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1-Carboxyfluorenone: an Intramolecularly Hydrogen-Bonded γ-Keto Acid

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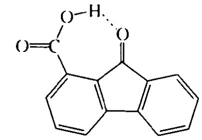
Abstract

9-Oxo-9*H*-fluorene-1-carboxylic acid, $C_{14}H_8O_3$, adopts a planar conformation with the carboxyl group internally hydrogen bonded to the ketone O atom. The molecules stack in the *a* direction [$a = 3.809(1)$ Å], with an interplanar separation of 3.496 (4) Å.

Comment

The crystalline states of acetic and formic acid involve chains (catemers) created by repeating intermolecular O—H···O═C hydrogen bonds (Jones & Templeton, 1958; Nahringbauer, 1978), a pattern otherwise rare among carboxylic acids, which typically form hydrogen-bonded dimers (Leiserowitz, 1976). Our continuing study of the X-ray structures of simple keto–carboxylic acids concerns such hydrogen-bonding motifs, of which four are known. The commonest motif consists of acid dimers, with the ketone group not involved in the hydrogen bonding. Less common is the motif in which intermolecular carboxy-to-ketone hydrogen bonds repeat along one cell axis to yield a catemer. A rare third arrangement involves an internal hydrogen bond and one instance is known of acid-to-ketone dimerization. We have previously discussed numerous examples of these hydrogen-bonding motifs (Thompson, Lalancette & Vanderhoff, 1992; Coté, Thompson & Lalancette, 1996).

We have recently examined and are reporting separately an example of an internally hydrogen-bonded β-keto acid (Thompson, Lalancette & Coté, 1996). Apart from this β-keto acid and several α,β-unsaturated β′-oxo acids which are not strictly ketones, this internal hydrogen-bonding motif has been found in only a few γ-keto acids, which require seven-membered hydrogen-bonded rings (Griffe, Durant & Pieret, 1972; Sheldrick & Trowitzsch, 1983; Halfpenny, 1990), and one ε-keto acid (Abell, Morris & McKee, 1990). With respect to the six non-H atoms of the hydrogen-bonded ring, these γ-keto acids have a number of features in common: (i) sp^2 hybridization at the α and β positions, (ii) skeletal features that enforce coplanarity of at least four consecutive atoms, (iii) conjugation or other effects that encourage coplanarity even in the rotationally unconstrained heavy atoms, and (iv) skeletal factors that favor internal angles wider than 120°. The commercially available title compound, (I), was selected as a promising candidate for internal hydrogen bonding, embodying as it does all of the above features, and its crystal structure determination is reported here.



(I)

Fig. 1 presents a view of compound (I) with its numbering scheme. The condensed ring system is planar, with the carboxy group lying in the molecular plane (the mean deviation of all non-H atoms from this plane is 0.021 Å), internally hydrogen bonded to the ketone (Table 2), only the second instance of this we have encountered in our work. This arrangement requires an antiplanar (or *s-trans*) carboxy conformation, which is less stable than the synplanar conformation by energies estimated variously as 2–4 kcal mol^{-1} (Leiserowitz, 1976) and 1.5–5.5 kcal mol^{-1} (Gandour, 1981). The dimensions of the carboxy group and the location of the carboxy H atom unequivocally establish that there is no disorder of this group, as is occasionally found in dimeric acids.

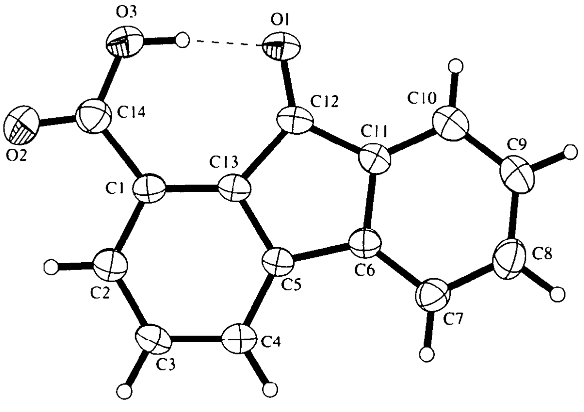


Fig. 1. A view of compound (I) showing the atomic numbering scheme, with ellipsoids drawn at the 30% probability level.

The internal angles of the hydrogen-bonding system all lie within typical ranges, with the exception of the C12—O1···H3*B* angle. Catemeric and dimeric arrangements favor O—H···O angles in the range 155–180° (Thompson, Lalancette & Vanderhoff, 1992) and in (I), this angle is 174 (4)°, which is achieved principally by narrowing of the C═O···H angle to 104 (1)°. This latter angle is significantly smaller than that preferred (114–156°) in surveyed catemeric (Thompson, Lalancette &

Vanderhoff, 1992) and acid-dimer cases (Lifson, Hagler & Dauber, 1979), and narrower even than those listed for other internally hydrogen-bonded γ-keto acids (Griffe, Durant & Pieret, 1972). The wide C13—C1—C14 angle [127.8 (3)°] at the point of attachment of the carboxy group suggests accommodation of angle strain for the sake of the internal hydrogen bond.

The cell contains a screw-related pair of molecules centrosymmetric to a second pair of molecules of opposite conformational handedness, all stacking in the shallow dimension of the cell. The tilt of the molecules relative to the cell produces an interplanar separation of 3.496 (4) Å, slightly less than the repeat distance [a = 3.809 (1) Å]. The interplanar distance in graphite is 3.354 Å (Nelson & Riley, 1945), in benzene is 3.8 Å (Cox, 1932) and in phenanthrene is 3.55 Å (Trotter, 1963).

Of the four isomers of carboxyfluorenone, the literature yields UV–visible spectral data for only the title compound, thus preventing comparisons. The bright orange color of (I), however, denotes a significant increase in conjugation relative to the other three isomers, which are described, like fluorenone itself, as yellow. This is consistent with the carboxy coplanarity found for (I) in the present study. In contrast, the conformation found by X-ray determination for the 4-carboxy isomer involves a 26.5° dihedral twist out of the ring plane by the dimerized carboxy group (Kennard, Smith & Katekar, 1981).

The solid-state IR spectrum (KBr disc) of (I) has two strong absorptions in the C=O stretching region. The narrower and more intense absorption at 1745 cm^{-1} is assigned to the free carboxy C=O group and the weaker at 1672 cm^{-1} to the ketone. These assignments are consistent with known patterns of C=O shifts associated with the removal and introduction of hydrogen bonding, as we have previously exemplified (Vanderhoff, Lalancette & Thompson, 1990). These bands, previously reported at similar positions in both Nujol (Josien & Fuson, 1951) and KBr (Resplandy & Le Roux, 1968), are found at 1733 and 1724 cm^{-1} in dioxane solution (Bowden & Taylor, 1971).

Experimental

The title compound was purchased from the Aldrich Chemical Co. Inc., Milwaukee, WI, USA, and recrystallized from formic acid at room temperature.

Crystal data

$C_{14}H_8O_3$
$M_r = 224.2$
Monoclinic
$P2_1/c$
$a = 3.809\ (1)$ Å
$b = 19.911\ (2)$ Å
$c = 13.206\ (2)$ Å
$\beta = 91.28\ (1)°$
$V = 1001.3\ (3)$ Å^3
$Z = 4$
$D_x = 1.487$ Mg m^{-3}
$D_m = 1.484\ (1)$ Mg m^{-3}
D_m measured by flotation in cyclohexane/CCl_4

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 14 reflections
$\theta = 5.4–11.1°$
$\mu = 0.105$ mm^{-1}
$T = 296\ (1)$ K
Flat plate
0.52 × 0.16 × 0.05 mm
Deep orange

Data collection

Siemens *P*4 diffractometer
$2\theta/\theta$ scans
Absorption correction: face-indexed numerical (*SHELXL*93; Sheldrick, 1993)
$T_{\min} = 0.979$, $T_{\max} = 0.994$
2046 measured reflections
1767 independent reflections

736 observed reflections [$F > 4\sigma(F)$]
$R_{\rm int} = 0.05$
$\theta_{\max} = 25.0°$
$h = 0 \rightarrow 4$
$k = 0 \rightarrow 23$
$l = -15 \rightarrow 15$
3 standard reflections monitored every 97 reflections intensity decay: 1.35%

Refinement

Refinement on F^2
$R(F) = 0.047$
$wR(F^2) = 0.091$
$S = 1.02$
1766 reflections
159 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0371P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.277$
$\Delta\rho_{\max} = 0.168$ e Å^{-3}
$\Delta\rho_{\min} = -0.147$ e Å^{-3}

Extinction correction: *SHELXL*93
Extinction coefficient: 0.016 (1)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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	−0.0881 (6)	0.27179 (11)	0.26039 (15)	0.0636 (7)
O2	0.0334 (8)	0.49059 (13)	0.1874 (2)	0.0873 (9)
O3	−0.1156 (7)	0.40180 (12)	0.2733 (2)	0.0725 (8)
C1	0.1518 (8)	0.38655 (15)	0.1088 (2)	0.0458 (8)
C2	0.2743 (8)	0.4208 (2)	0.0250 (2)	0.0521 (9)
C3	0.4056 (9)	0.3880 (2)	−0.0582 (2)	0.0553 (9)
C4	0.4185 (8)	0.3183 (2)	−0.0615 (2)	0.0507 (8)
C5	0.2934 (8)	0.28303 (13)	0.0206 (2)	0.0430 (8)
C6	0.2718 (8)	0.21019 (14)	0.0368 (2)	0.0450 (8)
C7	0.3653 (8)	0.1570 (2)	−0.0239 (2)	0.0549 (9)
C8	0.3107 (10)	0.0922 (2)	0.0116 (3)	0.0670 (10)
C9	0.1791 (9)	0.0807 (2)	0.1063 (3)	0.0671 (10)
C10	0.0819 (9)	0.1336 (2)	0.1673 (3)	0.0602 (10)
C11	0.1337 (8)	0.19818 (15)	0.1317 (2)	0.0462 (8)
C12	0.0506 (8)	0.2634 (2)	0.1781 (2)	0.0468 (8)
C13	0.1628 (8)	0.31636 (15)	0.1054 (2)	0.0430 (8)
C14	0.0197 (9)	0.4304 (2)	0.1926 (2)	0.0602 (10)

Table 2. *Selected geometric parameters (Å, °)*

O1—C12	1.230 (3)	C5—C6	1.469 (4)
O2—C14	1.202 (4)	C6—C7	1.380 (4)
O3—C14	1.322 (4)	C6—C11	1.391 (4)
C1—C2	1.390 (4)	C7—C8	1.389 (4)
C1—C13	1.399 (4)	C8—C9	1.376 (4)
C1—C14	1.505 (4)	C9—C10	1.381 (4)

C2—C3	1.381 (4)	C10—C11	1.385 (4)
C3—C4	1.389 (4)	C11—C12	1.474 (4)
C4—C5	1.386 (4)	C12—C13	1.495 (4)
C5—C13	1.402 (4)		
C14—O3—H3*B*	114 (2)	O1—C12—C13	127.3 (3)
C2—C1—C14	115.1 (3)	C1—C13—C12	132.4 (3)
C13—C1—C14	127.8 (3)	O2—C14—O3	119.6 (3)
O1—C12—C11	126.0 (3)	O3—C14—C1	119.0 (3)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3—H3*B*···O1	0.93 (4)	1.66 (4)	2.596 (3)	174 (4)

All non-carboxy H atoms were placed in calculated positions and allowed to refine as riding. The carboxy H3*B* atom was found in an electron density difference map and the positional parameters were refined, but the displacement parameter was fixed.

Data collection: *XSCANS* (Siemens, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXTL/PC* (Sheldrick, 1990*b*), *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: FG1139). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Photochromic Pyrido-Annelated 2,2-Dimethylchromene

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Abstract

An X-ray analysis of the title photochromic pyrido-annelated 2,2-dimethylchromene, 3,3-dimethylpyrano-[3,2-*f*]quinoline, has been undertaken. It forms a crystallohydrate, $C_{14}H_{13}NO.H_2O$. The influence of the molecular structure on its photochemical properties has been investigated.

Comment

Aldoshin *et al.* (1995) have discussed the structure and photochemical properties of 2,2-diphenylchromene derivatives. Elongation of the C_{sp^3}—O bond, the rupture of which is responsible for the photochemical properties of chromenes, was shown to be due to steric repulsions at the sp^3 centre. Two different arrangements of the mutually orthogonal phenyl rings relative to the pyran O atom were revealed, the steric influence of each on the C—O bond length being the same. Changes in photochemical activity of different diphenylchromene derivatives are related to the specific structure of the pyran fragment of the molecule. The stability of open forms of diphenylchromenes depends on the π-system size and on the efficiency of π-conjugation in this system. In relation to this, it would be interesting to study the structure and photochemical properties of 2,2-dimethylchromene, the methyl groups of which have a steric influence on the sp^3 centre only. On the other hand, from such an investigation, the effect of