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Structures of Two Strong Brønsted Acids: (I) Fluorosulfuric Acid and (II) Trifluoromethanesulfonic Acid†

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Abstract. (I) Fluorosulfuric acid, $FSO_2(OH)$, $M_r = 100{\cdot}07$, orthorhombic, $P2_12_12_1$, $a = 4{\cdot}868$ (4), $b = 6{\cdot}736$ (5), $c = 9{\cdot}359$ (7) Å, $V = 306{\cdot}9$ Å^3, $Z = 4$, $D_x = 2{\cdot}17$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}85$ mm^{-1}, $F(000) = 200$, $T = 123$ K, $R = 0{\cdot}025$ for 925 unique observed reflections. Slightly distorted tetrahedral molecules are linked by hydrogen bonds O—H···O [O···O: 2·643 (1) Å] to form infinite chains along the *c*-axis direction. (II) Trifluoromethanesulfonic acid, $CF_3SO_2(OH)$, $M_r = 150{\cdot}07$, monoclinic, $P2_1/n$, $a = 4{\cdot}947$ (3), $b = 11{\cdot}260$ (6), $c = 8{\cdot}457$ (6) Å, $\beta = 99{\cdot}21$ (5)°, $V = 465{\cdot}0$ Å^3, $Z = 4$, $D_x = 2{\cdot}14$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}66$ mm^{-1}, $F(000) = 296$, $T = 173$ K, $R = 0{\cdot}058$ for 1157 unique observed reflections. Molecules with a nearly staggered conformation around the C—S bond and a slightly distorted tetrahedral coordination of the S atom are linked by hydrogen bonds O—H···O [O···O: 2·640 (4) Å] to form infinite chains along [101].

Experimental. A single crystal of (I) was obtained from a solution of (I) in anhydrous HF by a miniature zone-melting technique. Crystal growth of (II) was achieved by slow cooling of a solution of (II) in anhydrous HF (solutions sealed in capillaries of Teflon PFA, diameter 0·3 mm). Syntex $P2_1$ diffractometer with modified LT device and graphite monochromator. Lattice constants from setting angles of 15 strong reflections with $31 < 2\theta < 33°$ for (I) and $17 < 2\theta < 32°$ for (II). Intensities by variable ω-scan method. Three standard reflections (measured after every fifty reflections) with only small random variations. No absorption correction applied. Criterion for unobserved reflections $I < 1{\cdot}96\sigma(I)$. (I) 949 unique reflections measured with $\sin\theta/\lambda$ up to $0{\cdot}857$ Å^{-1} and $0 \le h \le 8$, $0 \le k \le 11$, $0 \le l \le 16$; twelve reflections with too high intensities remeasured with lower tube power and put on a common scale. (II) 1332 unique reflections measured with $\sin\theta/\lambda$ up to $0{\cdot}704$ Å^{-1} and $0 \le h \le 6$, $0 \le k \le 15$, $-11 \le l \le 11$; five reflections with too high intensities not remeasured; fourteen reflections discarded at an advanced state of refinement because of adverse measuring conditions.

Direct methods applied to solve phase problem, full-matrix least-squares refinement based on F magnitudes with observed reflections, weight according to $w = [\sigma^2(F) + gF_o^2]^{-1}$. Isotropic correction of extinction by refining the parameter x in $F_c^* = F_c/[1 + 0{\cdot}002x(F_c^2)/\sin 2\theta]^{1/4}$. H atoms located by difference-Fourier method. Complex atomic scattering factors from *International Tables for X-ray Crystallography* (1974). (I) In final refinement 51 parameters varied: one scale factor, one extinction parameter, coordinates of all atoms, anisotropic and isotropic thermal parameters for non-H atoms and H atom, respectively; $g = 0{\cdot}0004$, $x = 0{\cdot}005$ (1), $wR = 0{\cdot}034$, $S = 1{\cdot}471$; $(\Delta/\sigma)_{\max}$ in last cycle 0·003; $\Delta\rho_{\min}$ and $\Delta\rho_{\max}$ in final difference map $-0{\cdot}80$ and $+0{\cdot}46$ e Å^{-3}, respectively. Refinement of the inverted molecule resulted in slightly higher values for R (0·026), wR (0·035) and S (1·535). (II) In final refinement 78 parameters varied: one scale factor, one extinction parameter, coordinates of all atoms, anisotropic and isotropic thermal parameters for non-H atoms and H atom, respectively; $g = 0{\cdot}0004$, $x = 0{\cdot}008$ (4), $wR = 0{\cdot}099$, $S = 3{\cdot}731$; $(\Delta/\sigma)_{\max}$ in last cycle 0·001; $\Delta\rho_{\min}$ and $\Delta\rho_{\max}$ in final difference map $-0{\cdot}54$ and $+0{\cdot}89$ e Å^{-3}, respectively. Final atomic parameters of (I) and (II) are listed in Table 1,‡ selected interatomic distances and angles in Table 2. Fig. 1 shows sections of the infinite chains with atom labels, Fig. 2 stereo plots of the crystal structures. All calculations and drawings performed with the Nicolet (1983) *SHELXTL* program system on a Data General Eclipse S/140 computer.

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† Part 25 of the series *Fluorides and Fluoro Acids*. For part 24 see Poll, Lohmeyer & Mootz (1989). This work constitutes part of the Dissertation in progress of K. Bartmann, Universität Düsseldorf.

‡ Lists of structure factors and anisotropic thermal parameters for both structures have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52266 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates and (equivalent) isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

	x	*y*	*z*	*U**
(I)				
S	−0·16332 (5)	0·52793 (4)	0·91081 (3)	0·0127 (1)
F	0·1452 (2)	0·5013 (2)	0·8797 (1)	0·0247 (2)
O1	−0·2863 (2)	0·3830 (2)	0·8044 (1)	0·0192 (2)
O2	−0·2080 (3)	0·4484 (2)	1·0494 (1)	0·0225 (2)
O3	−0·2270 (3)	0·7279 (1)	0·8798 (1)	0·0210 (2)
H	−0·299 (8)	0·421 (5)	0·744 (3)	0·059 (9)
(II)				
S	0·06158 (16)	0·70125 (7)	0·26377 (9)	0·0204 (3)
F1	−0·2110 (6)	0·5293 (2)	0·3658 (3)	0·0416 (9)
F2	−0·2832 (6)	0·5520 (3)	0·1110 (4)	0·0474 (9)
F3	0·0916 (6)	0·4728 (2)	0·2266 (4)	0·0473 (10)
O1	0·1697 (5)	0·7149 (3)	0·1046 (3)	0·0283 (8)
O2	0·2940 (6)	0·6878 (3)	0·3862 (3)	0·0345 (9)
O3	−0·1487 (6)	0·7834 (2)	0·2792 (4)	0·0329 (9)
C	−0·0954 (7)	0·5534 (3)	0·2397 (5)	0·0271 (10)
H	0·049 (18)	0·760 (6)	0·021 (12)	0·096 (24)

*For the non-H atoms calculated with $U = \frac{1}{3}(U_{11}a^{*2}a^2 + U_{23}bcb^*c^*\cos\alpha + \ldots)$.

Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

(I)			
S—O1	1·518 (1)	S—O2	1·420 (1)
S—O3	1·412 (1)	S—F	1·540 (1)
O1—H	0·63 (3)	O1···O2^i	2·643 (1)
H···O2^i	2·02 (3)		
O1—S—O2	107·2 (1)	O1—S—O3	113·1 (1)
O2—S—O3	120·9 (1)	O1—S—F	100·7 (1)
O2—S—F	106·2 (1)	O3—S—F	106·6 (1)
O1—H···O2^i	173 (5)		

Symmetry code: (i) $-0{\cdot}5 - x,\ 1 - y,\ -0{\cdot}5 + z$.

(II)			
S—O1	1·534 (3)	S—O2	1·427 (3)
S—O3	1·414 (4)	S—C	1·835 (4)
C—F1	1·316 (5)	C—F2	1·313 (4)
C—F3	1·313 (5)	O1—H	0·99 (9)
O1···O2^i	2·640 (4)	H···O2^i	1·67 (8)
O1—S—O2	107·1 (2)	O1—S—O3	112·4 (2)
O2—S—O3	121·5 (2)	O1—S—C	101·2 (2)
O2—S—C	105·2 (2)	O3—S—C	107·4 (2)
S—C—F1	109·2 (3)	S—C—F2	109·5 (3)
S—C—F3	110·2 (3)	F1—C—F2	109·1 (3)
F1—C—F3	109·2 (3)	F2—C—F3	109·7 (3)
O1—H···O2^i	167 (7)		

Symmetry code: (i) $-0{\cdot}5 + x,\ 1{\cdot}5 - y,\ -0{\cdot}5 + z$.

Related literature. IR spectrum of (I) in the solid state (Savoie & Giguère, 1964); electron diffraction study of (II) (Schultz, Hargittai & Seip, 1981).

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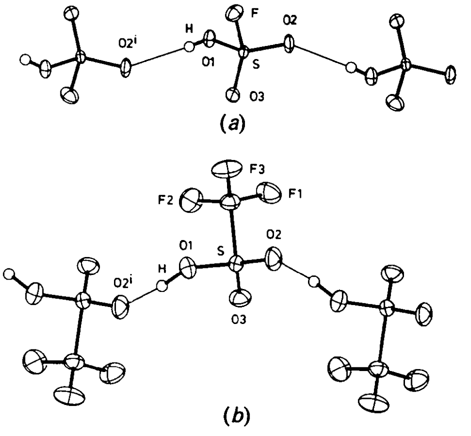

Fig. 1. Sections of infinite chains of hydrogen-bonded molecules of (*a*) (I) and (*b*) (II). Thermal ellipsoids correspond to the 50% probability level; H atoms are of arbitrary size.

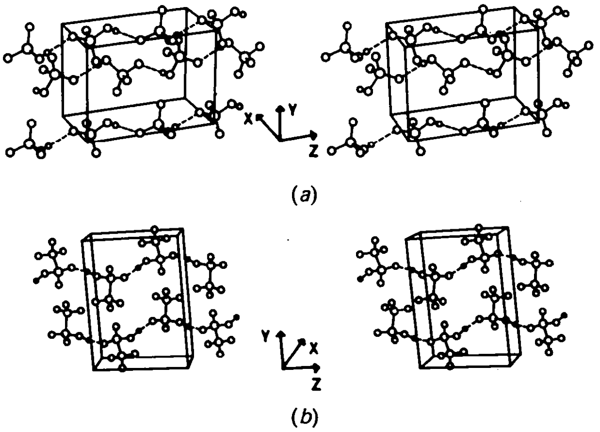

Fig. 2. Stereo plots of the crystal structures of (*a*) (I) and (*b*) (II). Atoms are of arbitrary size; hydrogen bonds are shown by broken lines.

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