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9*H*-Fluorene-2-carboxaldehyde

Allison J. Dobson and Roger E. Gerkin

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, USA. E-mail: gerkin@chemistry.ohio-state.edu

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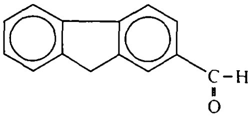
Abstract

The title compound, $C_{14}H_{10}O$, crystallized in the centrosymmetric space group $P2_1/c$ with a single molecule in the asymmetric unit. The C—H···O interaction having the shortest C···O distance involves the ring-bridging C9 atom and one of its H atoms, and results in the formation of a cyclic dimer about a center of symmetry. The molecular core is nearly planar. The dihedral angle between the best-fit plane of the ring to which the aldehyde group is attached and the plane of the aldehyde group is 4.4 (9)°. In a number of respects the molecular disposition is similar to that previously determined for the geometrically similar dibenzofuran-4-carboxaldehyde molecule.

Comment

Fluorene-2-carboxaldehyde, (I), is of interest as a crystalline solid because of its potential for significantly attractive C—H···O interactions and for comparison with the structure of dibenzofuran-4-carboxaldehyde (hereafter, DBFC) (Fitzgerald *et al.*, 1991), the idealized molecular geometry of which is similar.



(I)

The title aldehyde crystallized in the centrosymmetric space group $P2_1/c$ with one molecule in the asymmetric unit. The refined molecule and the numbering scheme are shown in Fig. 1. The C—H···O interaction with the shortest C···O distance involves atoms C9, H9*A* and $O1^{i}$ [symmetry code: (i) $2-x$, $1-y$, $1-z$] and is responsible for the formation of a cyclic dimer about a center of symmetry; the first-level graph-set descriptor (Bernstein *et al.*, 1995) is $R_2^2(14)$. The geometric parameters characterizing this interaction are $C_{donor}\cdots O_{acceptor}$ = 3.501 (2), $H\cdots O_{acceptor}$ = 2.55 (1) Å and C_{donor}—$H\cdots O_{acceptor}$ = 138 (1)°, values which fall well within the Taylor & Kennard (1982) criteria for significantly attractive interactions. As shown in Fig. 2, the molecules are further oriented such that the aldehyde groups of pairs of molecules are apposed. This suggests that a second C—H···O interaction, C14—$H2\cdots O1^{ii}$ [symmetry code: (ii) $2-x$, $\frac{1}{2}+y$, $\frac{3}{2}-z$], plays a significant role in the structural organization; its geometric parameters are $C_{donor}\cdots O_{acceptor}$ = 3.218 (2), $H\cdots O_{acceptor}$ = 2.75 (1) Å and C_{donor}—$H\cdots O_{acceptor}$ = 129 (1)°, values which also fall well within the Taylor & Kennard (1982) limits. This second interaction produces a pattern whose first-level descriptor is *C*(3), a chain which propagates along **b**. The consequence of these interactions is a layering along **a** such that the aldehyde groups and C—H···O interactions occur near 0 and 1**a** and that only C—H interactions occur near 0.5**a**. Although in Fig. 2 it may appear that there would be significant steric interference of H1 and $H1^{i}$, they are separated by 2.56 Å, a distance significantly greater than their Bondi (1964) van der Waals radius sum (2.40 Å); similarly, O1 and $H2^{ii}$ are separated by 3.02 (1) Å, a distance significantly greater than their radius sum (2.70 Å).

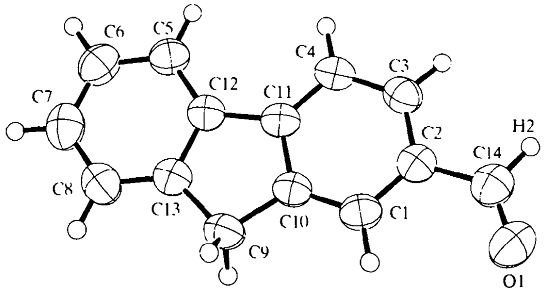


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of fluorene-2-carboxaldehyde showing the numbering scheme. Displacement ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small.

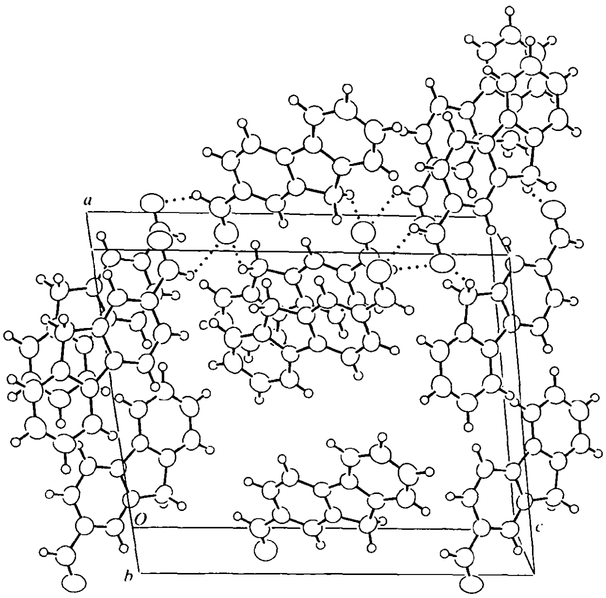


Fig. 2. *ORTEP*II (Johnson, 1976) packing diagram of fluorene-2-carboxaldehyde. Displacement ellipsoids are drawn at 50% probability for all atoms except H, for which they have been set artificially small. C—H···O interactions are depicted by dashed lines.

Each of the rings in (I) is very nearly planar, the maximum and average deviations of ring C atoms from the best-fit planes describing them being, respectively, 0.006 (1) and 0.003 (2) Å for C1–C4/C10/C11, 0.003 (1) and 0.002 (1) Å for C9–C13, and 0.003 (2) and 0.002 (1) Å for C5–C8/C12–C13. The entire molecular core, C1–C13, is also nearly planar, the maximum and average deviations as above being 0.018 (1) and 0.009 (6) Å, respectively; more precisely, (I) is slightly boat-shaped, the dihedral angle between the benzenoid rings being 1.22 (7)°. Moreover, the aldehyde C atom, C14, lies only 0.009 (1) Å out of this plane. The molecular disposition is thus quite similar to that of DBFC. In particular, the core of DBFC is also boat-shaped, with a dihedral angle between the benzenoid rings of 1.4 (1)°, and the least planar ring is the one carrying the aldehyde substituent. In DBFC, the dihedral angle between the plane of the aldehyde group and that of the ring to which it is attached is 3.2 (7)°; in (I), the corresponding angle is 4.4 (9)°. In (I), the dihedral angle between the two sets of non-parallel ring planes is 67.47 (2)°.

Compound (I) is further similar to DBFC in that the principal C—H···O interaction in the latter also involves a center of symmetry, and forms a cyclic dimer with first-level graph-set descriptor $R_2^2(18)$. However, in DBFC, a second significant C—H···O interaction (involving the heterocyclic O atom) also forms a cyclic dimer about the same center, with first-level graph-set descriptor $R_2^2(8)$, as shown in Fig. 1 of Fitzgerald *et al.* (1991).

Finally, in both structures, the aldehyde H atom [H2 in (I)] is slightly crowded by the closest ring H atom [H3 in (I)]; in (I), the separation is 2.35 (1) Å, while the Bondi (1964) radius sum is 2.40 Å. In both molecules, this H-atom–H-atom crowding could be relieved by rotation of the aldehyde group, but the attendant decreases in the attractive C—H···O interactions apparently outweigh the stability gains from the lowered H-atom repulsions and the rotations do not occur.

It may be noted that (I) and DBFC are dissimilar in that the ring-bridging atom is a donor in (I) but an acceptor in DBFC.

Distances and angles of special interest are given in Table 1; all distances and angles fall within normal ranges. The closest intermolecular approaches in this structure, excluding pairs of atoms in C—H···O interactions, are between C6 and H7^{iii} [symmetry code: (iii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$] and are merely 0.02 Å less than the sum of the corresponding Bondi (1964) van der Waals radii.

Experimental

Fluorene-2-carboxaldehyde was obtained as a pale-yellow crystalline powder from the Aldrich Chemical Company. This solid was dissolved in ether. The solution was treated with decolorizing carbon and filtered. Room-temperature evaporation of the filtrate produced rods and plates, one of which was cut to provide the experimental sample.

Crystal data

$C_{14}H_{10}O$
$M_r = 194.23$
Monoclinic
$P2_1/c$
$a = 14.171$ (2) Å
$b = 4.338$ (2) Å
$c = 16.217$ (2) Å
$\beta = 99.64$ (1)°
$V = 982.8$ (4) Å^3
$Z = 4$
$D_x = 1.313$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 13.0$–17.2°
$\mu = 0.076$ mm^{-1}
$T = 296$ K
Cut plate
0.42 × 0.42 × 0.15 mm
Colorless

Data collection

Rigaku AFC-5*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2677 measured reflections
2276 independent reflections
1423 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.021$
$\theta_{\rm max} = 27.56°$
$h = 0 \rightarrow 18$
$k = 0 \rightarrow 5$
$l = -21 \rightarrow 20$
6 standard reflections every 150 reflections intensity decay: 6.2%

Refinement

Refinement on F^2
$R(F) = 0.042$
$wR(F^2) = 0.065$
$S = 1.71$
2276 reflections
148 parameters
H atoms: see below
$w = 1/\sigma^2(F^2)$

$(\Delta/\sigma)_{\rm max} < 0.01$
$\Delta\rho_{\rm max} = 0.21$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.22$ e Å^{-3}
Extinction correction: none
Scattering factors from Stewart *et al.* (1965) (H) and Creagh & McAuley (1992) (C, O)

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

O1—C14	1.211 (2)	C2—C14	1.470 (2)
O1—C14—C2	124.9 (2)	C2—C14—H2	115.0 (7)
O1—C14—H2	120.1 (7)		

Scan widths were (1.60 + 0.30tanθ)° in ω, with a background/scan time ratio of 0.5. The data were corrected for Lorentz and polarization effects. A linear correction for decay was applied. The Laue group assignment, systematic absences and centrosymmetric intensity statistics indicated space group $P2_1/c$ (No. 14); since refinement proceeded well, it was adopted. Difference Fourier methods were used to locate the initial H-atom positions and the H atoms were then refined isotropically. The refined C—H distances ranged from 0.93 (2) to 0.98 (2) Å, with a mean value of 0.96 (1) Å; subsequently, the ring H atoms, excepting H9*A* and H9*B*, were made canonical, with C—H = 0.98 Å and with $U_{\rm iso} = 1.2U_{\rm eq}$(attached C atom). Atoms H2, H9*A* and H9*B* were refined isotropically. Since during least-squares refinement, the extinction coefficient was predicted to be negative, it was not included in the model. The maximum positive residual peak is located ~0.75 Å from C11 and C12; the maximum negative peak is located near the center of the ring carrying the aldehyde group.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). 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* and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1406). Services for accessing these data are described at the back of the journal.

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3,6-Dichlorophthalic Anhydride

Doyle Britton

Department of Chemistry, University of Minnesota, Minneapolis, MN 55455-0431, USA. E-mail: britton@chemsun.chem.umn.edu

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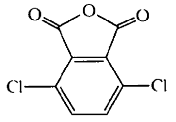
Abstract

The molecular structure of 3,6-dichlorophthalic anhydride, $C_8H_2Cl_2O_3$, is normal. The molecules pack in ribbons held together by O···Cl, O···H and Cl···H interactions. The ribbons pack in a herring-bone arrangement.

Comment

The packing motifs of 4,5-dichlorophthalic anhydride, 4,5-dibromophthalic anhydride and 4,5-benzofurazan 1-oxide are closely related and involve two-dimensional sheets of molecules held together by Cl···O or Br···O and C—H···O or C—H···N interactions (Ojala *et al.*, 1998). In 3,6-dibromobenzofurazan 1-oxide, the molecules are again arranged in two-dimensional sheets, with two different kinds of sheets occurring in the same structure (Britton, 1992). The structure of the title compound, (I), has been determined, to see whether there is a similar packing arrangement based on two-dimensional sheets.



(I)

The anisotropic displacement ellipsoids and the atom-labeling scheme are shown in Fig. 1. The bond lengths and angles are normal. The molecule deviates slightly from planarity. Each ring is close to planarity but the two rings are bent from coplanarity by 1.8 (1)°. This is similar to the situation in both phthalic anhydride (Bates & Cutler, 1977) and 3-methylphthalic anhydride (Bocelli & Cantoni, 1995). In addition, the Cl atoms and the exocyclic-O atoms are bent out of the planes of the rings to relieve the crowding between them. This is similar to the behavior in tetrachlorophthalic anhydride (Rudman, 1971).

The packing (Fig. 2) does not include two-dimensional layers. Using the van der Waals radii suggested by Pauling (1960), there are five intermolecular distances shorter than normal. The O3 and Cl1 atoms

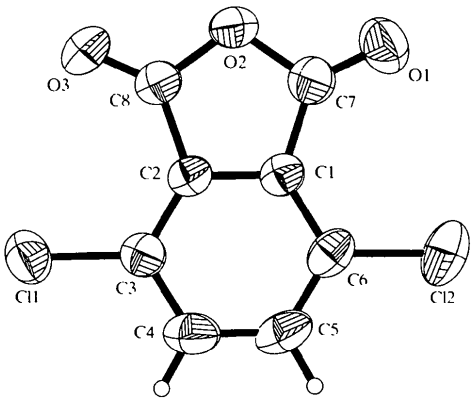


Fig. 1. The molecular structure of 3,6-dichlorophthalic anhydride, showing the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level; H atoms are shown as spheres of arbitrary size.