Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	$U_{\rm eq}$
S1	0.41431 (9)	0.42445 (6)	0.2751 (1)	0.0439 (2)
S2	0.54843 (8)	0.18915 (6)	0.2103 (1)	0.0408 (2)
S3	0.12666 (8)	0.14367 (5)	0.09422 (9)	0.0329 (2)
O1	0.6844 (2)	0.2526 (2)	0.3005 (3)	0.0612 (7)
O2	0.5455 (2)	0.0841 (2)	0.3030 (3)	0.0542 (6)
O3	0.2072 (2)	0.0890 (1)	−0.0312 (2)	0.0446 (5)
O4	−0.0496 (2)	0.1730 (2)	0.0127 (3)	0.0456 (5)
C2	0.3715 (3)	0.2876 (2)	0.2048 (3)	0.0325 (6)
C3	0.2123 (3)	0.2732 (2)	0.1759 (3)	0.0286 (6)
C4	−0.0462 (3)	0.3980 (2)	0.2043 (4)	0.0397 (7)
C5	−0.1066 (3)	0.5056 (3)	0.2445 (4)	0.0484 (8)
C6	−0.0101 (4)	0.5944 (2)	0.2920 (4)	0.0533 (9)
C7	0.1513 (4)	0.5770 (2)	0.3058 (4)	0.0466 (8)
C8	0.2149 (3)	0.4667 (2)	0.2662 (3)	0.0351 (7)
C9	0.1183 (3)	0.3769 (2)	0.2131 (3)	0.0304 (6)
C10	0.5337 (3)	0.1619 (2)	−0.0323 (4)	0.0475 (8)
C11	0.5231 (4)	0.2669 (3)	−0.1518 (5)	0.063 (1)
C12	0.1801 (3)	0.0574 (2)	0.3079 (4)	0.0399 (7)
C13	0.1194 (4)	0.1145 (3)	0.4607 (4)	0.0555 (9)

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

S1—C2	1.724 (2)	S3—O4	1.435 (2)
S1—C8	1.726 (3)	S3—C3	1.783 (2)
S2—O1	1.437 (2)	S3—C12	1.766 (3)
S2—O2	1.432 (2)	C2—C3	1.367 (3)
S2—C2	1.789 (2)	C3—C9	1.450 (3)
S2—C10	1.758 (3)	C10—C11	1.504 (4)
S3—O3	1.435 (2)	C12—C13	1.506 (4)
C2—S1—C8	91.4 (1)	S1—C2—S2	113.9 (1)
O1—S2—O2	118.6 (1)	S1—C2—C3	113.2 (2)
O1—S2—C2	103.8 (1)	S2—C2—C3	132.5 (2)
O1—S2—C10	108.5 (1)	S3—C3—C2	124.3 (2)
O2—S2—C2	108.1 (1)	S3—C3—C9	123.4 (2)
O2—S2—C10	109.1 (1)	C2—C3—C9	112.2 (2)
C2—S2—C10	108.3 (1)	S1—C8—C7	125.7 (2)
O3—S3—O4	117.5 (1)	S1—C8—C9	112.3 (2)
O3—S3—C3	107.5 (1)	C3—C9—C4	130.4 (2)
O3—S3—C12	109.3 (1)	C3—C9—C8	110.9 (2)
O4—S3—C3	107.5 (1)	S2—C10—C11	114.7 (2)
O4—S3—C12	109.0 (1)	S3—C12—C13	113.3 (2)
C3—S3—C12	105.3 (1)		

The space group was determined based on a statistical analysis of intensity distribution and the successful solution and refinement of the structure.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1994). Program(s) used to solve structure: *SAPI*91 (Fan, 1991). Program(s) used to refine structure: *TEXSAN*. 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: AS1212). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Fluorene-1-carboxylic Acid

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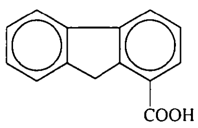
Abstract

In fluorene-1-carboxylic acid, $C_{14}H_{10}O_2$, the sole hydrogen bond is of the cyclic dimer type about a center of symmetry. The carboxyl H atom is ordered. Distances in the fluorene core are very similar to those in fluorene itself; the fluorene core dihedral angle is, however, larger than in fluorene.

Comment

The structure of fluorene-1-carboxylic acid was of interest both because of the potential for hydrogen bonding and because of the possibility of comparisons of the fluorene core geometry with that of fluorene itself, as determined by Belsky, Zavodnik & Vozzhennikov (1984) at 295 K and Gerkin, Lundstedt & Reppart (1984) at 159 K .

In the present structure (I), hydrogen bonding is of the cyclic dimer type about a center of symmetry. There is only a single hydrogen bond and this has O(1) as donor and O(2ⁱ) as acceptor [symmetry operator: (i) 1 − *x*, 1 − *y*, −*z*]; the donor–acceptor distance, 2.632 (4) Å, is well below the average for organic O···O hydrogen bonds (2.77 Å, Ceccarelli, Jeffrey & Taylor, 1981) and indicates a strong hydrogen bond. The interatomic distances in the carboxyl group (Table 2) are entirely consistent with an ordered carboxyl H atom.



(I)

In the fluorene structure a mirror plane bisects the molecule, while in the present structure distances in the fluorene core display pseudo-mirror symmetry: the r.m.s. deviation within the seven pairs of distances in the core that would be identical under mirror symmetry is 0.007 (5) Å. Moreover, the seven means of these seven pairs of values differ from the corresponding unique values in fluorene such that the r.m.s. deviation between the two sets of values is 0.007 (6) for the low-temperature fluorene data (Gerkin *et al.*, 1984) and 0.010 (8) for the room temperature fluorene data (Belsky *et al.*, 1984). Thus, with respect to bond distances, there is no significant difference between the two halves of the present fluorene core, nor between this fluorene core and the parent molecule at room or low temperature. There is, of course, a unique core bond, here labelled C(11)—C(12), which is bisected by the mirror plane in fluorene. The present value is 1.471 (4) Å, while for fluorene it is 1.472 (3) Å at low temperature (Gerkin *et al.*, 1984) and 1.491 (8) Å at room temperature (Belsky *et al.*, 1984). Gerkin *et al.* (1984) discussed the discrepancy of the two earlier values of this bond distance for fluorene; considering the present core value, it appears that the Belsky *et al.* (1984) value may simply be slightly in error.

Concerning the planarity of fluorene itself, Gerkin *et al.* (1984) demonstrated that the molecule is slightly non-planar both at low temperature and at room temperature [contrary to Belsky *et al.* (1984)]. For the fluorene core in the present molecule we have chosen best-fit planes for atoms C(1)–C(4), C(10) and C(11), and for C(5)–C(8), C(12) and C(13) to define the molecular dihedral angle. The maximum deviation of any of the defining atoms from the first plane is 0.002 Å and from the second, 0.008 Å; thus, the presence of the carboxyl group is associated with a slight rumpling of the second plane. Further, the dihedral angle is 3.1 (1)°, larger than for fluorene at room temperature [0.8 (2)°] or low temperature [1.28 (4)°]. The presence of the carboxyl group is thus also associated with slight plane 'displacement' as well as plane rumpling. The dihedral angle between the carboxyl group plane and the plane to which it is attached (the first plane above) is 4.3 (2)°.

Excluding the hydrogen bond, the closest approaches of two molecules in this structure are between H(1) and H(1^{i}), C(14) and H(1^{i}) and O(2) and H(3^{ii}) [symmetry operators: (i) $1 - x, 1 - y, -z$; (ii) $-1 + x, 1 + y, z$], all of which are at least 0.2 Å less than the sums of the corresponding van der Waals radii (Bondi, 1964).

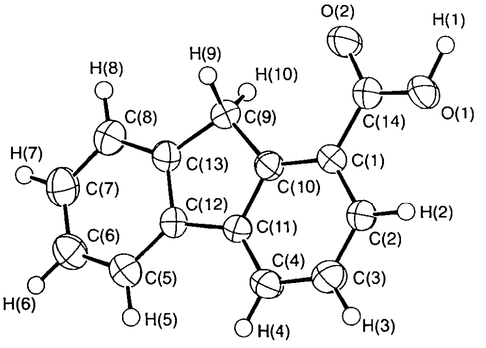


Fig. 1. An *ORTEP*II (Johnson, 1976) drawing of fluorene-1-carboxylic acid showing our numbering scheme. Displacement ellipsoids are drawn at 50% probability for all atoms except H for which they have been set artificially small.

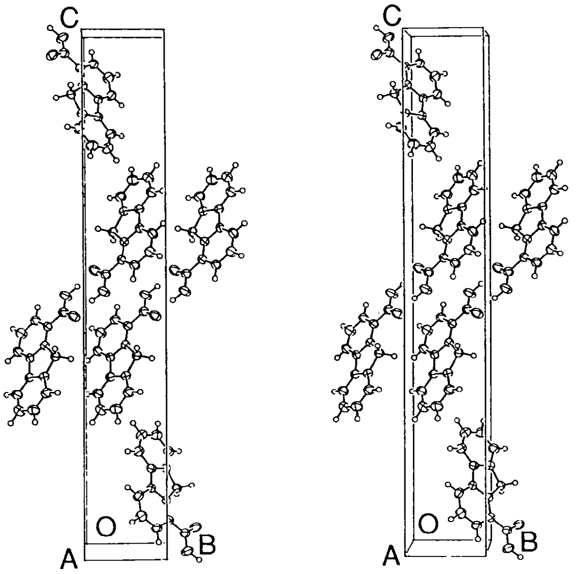


Fig. 2. A stereoview (*ORTEP*II; Johnson, 1976) of the title structure including a unit cell and two additional molecules, from a direction almost along the *a* axis. Two instances of the cyclic dimer hydrogen bonding are apparent. Displacement ellipsoids are drawn at 50% probability for all atoms except H for which they have been set artificially small.

Experimental

Fluorene-1-carboxylic acid (Aldrich Chemical Company) was dissolved in chloroform and the solution was filtered. The filtrate was evaporated slowly at room temperature to yield colorless columns. A cut column was mounted with epoxy cement on a glass fiber and was analyzed with graphite-monochromated radiation.

Crystal data

$C_{14}H_{10}O_2$
$M_r = 210.23$
Monoclinic
$P2_1/c$
$a = 5.564\ (2)$ Å
$b = 5.327\ (2)$ Å
$c = 34.038\ (2)$ Å
$\beta = 92.81\ (2)°$
$V = 1007.8\ (6)$ Å^3
$Z = 4$
$D_x = 1.385$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15.4$–$17.4°$
$\mu = 0.086$ mm^{-1}
$T = 296$ K
Cut column
0.34 × 0.27 × 0.27 mm
Colorless

Data collection

AFC-5*S* diffractometer
ω scans
Absorption correction: none
2806 measured reflections
2553 independent reflections
1168 observed reflections [$I > 3\sigma(I)$]
$R_{\rm int} = 0.033$

$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 7$
$k = 0 \rightarrow 6$
$l = -44 \rightarrow 44$
6 standard reflections monitored every 150 reflections intensity variation: ±3.4%

Refinement

Refinement on F
$R = 0.054$
$wR = 0.066$
$S = 2.06$
1168 reflections
158 parameters
H-atom treatment: see below
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = <0.01$
$\Delta\rho_{\max} = 0.26$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}

Extinction correction: Zachariasen (1963, 1968)
Extinction coefficient: $1.0\ (4) \times 10^{-6}$
Atomic scattering factors from Stewart, Davidson & Simpson (1965) (H), Cromer & Waber (1974) (C, O)

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	$U_{\rm eq}$
O(1)	0.7083 (5)	0.2582 (5)	0.00564 (7)	0.0600 (9)
O(2)	0.4088 (5)	0.3720 (5)	0.04288 (7)	0.0570 (8)
C(1)	0.6628 (6)	0.0359 (6)	0.06474 (9)	0.0391 (10)
C(2)	0.8499 (7)	−0.1235 (7)	0.05526 (9)	0.045 (1)
C(3)	0.9300 (7)	−0.3106 (8)	0.08096 (10)	0.053 (1)
C(4)	0.8255 (7)	−0.3435 (7)	0.11657 (10)	0.048 (1)
C(5)	0.5036 (7)	−0.3389 (7)	0.19409 (10)	0.049 (1)
C(6)	0.3391 (7)	−0.3001 (8)	0.22239 (10)	0.053 (1)
C(7)	0.1688 (7)	−0.1134 (9)	0.21826 (10)	0.056 (1)
C(8)	0.1602 (7)	0.0452 (8)	0.18582 (10)	0.050 (1)
C(9)	0.3516 (7)	0.1440 (7)	0.11844 (10)	0.041 (1)
C(10)	0.5557 (6)	0.0037 (6)	0.10042 (9)	0.0372 (9)
C(11)	0.6390 (6)	−0.1872 (6)	0.12611 (9)	0.0371 (9)
C(12)	0.4947 (6)	−0.1836 (7)	0.16118 (9)	0.0380 (9)
C(13)	0.3241 (6)	0.0074 (7)	0.15705 (9)	0.0398 (10)
C(14)	0.5850 (7)	0.2348 (7)	0.03680 (9)	0.043 (1)
H(1)	0.656 (8)	0.406 (11)	−0.012 (1)	0.12 (2)
H(9)	0.388 (6)	0.329 (7)	0.125 (1)	0.05 (1)
H(10)	0.203 (6)	0.144 (7)	0.102 (1)	0.05 (1)

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

C(1)—C(2)	1.394 (5)	C(9)—C(13)	1.517 (5)
C(1)—C(10)	1.389 (4)	C(10)—C(11)	1.405 (5)
C(2)—C(3)	1.385 (5)	C(11)—C(12)	1.471 (4)
C(3)—C(4)	1.381 (5)	C(12)—C(13)	1.394 (4)
C(4)—C(11)	1.382 (5)	C(9)—H(9)	1.03 (4)
C(5)—C(6)	1.377 (5)	C(9)—H(10)	0.97 (3)
C(5)—C(12)	1.392 (4)	C(1)—C(14)	1.474 (5)
C(6)—C(7)	1.376 (5)	C(14)—O(1)	1.297 (4)
C(7)—C(8)	1.389 (5)	C(14)—O(2)	1.248 (4)
C(8)—C(13)	1.385 (4)	O(1)—O(2)	2.227 (4)
C(9)—C(10)	1.515 (5)	O(1)—H(1)	1.03 (5)
C(2)—C(1)—C(10)	118.9 (3)	C(5)—C(12)—C(13)	120.8 (3)
C(1)—C(2)—C(3)	120.9 (3)	C(11)—C(12)—C(13)	108.9 (3)
C(2)—C(3)—C(4)	120.6 (3)	C(8)—C(13)—C(9)	129.8 (3)
C(3)—C(4)—C(11)	118.9 (3)	C(8)—C(13)—C(12)	120.2 (3)
C(6)—C(5)—C(12)	118.4 (3)	C(9)—C(13)—C(12)	109.9 (3)
C(5)—C(6)—C(7)	121.0 (3)	C(10)—C(9)—H(9)	114 (1)
C(6)—C(7)—C(8)	121.1 (3)	C(10)—C(9)—H(10)	114 (1)
C(7)—C(8)—C(13)	118.4 (4)	C(13)—C(9)—H(9)	107 (1)
C(10)—C(9)—C(13)	102.9 (3)	C(13)—C(9)—H(10)	111 (1)
C(1)—C(10)—C(9)	130.9 (3)	H(9)—C(9)—H(10)	105 (2)
C(1)—C(10)—C(11)	119.4 (3)	C(2)—C(1)—C(14)	119.2 (3)
C(9)—C(10)—C(11)	109.6 (3)	C(10)—C(1)—C(14)	121.9 (3)
C(4)—C(11)—C(10)	121.2 (3)	C(1)—C(14)—O(1)	116.5 (3)
C(4)—C(11)—C(12)	130.1 (3)	C(1)—C(14)—O(2)	121.4 (3)
C(10)—C(11)—C(12)	108.6 (3)	O(1)—C(14)—O(2)	122.0 (3)
C(5)—C(12)—C(11)	130.3 (3)	C(14)—O(1)—H(1)	114 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···A	H···A	D···A	D—H···A
O(1)—H(1)···O(2$^{\rm i}$)	1.60 (6)	2.632 (4)	176 (4)

Symmetry code: (i) $1 - x, 1 - y, -z$.

Scan widths were $(1.35 + 0.35\tan\theta)°$ in ω, with a background/scan time ratio of 0.5. No correction was required for decay or absorption but the data were corrected for Lorentz and polarization effects. The Laue symmetry, the observed reflection-limiting conditions and the intensity statistics indicated the space group to be $P2_1/c$; refinement proceeded well, and it was adopted. The direct methods program *SHELXS*86 (Sheldrick, 1985) was used to obtain the initial positions of the C and O atoms. Fourier difference methods were used to locate initial H-atom positions. Full-matrix least-squares refinement was performed in *TEXSAN* (Molecular Structure Corporation, 1989). In later stages of the refinement, aromatic ring H atoms were assigned fixed geometry (C—H = 0.98 Å) and isotropic displacement parameters of magnitude 1.2 times those of the attached C atoms. The carboxyl H atom and the two H atoms bonded to C(9) were refined isotropically. Also in later stages, a secondary-extinction parameter was included in the least-squares refinement; the maximum effect of extinction was 5.4% of F_o for (114). The greatest positive residual electron density, 0.26 e Å^{-3}, occurred approximately 1 Å from C(1) and C(2), while the greatest negative density, −0.19 e Å^{-3}, occurred approximately 1.4 Å from C(10) and C(11).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN*. Program(s) used to solve structure: *SHELXS*86. Program(s) used to refine structure: *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, least-squares-planes data, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1185). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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An Unusual C(sp^2)—H···Cl Interaction in the Solid State: Reinvestigation of 4,6-Dimethylpyrimidine-2-thione Hydrochloride Monohydrate

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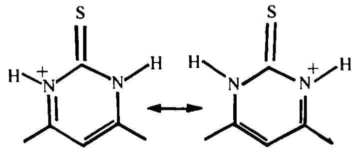
Abstract

The crystals of $C_6H_9N_2S^+.Cl^-.H_2O$ are composed of 4,6-dimethyl-2-thioxopyrimidinium cations, Cl^- anions and water molecules of crystallization. The Cl^- ion and the water O(1*W*) atom are strongly bonded to the cation by N—H···Cl and N—H···O hydrogen bonds, forming a hydrated molecule. The cation is almost coplanar with the Cl^- anion while the water O(1*W*) atom deviates significantly from the plane of the cation. The molecules form stacks along the *z* axis with an interplanar distance of 3.62 Å. A three-dimensional network of hydrogen bonds links molecules in consecutive planes with H_2O molecules and Cl^- ions in the lattice cavities and thus stabilizes the molecular packing. The lattice exhibits an unusual C(sp^2)—H···Cl interaction, bridging consecutive molecular chains.

Comment

A single-crystal X-ray diffraction study of the title compound was undertaken for a critical re-examination (Battaglia, Corradi, Battistuzzi & Manfredini, 1986) of its crystal structure and also to compare it with the adduct of the same molecule and thiourea (Seth & Sur, 1995). This is important due to its antibacterial, antiviral and antimicrobial properties (Coutts & Casy, 1975; Rosenfield, Berneds, Gelmini, Stephan & Mascharak, 1987). Pyrimidinethiones are also important sulfur-containing components of minor nucleobases; 2- and 4-thiouracil and 2-thiocytosine are normal constituents of some tRNA species. As essential components, they can inhibit RNA synthesis under certain conditions, leading to antitumour and antithyroid activity (Abbot, Goodgame & Jeeves, 1978).

The present study reveals that the crystals of $C_6H_8N_2S.HCl.H_2O$ are composed of 4,6-dimethylpyrimidine-2-thione (dtm) cations, Cl^- anions and water molecules of crystallization. The dtm moieties are almost coplanar with the Cl^- anions [deviation 0.007 (1) Å] while the water O(1*W*) atoms deviate considerably from these planes [−0.324 (3) Å]. The adduct is characterized by a monoprotonated pyrimidine nucleus, whereas in the present case it is protonated at both N(1) and N(2) rather than at the S(1) atom, providing the maximum opportunity for delocalization of the resulting positive charge over almost the entire dtm ion. Thus, the pyrimidine ring of the title compound has appreciable and identical contributions from equivalent canonical structures (I) and (II).



(I) (II)

This isovalent resonance, along with the stability gained due to strong hydrogen bonding with the O atom and Cl^- anion on both sides, serve as the potential factors in directing the dtm moiety towards simultaneous thionation and protonation. In the dtm cation, the positive charges on both ring N atoms may also be