372 (6)	0.5922 (5)	−0.2994 (3)	0.088 (2)
C8*A*	0.1147 (5)	0.7572 (3)	0.1854 (2)	0.066 (1)
C8*B*	−0.6299 (6)	0.5183 (4)	−0.2804 (3)	0.085 (2)
C9*A*	0.3272 (4)	0.8041 (3)	0.2829 (2)	0.063 (1)
C9*B*	−0.4260 (6)	0.4591 (3)	−0.1813 (3)	0.085 (2)
C10*A*	0.3738 (4)	0.7482 (3)	0.3555 (2)	0.054 (1)
C10*B*	−0.3770 (5)	0.5110 (3)	−0.1076 (3)	0.065 (2)
C11*A*	0.2815 (4)	0.6618 (3)	0.3665 (2)	0.046 (1)
C11*B*	−0.4628 (4)	0.6014 (3)	−0.0957 (2)	0.053 (1)
C12*A*	0.1727 (4)	0.6569 (3)	0.3008 (2)	0.045 (1)
C12*B*	−0.5705 (4)	0.6117 (3)	−0.1623 (2)	0.054 (1)
C13*A*	0.1996 (4)	0.7410 (3)	0.2520 (2)	0.052 (1)
C13*B*	−0.5477 (5)	0.5282 (3)	−0.2123 (3)	0.066 (2)
C14*A*	0.2182 (4)	0.5082 (3)	0.4519 (2)	0.050 (1)
C14*B*	−0.5149 (4)	0.7543 (3)	−0.0074 (2)	0.053 (1)
H*A*	0.159 (6)	0.429 (4)	0.532 (3)	0.16 (2)
H*B*	−0.571 (5)	0.831 (4)	0.072 (3)	0.13 (2)

Table 4. *Selected geometric parameters (Å, °) for β-fluorene-4-carboxylic acid*

C1*A*—C2*A*	1.384 (5)	C1*B*—C2*B*	1.383 (6)
C1*A*—C10*A*	1.383 (5)	C1*B*—C10*B*	1.370 (5)
C2*A*—C3*A*	1.379 (5)	C2*B*—C3*B*	1.379 (5)
C3*A*—C4*A*	1.395 (5)	C3*B*—C4*B*	1.387 (5)
C4*A*—C11*A*	1.407 (4)	C4*B*—C11*B*	1.406 (5)
C5*A*—C6*A*	1.382 (5)	C5*B*—C6*B*	1.383 (5)
C5*A*—C12*A*	1.396 (5)	C5*B*—C12*B*	1.390 (5)
C6*A*—C7*A*	1.389 (5)	C6*B*—C7*B*	1.380 (6)
C7*A*—C8*A*	1.368 (5)	C7*B*—C8*B*	1.378 (6)
C8*A*—C13*A*	1.379 (5)	C8*B*—C13*B*	1.380 (5)
C9*A*—C10*A*	1.499 (5)	C9*B*—C10*B*	1.498 (5)
C9*A*—C13*A*	1.486 (5)	C9*B*—C13*B*	1.488 (6)
C10*A*—C11*A*	1.403 (4)	C10*B*—C11*B*	1.409 (5)
C11*A*—C12*A*	1.477 (5)	C11*B*—C12*B*	1.487 (5)
C12*A*—C13*A*	1.400 (4)	C12*B*—C13*B*	1.400 (5)
C4*A*—C14*A*	1.482 (4)	C4*B*—C14*B*	1.481 (5)
C14*A*—O1*A*	1.308 (4)	C14*B*—O1*B*	1.311 (4)
C14*A*—O2*A*	1.219 (4)	C14*B*—O2*B*	1.216 (4)
C10*A*—C9*A*—C13*A*	103.4 (3)	C10*B*—C9*B*—C13*B*	103.6 (4)
C9*A*—C10*A*—C11*A*	110.2 (3)	C9*B*—C10*B*—C11*B*	110.3 (4)
C10*A*—C11*A*—C12*A*	107.7 (3)	C10*B*—C11*B*—C12*B*	107.4 (4)
C11*A*—C12*A*—C13*A*	108.2 (3)	C11*B*—C12*B*—C13*B*	108.3 (4)
C9*A*—C13*A*—C12*A*	110.4 (3)	C9*B*—C13*B*—C12*B*	110.4 (4)
C3*A*—C4*A*—C14*A*	116.9 (3)	C3*B*—C4*B*—C14*B*	116.7 (4)
C11*A*—C4*A*—C14*A*	124.0 (3)	C11*B*—C4*B*—C14*B*	123.9 (4)
C4*A*—C14*A*—O1*A*	114.4 (3)	C4*B*—C14*B*—O1*B*	114.6 (4)
C4*A*—C14*A*—O2*A*	123.6 (3)	C4*B*—C14*B*—O2*B*	124.0 (4)
O1*A*—C14*A*—O2*A*	122.0 (3)	O1*B*—C14*B*—O2*B*	121.4 (3)

Table 5. *Hydrogen bonds in α- and β-fluorene-4-carboxylic acid (Å, °)*

The criteria for inclusion of hydrogen bonds in this table are (*a*) the H atom must be closer to the acceptor atom than is the donor atom, and (*b*) the donor–acceptor distance must be less than 3.2 Å.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
α phase				
O1—H1···O2$^{\text{i}}$	0.90 (4)	1.77 (4)	2.644 (3)	163 (4)
β phase				
O1*A*—H*A*···O2*B*$^{\text{ii}}$	0.96 (5)	1.68 (5)	2.628 (4)	171 (5)
O1*B*—H*B*···O2*A*$^{\text{iii}}$	0.92 (5)	1.75 (5)	2.662 (4)	173 (4)

Symmetry codes: (i) $1 - x, -1 - y, 1 - z$; (ii) $-\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $-\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$.

The nine ring-H atoms were assigned fixed geometry (C—H = 0.98 Å) and isotropic displacement parameters of magnitude 1.2 times those of the associated C atoms. The carboxylic H atoms were refined isotropically.

For both compounds, 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 structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *TEXSAN*; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and stereo drawings have been deposited with the IUCr (Reference: FG1130). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Xanthene-9-carboxylic Acid

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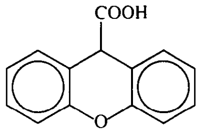
Abstract

In xanthene-9-carboxylic acid, $C_{14}H_{10}O_3$, hydrogen bonding is of the cyclic dimer type but involves two crystallographically inequivalent molecules and does not occur about a center of symmetry. The carboxylic H atoms are ordered. The dihedral angle (fold angle) of the xanthene core is 14.2 (1)° for molecule *A* and 11.3 (2)° for molecule *B*. The planes of the carboxyl groups are almost perpendicular to the xanthene cores.

Comment

In the title structure, (I), hydrogen bonding is of the cyclic dimer type but it involves two crystallographically inequivalent molecules and does not occur about a center of symmetry. There are, therefore, two inequivalent hydrogen bonds involving the O1*A* and O1*B* atoms as donors and the O2*B* and O2*A* atoms as acceptors. The donor–acceptor distances of 2.647 (4) and 2.650 (4) Å are somewhat below the average for organic O···O hydrogen bonds (2.77 Å; Ceccarelli, Jeffrey & Taylor, 1981) and indicate strong hydrogen bonds. The interatomic distances in the carboxyl groups (Table 2) are entirely consistent with ordered carboxyl H atoms.



(I)

The xanthene cores show pseudo-mirror symmetry; for the eight pairs of core bond distances that would be identical under mirror symmetry, the r.m.s. difference within pairs is 0.011 (8) Å for molecule *A* and 0.010 (8) Å for molecule *B*. Moreover, the averages of these pairs of values for the *A* and *B* molecules have an r.m.s. difference of only 0.006 (8) Å. The calculation of grand means is therefore justified. For comparison, the xanthene core values obtained for methyl 9-xanthenyl ketone (Rochlin & Rappoport, 1992) have been chosen and will be cited in square brackets. The grand mean of the ring bond lengths involving the C9 atom is 1.507 (7) Å [1.516 (4) Å], of those involving O10 is 1.377 (6) Å [1.392 (3) Å] and of the aromatic (outer ring) bonds is 1.380 (10) Å [1.391 (4) Å]. The mean values for the central ring angles, C12—C9—C13 and C11—O10—C14, are 111.5 (3) [109.4 (2)] and 118.5 (3)° [116.4 (2)°], respectively.

The central ring of the xanthene core of each molecule is in a boat conformation (Fig. 1), with atoms C9 and O10 on the same side of the plane defined by atoms C11, C12, C13 and C14. The angle between this latter plane and the carboxyl group plane is 86.3 (6)° for molecule *A* and 84.8 (7)° for molecule *B*.

Overall, the xanthene core of each molecule is V-shaped with atoms C1–C4, C13, C14, C9 and O10 defining one plane and atoms C5–C8, C11, C12, C9 and O10 defining the other, with C9 and O10 lying on the line of intersection. The mean distances of the respective atoms from these least-squares best-fit planes are 0.016 and 0.016 Å for molecule *A*, and 0.017 and 0.021 Å for molecule *B*. The dihedral angle (folding angle) is 14.2 (1)° for *A* and 11.3 (2)° for *B*; for methyl 9-xanthenyl ketone (Rochlin & Rappoport, 1992), this value was found to be 30.1°, while for 9-isopropylxanthene (Chu & Yang, 1977) it was 21.9°.

In the present structure, all of the closest intermolecular approaches of atoms, excluding those participating in hydrogen bonding, involve H and O atoms or H and C atoms. With respect to the sums of the van der Waals radii (Bondi, 1964) of the involved atoms, only four interatomic approaches show deficits, the maximum deficit being 0.11 Å for the atom pair C14*A*···H3*B*$^{\text{i}}$ [symmetry code: (i) $1-x$, $1-y$, $-\frac{1}{2}+z$].

A point of particular interest is that with respect to a pair of hydrogen-bonded partners, the 'midpoint' of the cyclic portion is a pseudo-center of symmetry. There is, however, no pseudo-center which relates such a hydrogen-bonded dimer to another hydrogen-bonded dimer. A somewhat similar occurrence was

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