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Crystal Structure of (Fluorosulfonyl)fluoroacetic Acid: A Novel Four-Center Hydrogen-Bond System Involving a C−H Donor

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The crystal structure of $FSO_2CFHCOOH$ has been determined by a single-crystal X-ray study. The crystals are monoclinic, of space group $P2_1/c$, and have the following cell parameters: $a = 5.0164(6)$ Å, $b = 9.658(2)$ Å, $c = 11.061(2)$ Å, $\beta = 90.54(1)°$, $Z = 4$. The carboxyl groups of the molecules form the usual hydrogen-bonded, centrosymmetric dimers, but each molecule also interacts with three other neighboring molecules by hydrogen bonds from the methine hydrogen to two sulfonyl oxygens and to a carbonyl oxygen, making a four-center system. The extensive network of hydrogen bonding in this material appears to be responsible for its existence as a solid. This material has also been characterized by ^1H, ^{13}C, and ^{19}F NMR, IR, and mass spectroscopy.

Introduction

Since the title compound, **1**, has a higher melting point (50−51 °C) than that of the related compounds FSO_2CH_2COOH (37 °C)[1] and FSO_2CF_2COOH (liquid, bp 153 °C)[2] and since relatively few crystal structures of compounds containing the $-SO_2F$ group attached to carbon are known,[3−12] we decided to investigate the crystalline nature of **1**. Although it was first prepared in 1961,[13] only its melting point was reported, and we therefore undertook further characterization of this compound.

Experimental Section

X-ray Work. A crystal of dimensions 0.09 × 0.22 × 0.25 mm was placed in a special glass capillary in a drybox under a nitrogen atmosphere. The tube was then sealed. The orientation parameters and cell dimensions were obtained from the setting angles of an Enraf-Nonius CAD-4 diffractometer for 25 centered reflections in the range $15° < \theta < 17°$. The data were corrected for crystal decay during data collection (2.9% on I over 16 h). The systematic absences indicated the space group $P2_1/c$. A MITHRIL[14] E map showed all the non-hydrogen atoms. The hydrogen atoms were located in a difference map after anisotropic refinement of the other atoms and refined isotropically. The final difference synthesis was featureless. The TEXSAN program suite,[15] incorporating complex atomic scattering factors,[16] was used in all calculations.

Instrumentation. IR spectra were taken on a Nicolet 20DX spectrophotometer, fluorine NMR spectra were taken on a Varian EM390 operating at 84.67 MHz, and proton and carbon-13 NMR spectra were taken on a Bruker AMX-400 operating at 400.1 MHz for ^1H and at 100.6 MHz for ^{13}C. The mass spectrum was obtained on a VG 7070 HS spectrometer with an ionization potential of 70 eV. Elemental analysis was carried out by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

Synthesis. **1** was prepared by hydrolysis of trifluoroethylene sultone ($\overline{CFHCF_2O}SO_2$)[17] according to the literature[13] and purified by vacuum distillation. The distillate bubbled briefly in the receiving vessel, suggesting some decarboxylation. The liquid crystallized upon standing overnight in the stoppered receiving flask. The hygroscopic crystals were washed with $CFCl_3$. The ^1H and ^{19}F NMR spectra of the washings were consistent with the presence of the decarboxylation product, FSO_2CFH_2. A sample of **1** melted at 50−51 °C (uncorrected) in a sealed capillary.

IR (liquid film on AgCl plates): 3627 (m, OH, unassoc), 3600−2500 (m, br, OH, assoc), 2973 (ms, CH), 1771 (vs, C═O), 1623 (w), 1441 (vs, SO_2 asym), 1306 (w), 1258 (ms), 1230 (s, SO_2 sym), 1190 (ms), 1131 (s, CF), 920 (w), 871 (m), 843 (ms), 815 (ms), 766 (m), 716 (w), 604 (m), 578 (m), 469 (w), 449 cm^{-1} (m).

^1H NMR (in CD_3CN; shifts in ppm relative to internal $(CH_3)_4Si$): 8.93 (br, OH), 6.37 (dd, CH), $J(H-SO_2F) = 3.7$ Hz, $J(H-CF) = 45.1$ Hz.

^{19}F NMR (in $CDCl_3$; shifts in ppm relative to internal $CFCl_3$): 50 (dd, SO_2F), −184 (dd, CF), $J(F-F) = 7.8$ Hz.

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Table 1. Crystallographic Data for **1**

empirical formula	$C_2H_2F_2O_4S$	Z	4
fw	160.09	ρ_{calc}	1.984 g/cm^3
space group	$P2_1/c$	T	21 °C
a	5.0164(6) Å	λ	0.710 73 Å
b	9.658(2) Å	μ	5.65 cm^{-1}
c	11.061(2) Å	$R(F_o)^a$	0.046
β	90.54(1)°	$R_w(F_o)^b$	0.052
V	535.9(3) Å^3		

[a] $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w(F_o) = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 2. Fractional Atomic Coordinates and B_{eq} Values for **1**

atom	x	y	z	B_{eq},^{a} Å^2
S	0.8397(2)	0.6211(1)	0.1416(1)	3.85(5)
F1	0.5712(7)	0.5686(4)	0.1045(3)	9.4(2)
F2	0.5768(6)	0.8075(3)	0.2472(2)	6.0(2)
O1	0.9977(10)	0.5069(4)	0.1651(3)	8.1(2)
O2	0.9133(8)	0.7206(4)	0.0571(3)	7.0(2)
O3	0.7875(7)	0.5170(4)	0.4084(3)	4.4(2)
O4	0.3993(6)	0.6317(3)	0.4052(3)	4.7(2)
C1	0.7506(9)	0.7068(4)	0.2788(3)	3.4(2)
C2	0.6280(8)	0.6113(4)	0.3725(3)	3.3(2)
H1^b	0.916(7)	0.743(4)	0.304(3)	2.5(8)
H2^b	0.745(11)	0.473(7)	0.465(6)	10(2)

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

Table 3. Bond Lengths (Å) and Angles (deg) for **1**

S−F1	1.493(3)	O3−C2	1.274(5)
S−O1	1.381(4)	O3−H2	0.78(7)
S−O2	1.393(3)	O4−C2	1.222(5)
S−C1	1.789(4)	C1−C2	1.522(6)
F2−C1	1.350(5)	C1−H1	0.94(3)
F1−S−O1	107.2(3)	S−C1−C2	113.8(3)
F1−S−O2	107.1(2)	S−C1−H1	101(2)
F1−S−C1	99.1(2)	F2−C1−C2	110.4(4)
O1−S−O2	121.5(2)	F2−C1−H1	112(2)
O1−S−C1	110.9(2)	C2−C1−H1	113(2)
O2−S−C1	108.6(2)	O3−C2−O4	127.7(4)
C2−O3−H2	117(4)	O3−C2−C1	112.9(4)
S−C1−F2	106.2(3)	O4−C2−C1	119.4(4)

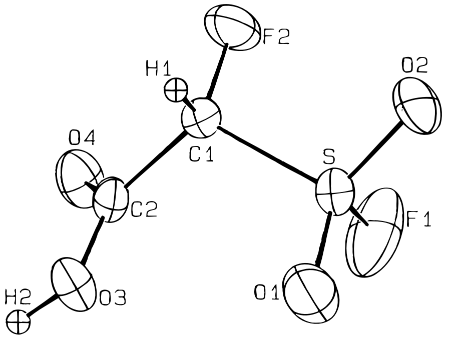

Figure 1. ORTEP view of **1** at 30% probability.

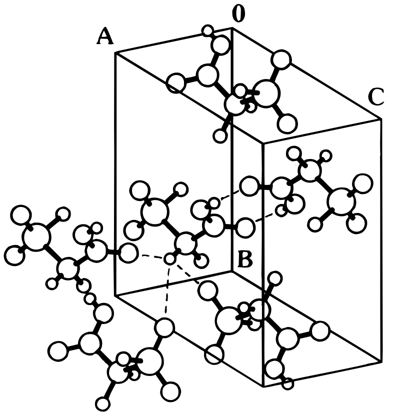

Figure 2. Unit cell for **1** showing hydrogen bonds (dashed lines).

^{13}C NMR (in CD_3CN; shifts in ppm relative to internal $(CH_3)_4Si$): 95.2 (CFH), $J(C-SO_2F) = 23.42$ Hz, $J(C-F) = 232.75$ Hz, $J(C-H) = 175.03$ Hz; 160.4 (COOH), $J(C-SO_2F) < 1$ Hz, $J(C-CF) = 23.2$ Hz, $J(C-CH) < 1$ Hz.

Mass spectrum (EI$^+$; 70 eV): m/z 161 $(MH)^+$, 160 $(M)^+$, 143 $(M - OH)^+$, 116 $(M - CO_2)^+$, 96 $(M - SO_2)^+$, 85 $(H_2SO_2F)^+$, 77 $(M - SO_2F)^+$, 68 $(HSOF)^+$, 67 $(SOF)^+$, 65 $(SO_2H)^+$, 64 $(SO_2)^+$, 60 $(C_2FOH)^+$, 51 $(SF,CF_2H)^+$, 49 $(CH_2FO)^+$, 48 $(CFOH)^+$, 46 $(CO_2H_2)^+$, 45 $(CO_2H)^+$, 44 $(CO_2)^+$.

Anal. Calcd for $C_2H_2O_4F_2S$: C, 15.01; H, 1.26; S, 20.03; F, 23.7. Found: C, 15.00; H, 1.31; S, 20.15; F, 23.3.

Results

Crystallographic and structural data for **1** are presented in Tables 1−3. The molecular geometry is shown in Figure 1, and the unit cell is shown in Figure 2. The *R* and *S* enantiomers form hydrogen-bonded centrosymmetric dimers in the manner characteristic of carboxylic acids. The O3···O4 intermolecular distance is 2.688(5) Å, comparable to that found in other fluorinated acetic acids in the solid phase.[18−20] The substituents on sulfur are staggered with respect to those on C1: the F1−S−C1−C2 dihedral angle is 60.1(4)°. The bond lengths and angles in the $C-SO_2F$ system are comparable to those in other compounds,[3−12] except that the S═O bond lengths are among the shortest reported so far (1.381 and 1.393 Å compared to 1.389−1.446 Å, average 1.412 Å), and the F1−S−C1 bond angle is less than that in the other compounds (99.1° compared to 99.9−111.0°, average 103.6°). The latter is due to a conformation induced by hydrogen bonding to the sulfonyl oxygens, as described below.

The hydrogen-bonded dimers are rather closely spaced in the lattice, as indicated by an intermolecular F1···F1 contact distance of 2.753(6) Å. This is much shorter than the closest intermolecular F···F contact in trifluoroacetic acid (3.02 Å)[20] and is at the van der Waals limit for intermolecular fluorine contact (2.60−2.78 Å).[21] That these fluorine atoms are in fact undergoing a repulsive interaction is indicated by the small F1−S−C1 bond angle of 99.1°. Both sulfonyl oxygen atoms are involved in hydrogen bonds from H1 on two neighboring molecules. This forces the SO_2F groups into a conformation that brings neighboring sulfonyl fluorine atoms into repulsive contact. There is an additional hydrogen bond between H1 and the carbonyl oxygen atom on a third neighboring molecule, forming a four-center system as shown in Figure 2. The latter interaction draws the carbonyl oxygen 0.020(3) Å out of the least-squares plane formed by the six heavy atoms of the hydrogen-bonded carboxyl groups. This is a significantly larger deviation than that of the carbonyl oxygen in fluoroacetic acid (0.004(5) Å),[18] bromofluoroacetic acid (0.0001(10) Å),[19] or trifluoroacetic acid (0.009(4) Å)[20] and is evidence of its interaction with H1. This type of system, in which a C−H hydrogen interacts with a carbonyl oxygen, is also found in acetic acid (H···O distance 2.409 Å)[22] and in fluoroacetic acid (H···O distance 2.29 Å).[18] Thus all oxygens and hydrogens in **1** are involved in intermolecular hydrogen bonds, as described in Table 4.

The significant IR bands and the ^1H and ^{19}F NMR chemical shifts for **1** are similar to those reported for its esters.[17,23] The

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Table 4. Hydrogen Bond Distances and Angles in **1**

D−H···A^{a}	D−H, Å	H···A, Å	D···A, Å	D−H···A, deg
C1−H1···O1^{a}	0.94(3)	2.61(4)	3.220(6)	123
C1−H1···O2^{b}	0.94(3)	2.83(3)	3.254(5)	109
C1−H1···O4^{c}	0.94(3)	2.87(3)	3.603(5)	136
O3−H2···O4^{d}	0.78(7)	1.91(7)	2.688(5)	175

[a] Symmetry operations: (a) $2 - x$, $^{1}/_{2} + y$, $^{1}/_{2} - z$; (b) x, $1^{1}/_{2} - y$, $^{1}/_{2} + z$; (c) $1 + x$, y, z; (d) $1 - x$, $1 - y$, $1 - z$.

methine hydrogen is very deshielded, as indicated by its chemical shift of 6.37 ppm, while the geminal fluorine nucleus is shielded, appearing at −184 ppm in the ^{19}F NMR spectrum. The ^{1}H chemical shift is comparable to that in methanes with three electron-withdrawing substituents: CHF_2COOH ($\delta = 5.99$ ppm),[24] CHF_2SO_2F ($\delta = 6.35$ ppm),[25] and $CH(SO_2F)_3$ ($\delta = 6.85$ ppm).[26]

Both the molecular ion and the $(MH)^+$ peaks were observed in the mass spectrum. The base peak was at $m/z = 44$, and the peak at $m/z = 116$ was very nearly equal in intensity. This is consistent with facile decarboxylation, which was also observed during distillation of **1**. The instability of various acetic acids disubstituted with strongly electron-withdrawing groups has been reported previously.[27−29]

Discussion

That hydrogen atoms bonded to carbon (in any hybridization) may participate in hydrogen bonding is now well established.[30−35] The hydrogens need not be acidic: methyl groups are known to act as donors, as in crystalline acetic acid.[22] Recent work has shown that hydrogen bonds, and particularly C−H···O interactions, have a longer range than previously thought, because the major component of the interaction is an electrostatic one.[31,36] Thus the use of a van der Waals contact distance as a criterion for recognizing a hydrogen bond is too limiting.[32,33] A (C−)H···O hydrogen bond length of 2.97 Å has been reported for 1,3-dimethyluracil,[33,37] and several (C−)H···O bond lengths in the range 2.63−3.26 Å have been proposed for three *N*,*N′*-diacylindigo species.[38] Long-range hydrogen bonds from C−H donors in fluorine-containing compounds have also been reported.[5,39] C−H···O bond angles are known to vary from approximately 90 to 180°.[31] Thus the data in Table 4 are well within the known ranges for C−H···O hydrogen bond lengths and angles.

Three-center hydrogen bonds (one hydrogen interacting with two acceptors) from C−H donors in crystals have been previously reported.[33,40,41] Four-center systems for any kind of donor are uncommon, but examples involving O−H and N−H donors are known.[33,42−46] To the best of our knowledge, **1** contains the first example of a four-center hydrogen-bond system involving a C−H donor in the solid phase.[47] In such multicenter systems, lengthening of neither the C−H bond[33] nor the covalent bond to the donor atom is necessarily observed, due to the weakness of the interaction. For example, there is a three-center system involving a C−H donor in 5-nitro-1-(β-D-ribosyluronic acid)uracil hydrate in which the bond length of the carbonyl acceptor group is a short 1.216 Å,[48] while in 1,5,*N*(*4*),*N*(*4*)-tetramethylcytosine, in which there is no hydrogen bonding, the carbonyl bond length is 1.240 Å.[49] Thus the fact that the S═O bond lengths in **1** are especially short does not argue against hydrogen bonding.

The methine hydrogen of **1** bears a substantial positive charge, as is indicated by its downfield NMR chemical shift. It is likely to be very acidic, since the methyl ester of **1** is known to form a salt with triethylamine.[23] A given molecule of **1** is hydrogen-bonded to four neighbors, and even if the strength of such long-range interactions is weak, cooperativity effects must not be ignored.[33] Such effects have been shown to play a role in the solid-phase structure of acetic acid,[50] which, unlike fluoroacetic acid and trifluoroacetic acid, does not form dimers in the solid phase but forms infinite chains in which the monomers are linked by O-H···O and C−H···O hydrogen bonds.[22] So although C−H···O interactions are believed to be weaker than O-H···O and N−H···O interactions, they can still be structure-determining.[38,51] We believe that the extensive hydrogen bonding of H1 in **1** is primarily responsible for the fact that it exists as a solid. The same phenomenon occurs in the only known solid-phase β-fluorosultone,[39] and presumably in FSO_2CH_2COOH, but to a lesser extent than in **1** due to the lack of the fluorine atom on the β-carbon. Note that FSO_2CF_2COOH should also form the usual hydrogen bonds with its carboxyl groups, but since additional hydrogen bonding from the β-carbon is impossible, this compound is a liquid at room temperature.

Supporting Information Available: A textual description of the structural analysis and tables of crystallographic data, details of the structure determination, atomic coordinates with *B* values, bond lengths and angles, dihedral and torsion angles, least-squares planes data, anisotropic thermal parameters, and intermolecular distances (11 pages). Ordering information is given on any current masthead page.

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