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3-Pentafluorothiopropionic acid

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Key indicators

Single-crystal X-ray study
T = 290 K
Mean σ(C–C) = 0.008 Å
R factor = 0.056
wR factor = 0.138
Data-to-parameter ratio = 10.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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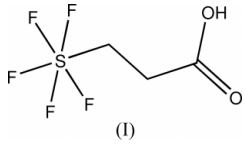
The crystal structure of 3-pentafluorothiopropionic acid, $C_3H_5F_5O_2S$, is reported. In the solid, the acid forms a dimeric unit, in which two molecules are held together by strong hydrogen bonds. The two molecules are arranged across an inversion center. The average literature structural parameters for the organic/organometallic pentafluorothio group are reported, and a short discussion of the geometry of this molecule in this context is given.

Comment

As part of our ongoing interest in the chemistry and structure of organic SF_5 and SO_2F groups and of the applications of compounds containing these groups (Schlueter *et al.*, 2001, and references therein), we have recently devised a method for the preparation of alkyl derivatives of SF_5, including the title compound, pentafluorothiopropionic acid, $SF_5(CH_2)_2CO_2H$, (I) (Winter & Gard, 2000). At the time the synthesis and spectroscopic characterization of the compound were published, the structure of this acid was not available. Since then we have been able to obtain crystals of sufficient quality for a structural characterization to be possible, and therefore we present it here.



(I)

The compound crystallizes as a hydrogen-bonded dimer, as is common for many carboxylic acids. The hydrogen-bonded oxygen···oxygen distance, 2.706 (5) Å, is well within the usual range for strong hydrogen bonds (Jeffrey, 1997). The SF_5C group is essentially octahedral, with four nearly identical S—F_{eq} bonds, a longer S—F_{ax} bond and a long S—C one. The equatorial fluorine atoms are slightly displaced away from the C atom, as shown by the fact that the F_{ax}—S—F_{eq} bond angles are all somewhat less than 90°. Finally, there are two short intramolecular contacts, F1···H2*A*, with a separation of 2.48 Å and an F1···H2*A*—C2 angle of 90°, and O1···H3*B*, with a separation of 2.53 Å and an O1···H3*B*—C3 angle of 100°. Although the *X*···H distances are very close to the sum of their respective van der Waals radii, the pronounced deviation of the *X*···H—C angle from linearity would suggest that, rather than being viewed as traditional hydrogen bonds, these should be thought of as forced contacts required by the geometry of the molecule in the crystal structure (Jeffrey, 1997).

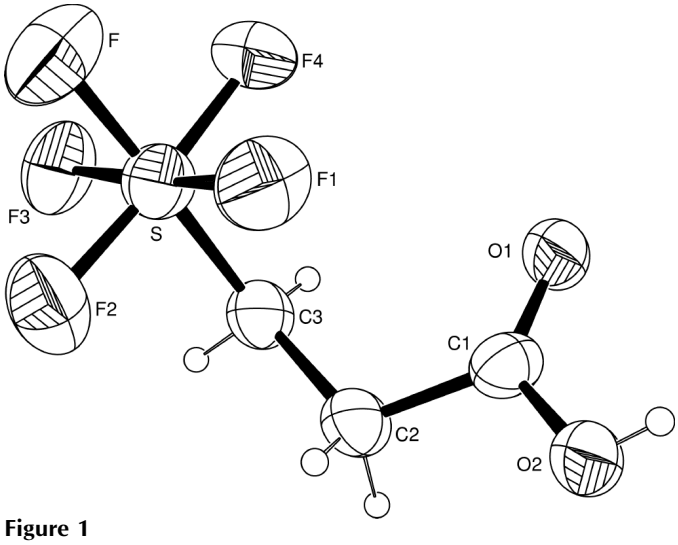


Figure 1
*ORTEP*3 (Farrugia, 1997) view of (I), showing the atom-numbering scheme (30% probability displacement ellipsoids).

Since a number of compounds containing the SF_5C- group have been structurally characterized, either by solid state X-ray diffraction, or by gas phase electron diffraction, it would therefore be useful to discuss the present molecule in the context of these results. However, the systematic analysis of the structure of this group has not yet been reported, and therefore we include here a brief literature survey of pertinent structural features.

A search of the Cambridge Structural Database reveals that the structures of 20 other organic or organometallic compounds containing the SF_5 group have been determined (Allen & Kennard, 1993; Refcodes: DIVPAZ, JANYAY, JEBNEZ, JEBNIM, JESJUM, KUYPEZ, KUYYUY, LANWEC, LAYHEY, LECRUG, LECSAN, LECSER, NALWIG, QAFGOT, YAMGIC, YAMGOI, ZEZNIB, ZEZNOH, ZEZNUN, ZOVZAL). Additionally, three molecules are known, whose structure was determined by gas phase electron diffraction (Gupta *et al.*, 1986; Weiss *et al.*, 1990; Gard *et al.*, 1998). From the set of X-ray structural determinations we know of, we obtain the following structural parameters. The SF_5C group tends towards a regular octahedron with five identical S—F bonds and a long S—C bond, with the following average bond lengths (population standard deviations given in parentheses): S—F_{ax} 1.574 (14) Å, S—F_{eq} 1.571 (14) Å, S—C 1.823 (28) Å, F_{ax}—S—C 177.1 (8)°, and F_{ax}—S—F_{eq} 88.1 (10)°.

The structures determined by gas phase electron diffraction are in agreement with this set of parameters. Thus, from the gas phase determinations, the S—F_{ax} and S—F_{eq} bonds have essentially identical lengths, at 1.560 Å, the F_{ax}—S—F_{eq} angle is 90°, and the F_{ax}—S—C angle does not deviate significantly from 180°.

Therefore, the structure reported here is in excellent agreement with the average parameters listed above. The S—C bond, with a length of 1.791 (6) Å, and the F_{ax}—S—F_{eq} angles, averaging 88.3 (12)°, are also well within the expected ranges.

Experimental

The compound was synthesized as described elsewhere (Winter & Gard, 2000) and crystals suitable for single-crystal X-ray diffraction were obtained by sublimation. Owing to the fact that, in the first experiments the crystal either sublimed off the glass fibre on which it was mounted, or absorbs water from the atmosphere, for the final experiment the sample was completely encapsulated in a thin layer of epoxy glue. This strategy was sufficient to allow data collection over a period of a few days.

Crystal data

$C_3H_5F_5O_2S$
M_r = 200.13
Monoclinic, $P2_1/n$
a = 5.737 (2) Å
b = 12.438 (2) Å
c = 9.777 (2) Å
β = 102.59 (2)°
V = 680.9 (3) Å^3
Z = 4
D_x = 1.952 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 56 reflections
θ = 7.9–23.4°
μ = 4.90 mm^{-1}
T = 290 (2) K
Block, colorless
0.40 × 0.20 × 0.10 mm

Data collection

Siemens $P4$ diffractometer
$\omega/2\theta$ scans
Absorption correction: multi-scan [*SORTAV* (Blessing, 1995) in *WinGX* (Farrugia, 1997)]
T_{min} = 0.245, T_{max} = 0.640
1737 measured reflections
1151 independent reflections
615 reflections with $I > 2\sigma(I)$
R_{int} = 0.066
θ_{max} = 67.3°
$h = -6 \rightarrow 1$
$k = -3 \rightarrow 14$
$l = -11 \rightarrow 11$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.138
S = 1.04
1151 reflections
106 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 0.377P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.047
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.0003 (9)

Table 1
Selected geometric parameters (Å, °).

S1—F2	1.569 (4)	S1—F4	1.584 (4)
S1—F3	1.575 (3)	S1—F1	1.582 (3)
S1—F5	1.581 (4)	S1—C3	1.791 (6)
F2—S1—F3	89.6 (2)	F5—S1—F1	87.51 (19)
F2—S1—F5	87.4 (3)	F4—S1—F1	89.3 (2)
F3—S1—F5	86.7 (2)	F2—S1—C3	91.6 (2)
F2—S1—F4	175.1 (2)	F3—S1—C3	91.4 (2)
F3—S1—F4	90.2 (2)	F5—S1—C3	177.8 (2)
F5—S1—F4	87.7 (2)	F4—S1—C3	93.3 (2)
F2—S1—F1	90.5 (2)	F1—S1—C3	94.4 (2)
F3—S1—F1	174.2 (2)		

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H···O1^{i}	0.810 (10)	1.921 (14)	2.706 (5)	163 (3)

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

All data were employed in the refinement with the exception of the ($\bar{3}$,10,3) reflection, which had strongly negative intensity. During the course of the refinement it became apparent that the displacement ellipsoids of the equatorial fluorine atoms were rather large. Attempts to model these atoms as part of a disordered group were fruitless, and we propose the elongated ellipsoids should only be attributed to thermal motion. The H atoms in the molecule were included using a riding model, except for the acid hydrogen which was located in a difference Fourier map, and refined with a distance restraint of 0.82 (2) Å. The refined isotropic displacement parameter (U) for the acid H atom is 0.013 (8) Å^2.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1999); software used to prepare material for publication: *SHELXL*97.

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