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5-Fluoro-1-indanone and 2,2-Dimethyl-5-fluoro-1-indanone

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Abstract

There are two independent molecules in the asymmetric unit of 5-fluoro-1-indanone (1), C_9H_7FO. The cyclopentene ring is planar in one of the molecules and slightly distorted into an envelope conformation in the other, with the CH_2 group adjacent to the carbonyl group lying 0.033 (2) Å out of the best plane of the other four atoms. The maximum deviation from coplanarity of all the non-H atoms of (1) is 0.038 (2) Å for one molecule and 0.019 (2) Å for the other. The two molecules are nearly parallel in the crystal, their best planes forming a dihedral angle of 4.1 (3)°. 2,2-Dimethyl-5-fluoro-1-indanone (2), $C_{11}H_{11}FO$, lies on a mirror plane in the crystal. Molecules of both (1) and (2) pack in hypercentric arrays. The C—F distances are 1.354 (2) and 1.360 (3) Å for (1) and 1.355 (2) Å for (2). The C=O distances are 1.218 (2) and 1.212 (3) Å for (1) and 1.220 (2) Å for (2).

Comment

The synthesis of 5-fluoro-1-indanone (1) and 2,2-dimethyl-5-fluoro-1-indanone (2) was required for their use as standards for 5-[18F]fluoro-1-indanone

and 2,2-dimethyl-5-[18F]fluoro-1-indanone. This work is part of an ongoing study involving nucleophilic substitution reactions with the [18F]fluoride ion on nitro-1-indanones and nitro-1,3-indandiones (Enas, Garcia, Mathis & Gerdes, 1993; VanBrocklin, Enas, Garcia & Hanrahan, 1993). Compound (1) was prepared according to the literature method of Quere & Maréchal (1971) and compound (2) was prepared by reacting 2,2-dimethyl-5-nitro-1-indanone with KF in dimethyl sulfoxide (Enas, Garcia, Mathis & Gerdes, 1993). Suitable crystals of (1) and (2) had m.p.'s of 303–304 and 336–337 K, respectively.

Structural data for compounds (1) and (2) are in agreement with those of indan-2,2-dicarboxylic acid (Garcia, Enas & Fronczek, 1994), 2-ethyl-2-nitroindan-1,3-dione (Garcia, Enas, Chang & Fronczek, 1993), 8-acetyl-2,2-difluoro-4-methyl-6H-1,3,2-indenodioxaborinane and 8-bromo-2,2-difluoro-4-methyl-6H-1,3,2-indenodioxaborinane (Garcia, Enas, VanBrocklin & Fronczek, 1993), 2-acylindan-1-one (Garcia, Enas & Fronczek, 1993) and 2,2-dimethyl-4,5-dinitroindan (Garcia, Enas & Fronczek, 1995).

The packing of molecules in the structure of (1) (Fig. 3) is hypercentric. The two independent molecules are related by a pseudocenter near $\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$ (0.263, 0.244, 0.257). The F and O atoms, however, do not conform to the pseudo-inversion and the molecules deviate slightly from being parallel, forming a dihedral angle of 4.1 (3)° with one another. The
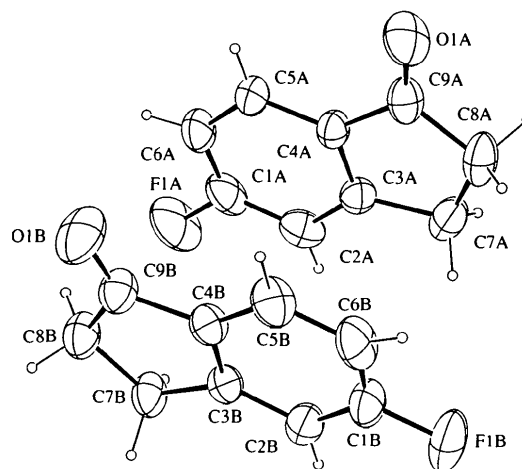

Fig. 1. *ORTEP* drawing (Johnson, 1965) of the asymmetric unit of (1) representing heavy atoms as 30% probability ellipsoids and H atoms as circles of arbitrary radii.

packing of (2) (Fig. 4) is also hypercentric, with *n*-glide related molecules related by a psudocenter at $\frac{1}{4}$, $\frac{1}{4}$, 0.245. This hypersymmetry caused some difficulty in the structure solution with multisolution direct methods typically yielding correctly oriented indan fragments misplaced with respect to the symmetry elements. The problem was circumvented using a misplaced fragment from *RANTAN* (Yao, 1981) for phase refinement in space group *P*1 using *DIRDIF* (Beurskens, 1984). This procedure yielded positions for the F and O atoms, which do not conform to the pseudosymmetry and thus led to the correct placement of the molecule with respect to the symmetry elements of *Pnma*.
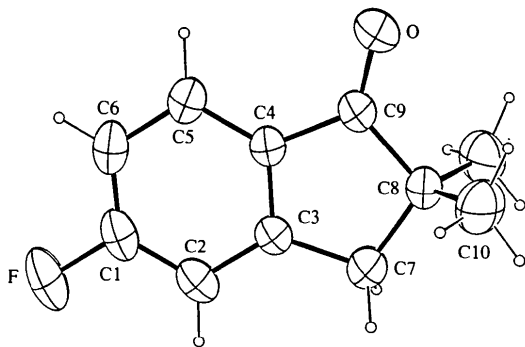

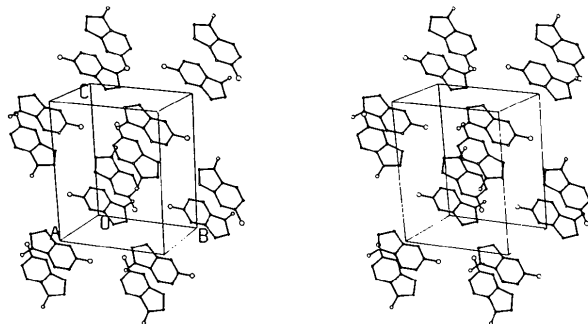Fig. 2. Compound (2) represented as in Fig. 1.

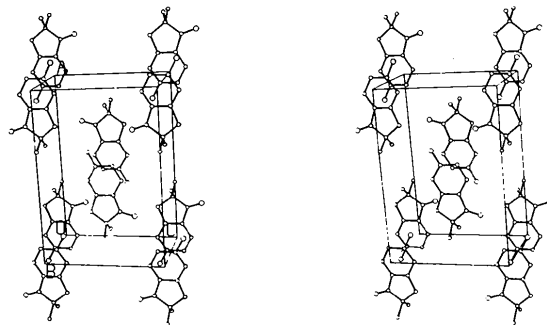Fig. 3. The unit cell of (1) illustrating the pseudocenter relating the two independent molecules.

Fig. 4. The unit cell of (2).

Experimental

Compound (1)

Crystal data

C$_9$H$_7$FO
M_r = 150.2
Triclinic
$P\bar{1}$
a = 6.6219 (3) Å
b = 9.4738 (13) Å
c = 12.462 (2) Å
α = 96.475 (11)°
β = 93.022 (7)°
γ = 107.315 (8)°
V = 738.5 (3) Å^3
Z = 4
D_x = 1.350 Mg m^{-3}

Cu $K\alpha$ radiation
λ = 1.54184 Å
Cell parameters from 25 reflections
θ = 20–30°
μ = 0.84 mm^{-1}
T = 297 K
Fragment
0.50 × 0.42 × 0.30 mm
Colorless
Crystal source: recrystallized from dichloromethane

Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: empirical
T_{min} = 0.941, T_{max} = 0.998
2924 measured reflections
2924 independent reflections

2381 observed reflections
$[I > 3\sigma(I)]$
θ_{max} = 75°
h = 0 → 8
k = -11 → 11
l = -15 → 15
3 standard reflections
frequency: 167 min
intensity decay: <3%

Refinement

Refinement on F
R = 0.056
wR = 0.076
S = 4.462
2381 reflections
256 parameters
All H-atom parameters refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.02F_o^2)^2]$
$(\Delta/\sigma)_{max} < 0.01$

$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = -0.18 e Å^{-3}
Extinction correction:
$(1 + gI_c)^{-1}$ applied to F_c
Extinction coefficient:
g = 1.42 (4) × 10^{-5}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

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

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
F1A	0.5986 (3)	0.6008 (2)	0.2135 (1)	10.60 (4)
O1A	0.0289 (2)	0.2361 (2)	0.5490 (1)	7.53 (4)
C1A	0.4901 (4)	0.5133 (2)	0.2833 (1)	6.57 (5)
C2A	0.5682 (3)	0.4044 (2)	0.3143 (2)	6.24 (5)
C3A	0.4555 (3)	0.3171 (2)	0.3871 (1)	4.75 (4)
C4A	0.2743 (3)	0.3430 (2)	0.4232 (1)	4.36 (3)
C5A	0.1992 (3)	0.4532 (2)	0.3881 (1)	5.25 (4)
C6A	0.3084 (4)	0.5389 (2)	0.3168 (2)	6.31 (5)
C7A	0.5019 (3)	0.1919 (2)	0.4387 (2)	6.14 (5)
C8A	0.3233 (3)	0.1406 (2)	0.5100 (2)	6.54 (5)
C9A	0.1851 (3)	0.2403 (2)	0.5005 (2)	5.32 (4)
F1B	0.3483 (2)	-0.1414 (1)	0.2153 (1)	9.93 (4)
O1B	-0.1661 (2)	0.3083 (2)	0.1080 (2)	8.75 (4)
C1B	0.2526 (3)	-0.0416 (2)	0.1851 (2)	6.30 (5)
C2B	0.3528 (3)	0.0556 (2)	0.1178 (2)	5.63 (4)
C3B	0.2533 (3)	0.1572 (2)	0.0898 (1)	4.51 (3)
C4B	0.0636 (3)	0.1580 (2)	0.1295 (1)	4.71 (4)
C5B	-0.0333 (3)	0.0582 (2)	0.1982 (2)	6.28 (5)

C6B	0.0632 (4)	−0.0445 (2)	0.2262 (2)	6.78 (5)
C7B	0.3281 (3)	0.2772 (2)	0.0184 (1)	5.52 (4)
C8B	0.1575 (3)	0.3546 (2)	0.0181 (2)	6.03 (4)
C9B	−0.0058 (3)	0.2774 (3)	0.0884 (2)	5.55 (4)

Table 2. *Geometric parameters* (Å, °) *for* (1)

F1A—C1A	1.354 (2)	F1B—C1B	1.360 (3)
O1A—C9A	1.218 (2)	O1B—C9B	1.212 (3)
C1A—C2A	1.367 (3)	C1B—C2B	1.364 (3)
C1A—C6A	1.373 (3)	C1B—C6B	1.374 (3)
C2A—C3A	1.392 (3)	C2B—C3B	1.383 (3)
C3A—C4A	1.382 (3)	C3B—C4B	1.376 (2)
C3A—C7A	1.511 (3)	C3B—C7B	1.506 (2)
C4A—C5A	1.384 (3)	C4B—C5B	1.385 (3)
C4A—C9A	1.467 (2)	C4B—C9B	1.473 (3)
C4A—C5A	1.384 (3)	C4B—C5B	1.385 (3)
C4A—C9A	1.467 (2)	C4B—C9B	1.473 (3)
C5A—C6A	1.361 (3)	C5B—C6B	1.378 (3)
C7A—C8A	1.513 (3)	C7B—C8B	1.519 (3)
C8A—C9A	1.508 (3)	C8B—C9B	1.498 (3)
F1A—C1A—C2A	117.5 (2)	F1B—C1B—C2B	117.8 (2)
F1A—C1A—C6A	117.8 (2)	F1B—C1B—C6B	117.5 (2)
C2A—C1A—C6A	124.6 (2)	C2B—C1B—C6B	124.7 (2)
C1A—C2A—C3A	116.5 (2)	C1B—C2B—C3B	116.5 (2)
C2A—C3A—C4A	119.6 (2)	C2B—C3B—C4B	120.5 (2)
C2A—C3A—C7A	129.6 (2)	C2B—C3B—C7B	127.9 (2)
C4A—C3A—C7A	110.8 (1)	C4B—C3B—C7B	111.6 (2)
C3A—C4A—C5A	121.9 (2)	C3B—C4B—C5B	121.5 (2)
C3A—C4A—C9A	110.1 (2)	C3B—C4B—C9B	109.4 (1)
C5A—C4A—C9A	128.1 (2)	C5B—C4B—C9B	129.1 (2)
C4A—C5A—C6A	118.9 (2)	C4B—C5B—C6B	118.7 (2)
C1A—C6A—C5A	118.5 (2)	C1B—C6B—C5B	118.1 (2)
C3A—C7A—C8A	105.0 (2)	C3B—C7B—C8B	104.5 (1)
C7A—C8A—C9A	106.6 (2)	C7B—C8B—C9B	106.6 (2)
O1A—C9A—C4A	126.7 (2)	O1B—C9B—C4B	126.2 (2)
O1A—C9A—C8A	125.8 (2)	O1B—C9B—C8B	125.9 (2)
C4A—C9A—C8A	107.5 (2)	C4B—C9B—C8B	107.9 (2)
F1A—C1A—C2A—C3A	179.2 (2)	C5A—C4A—C9A—O1A	−1.2 (3)
F1B—C1B—C6B—C5B	178.6 (2)	C5B—C4B—C9B—O1B	−0.7 (3)
C7A—C3A—C4A—C9A	0.1 (2)	C3A—C4A—C9A—C8A	−1.4 (2)
C7B—C3B—C4B—C9B	0.2 (2)	C3B—C4B—C9B—C8B	−0.1 (2)

Compound (2)

Crystal data

$C_{11}H_{11}FO$
$M_r = 178.2$
Orthorhombic
$Pnma$
$a = 13.992\ (1)$ Å
$b = 6.962\ (1)$ Å
$c = 9.788\ (1)$ Å
$V = 953.5\ (2)$ Å^3
$Z = 4$
$D_x = 1.241$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.54184$ Å
Cell parameters from 25 reflections
$\theta = 25–42°$
$\mu = 0.73$ mm^{-1}
$T = 296$ K
Fragment
$0.60 \times 0.45 \times 0.35$ mm
Colorless
Crystal source: recrystallized from hexane

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega–2\theta$ scans
Absorption correction: empirical
$T_{min} = 0.954,\ T_{max} = 0.993$
3070 measured reflections
1062 independent reflections

820 observed reflections
$[I > \sigma(I)]$
$R_{int} = 0.032$
$\theta_{max} = 75°$
$h = 0 \rightarrow 17$
$k = −12 \rightarrow 12$
$l = −8 \rightarrow 8$
3 standard reflections
frequency: 167 min
intensity decay: −8.8%

Refinement

Refinement on F
$R = 0.044$
$wR = 0.055$
$S = 2.152$
820 reflections
102 parameters
All H-atom parameters refined
$w = 4F_o^2/[\sigma^2(F_o^2) + (0.02F_o^2)^2]$
$(\Delta/\sigma)_{max} = 0.04$

$\Delta\rho_{max} = 0.15$ e Å^{-3}
$\Delta\rho_{min} = −0.15$ e Å^{-3}
Extinction correction:
$(1 + gI_c)^{-1}$ applied to F_c
Extinction coefficient:
$g = 1.10\ (3) \times 10^{-5}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
F	0.37429 (7)	1/4	0.6264 (1)	8.75 (4)
O	0.75078 (8)	1/4	0.2569 (1)	7.05 (3)
C1	0.4591 (1)	1/4	0.5597 (2)	5.90 (4)
C2	0.5408 (1)	1/4	0.6367 (2)	5.62 (4)
C3	0.6270 (1)	1/4	0.5672 (2)	4.52 (3)
C4	0.6269 (1)	1/4	0.4258 (2)	4.34 (3)
C5	0.5430 (1)	1/4	0.3512 (2)	5.28 (4)
C6	0.4569 (1)	1/4	0.4199 (2)	5.96 (4)
C7	0.7268 (1)	1/4	0.6239 (2)	5.99 (4)
C8	0.7930 (1)	1/4	0.4989 (2)	5.14 (4)
C9	0.7255 (1)	1/4	0.3762 (1)	4.76 (3)
C10	0.8546 (1)	0.4299 (3)	0.4919 (2)	8.08 (4)

Table 4. *Geometric parameters* (Å, °) *for* (2)

F—C1	1.355 (2)	C3—C7	1.502 (2)
O—C9	1.220 (2)	C4—C5	1.382 (2)
C1—C2	1.368 (2)	C4—C9	1.463 (2)
C1—C6	1.369 (3)	C5—C6	1.380 (2)
C2—C3	1.385 (2)	C7—C8	1.534 (2)
C3—C4	1.383 (2)	C8—C9	1.528 (2)
C8—C10	1.523 (2)		
F—C1—C2	117.8 (2)	C3—C7—C8	105.5 (1)
F—C1—C6	117.5 (2)	C7—C8—C9	104.7 (1)
C2—C1—C6	124.7 (2)	C7—C8—C10	112.2 (1)
C1—C2—C3	117.2 (2)	C2—C3—C7	128.9 (2)
C2—C3—C4	119.4 (1)	C4—C3—C7	111.7 (1)
C9—C8—C10	108.3 (1)	C10—C8—C10^i	110.7 (1)
C3—C4—C5	122.0 (1)	O—C9—C4	126.3 (1)
C3—C4—C9	109.3 (1)	O—C9—C8	125.0 (1)
C5—C4—C9	128.7 (1)	C4—C5—C6	118.9 (2)
C1—C6—C5	117.8 (2)	C4—C9—C8	108.8 (1)
C3—C7—C8—C10	117.3 (1)	C10—C8—C9—C4	−119.9 (1)
C10—C8—C9—O	60.1 (1)		

Symmetry code: (i) $x, \frac{1}{2} − y, z$.

Crystals of (1) and (2) were sealed in capillaries for data collection. Three octants of data were collected for compound (2). Programs used were *MolEN* (Fair, 1990), *SHELXS*86 (Sheldrick, 1990), *RANTAN* (Yao, 1981), *DIRDIF* (Beurskens, 1984), *PLUTO* (Motherwell & Clegg, 1978) and *ORTEP* (Johnson, 1965).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry for (1) and (2), and least-squares-planes data for (1) have been deposited with the IUCr (Reference: CR1124). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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cis,trans-3,3'-Sulfinylbis(acrylic acid)

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Abstract

The title compound, (*E,Z*)-4-thia-2,5-heptadienedioic acid 4-oxide, (C₆H₆O₅S), exhibits an atypical hydrogen-bonding network in which normal carboxylic acid dimers are not observed; one carbonyl O

atom is omitted from the scheme. The C—S—C angle [94.9 (1)°] is unusually compressed and the S—O bond [1.504 (2) Å] is somewhat lengthened.

Comment

In the course of the synthesis and study of the divinyl sulfurane (1), proof of the structure of its hydrolysis product (2) was sought. Much to our surprise, slow evaporation of a methanol solution of (2) afforded crystals of (3) rather than (2) (Ho, 1993). The product of isomerization of both *cis* double bonds of (2), namely (4), was not detected, even after prolonged reaction time. Thus (3) is thermodynamically more stable than (2) or (4). The structure of (3) is reported herein.
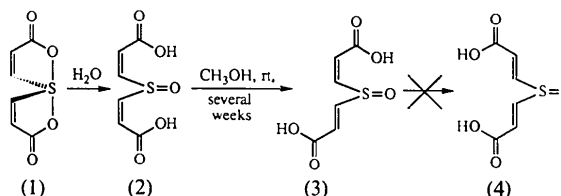
The hydrogen-bonding network is interesting (Fig. 2). The sulfoxide diacid contains two hydrogen-bond donor sites (the OH's) but three hydrogen-bond acceptor sites (two carbonyl and one sulfinyl O atom). In this case, one hydrogen-bond acceptor, the carbonyl O atom of the *cis* acrylic acid moiety (O4), is simply excluded from the hydrogen-bonding scheme. The usual model of carboxylic acid dimerization is not in evidence nor is any intramolecular hydrogen bond. Instead, there is a centrosymmetric dimer formed by two hydrogen bonds (*a* in Fig. 2) between the *trans* acrylic acid carbonyl (O2) and the *cis* acrylic acid hydroxyl (O5). This dimer is in turn bound by hydrogen bonds (*b* in Fig. 2), involving the sulfinyl O atom (O1) and the *trans* acrylic acid hydroxyl (O3), to a dimer in the adjacent unit cell arrived at by a translation along *c*. The relevant intermolecular contacts are O2···O5(−*x*, 1 − *y*, 1 − *z*) 2.683 (4) and O1···O3(*x*, *y*, 1 + *z*) 2.617 (4) Å. The length of the non-hydrogen-bonded carbonyl bond is 0.008 Å shorter than that of the hydrogen-bonded carbonyl. The presence of two non-equivalent carbonyls explains the IR spectrum of (3) (KBr) which shows a broad absorption of 1665 cm^{-1}, typical of α,β-unsaturated acids, and a sharp peak at 1709 cm^{-1} which may be assigned to the non-hydrogen-bonded carbonyl. This novel solution of the problem of one too many hydrogen-bond acceptors is reminiscent of the unusual hydrogen bonding observed in glycolic acid HOOC—CH₂OH, which forms a closed loop of six molecules (Ellison, Johnson & Levy, 1971; Pijper, 1971).