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Hydrogen Bond Studies. CVI.* The Crystal Structure of $2CF_3SO_3H.H_2O$

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The crystal structure of $2CF_3SO_3H.H_2O$ (trifluoromethanesulphonic acid hemihydrate) has been determined from three-dimensional single-crystal X-ray diffraction data at 85 K. The crystals are monoclinic, space group $C2/c$, with eight formula units in a unit cell of dimensions $a=21\cdot0364$ (24), $b=11\cdot4965$ (9), $c=8\cdot4848$ (9) Å, and $\beta=94\cdot524$ (16)°. The structure consists of H_3O^+ ions, $CF_3SO_3^-$ ions, and CF_3SO_3H molecules hydrogen-bonded together to form double layers. The oxonium ion is hydrogen-bonded to three different sulphonate ions in an asymmetric pyramidal bonding arrangement; the $O-H\cdots O$ distances are 2·542 (5), 2·576 (4), and 2·723 (4) Å. The sulphonate ion also accepts a hydrogen bond [2·558 (4) Å] from the acid molecule.

Introduction

This report is a continuation of a systematic investigation of the crystal structures of the hydrates of trifluoromethanesulphonic acid. The monohydrate formulated as $CF_3SO_3^-H_3O^+$ contains the oxonium ion (Spencer & Lundgren, 1973; Lundgren, Tellgren & Olovsson, 1975) whereas the $H_5O_2^+$ ion was found in the dihydrate (Delaplane, Lundgren & Olovsson, 1975). Crystallographic studies of the proton in various degrees of hydration as found in the hydrates of strong acids have been reviewed by Lundgren (1974*a*) and Lundgren & Olovsson (1975). In the present investigation the crystal structure of $2CF_3SO_3H.H_2O$ has been determined from single-crystal X-ray diffractometer data recorded at 85 K. The investigation of this compound is of particular interest as this is the first strong acid hydrate studied which contains two protons, which are equally easily dissociated from the acid, per water molecule. The hemihydrate of phosphoric acid, an acid which is considerably weaker than trifluoromethanesulphonic acid, exhibits a crystal structure consisting of phosphoric acid molecules hydrogen-bonded to water molecules (Dickens, Prince, Schroeder & Jordan, 1974). No transfer of proton from the acid to H_2O was found.

Crystal data

Trifluoromethanesulphonic acid hemihydrate, $2CF_3SO_3H.H_2O$,‡ F.W. 318·16. Monoclinic, $a=21\cdot0364(24)$,§ $b=11\cdot4965(9)$, $c=8\cdot4848(9)$ Å, $\beta=94\cdot524(16)$°, $V=2045\cdot62$ Å^3, $Z=8$, $D_x=2\cdot066$ g cm^{-3} at 85 K. μ(Cu $K\alpha$)$=59\cdot46$ cm^{-1}. Space group $C2/c$.

Experimental

Trifluoromethanesulphonic acid hemihydrate, $2CF_3SO_3H.H_2O$, melts incongruently at −15°C (Delaplane, Lundgren & Olovsson, 1975). Single crystals were grown on a Stoe–Philips semi-automatic two-circle diffractometer which had been modified for low-temperature studies. The technique for growing the crystals as well as a description of the cooling apparatus has been given previously by Olovsson (1960). An acid-water solution containing 70·6 mol. % acid was used; a higher concentration of acid than that of the exact composition of the hemihydrate was chosen to discourage the crystallization of the monohydrate upon cooling.

The unit-cell dimensions were measured at 85 K with the above-mentioned diffractometer using Cu $K\alpha$ radiation monochromatized with a graphite crystal [λ(Cu $K\alpha_1$)$=1\cdot54051$, λ(Cu $K\alpha_2$)$=1\cdot54433$ Å]. The cell parameters were determined from a least-squares refinement using the measured 2θ values of 101 axial reflexions from three different crystals mounted around [101], [001] and [010], respectively. The diffraction symmetry and systematic absences suggested one of the monoclinic space groups Cc or $C2/c$ (Nos. 9 and 15).

Intensity data for layers $h0l$ to $h10l$ were recorded at 85 K from the crystal mounted around [010]. The crystal was cylindrical and had a diameter of 0·16 mm. The measurements were made using the equi-inclination ω scan mode with a variable scan range. The expression used for the calculation of the scan range was that given by Freeman *et al.* (1970) and included terms which allowed for wavelength dispersion, divergence of the X-ray beam, crystal mosaicity, and margins of errors in the settings of the crystal and instrument. A total of 1816 independent reflexions were measured which corresponds to 85% of the reflexions within the unique quadrant of the Cu $K\alpha$ sphere. Of these 1567 had $I>3\sigma(I)$ where $\sigma(I)$ is based on counting statistics. A set of four standard reflexions was monitored within each layer. Decreases in in-

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‡ With regard to the ionic formulation, ($H_3O^+CF_3SO_3^-CF_3SO_3H$) this formulation is preferred to $CF_3SO_3H.\frac{1}{2}H_2O$.

§ Estimated standard deviations in the least significant digits are given in parentheses.

tensity for these reflexions varied from 2 to 7%. These decreases were approximately linear with respect to elapsed time for which a correction was later applied to all intensities.

A complementary set of 596 independent reflexions (layers *hk*0 to *hk*2) was measured similarly at 85 K from a second crystal mounted around [001]. This crystal was also cylindrical with a diameter of 0·16 mm. This set of intensities was used later only for determining the relative scale factors between layers in the previous data set using the program *INTERSCALE.*

The raw intensities for each data set were corrected for background effects, and standard deviations $\sigma(I)$ were assigned on the basis of counting statistics. The values of I and $\sigma(I)$ were corrected for Lorentz, polarization and absorption effects ($\mu=59{\cdot}46$ cm^{-1} at 85 K for Cu $K\alpha$) with the program *DATAPW.*

Structure determination and refinement

Direct methods were used to solve the structure. Normalized structure-factor amplitudes ($|E|$) were calculated from the first data set with the program *EFAK*. The statistical distribution of E values is compared in Table 1 with the theoretical values corresponding to centrosymmetric and non-centrosymmetric space groups (Karle, Dragonette & Brenner, 1965). The comparison strongly suggests a centrosymmetric space group, and the space group $C2/c$ was thus chosen. The structure was later refined successfully by least-squares techniques in this space group.

Table 1. *Statistical distribution of the normalized structure-factor amplitudes (E) compared with theoretical values*

	Experimental	Centrosymmetric	Non-centrosymmetric
$\langle\lvert E\rvert^2\rangle$	1·00	1·00	1·00
$\langle\lvert E^2-1\rvert\rangle$	0·944	0·968	0·736
$\langle\lvert E\rvert\rangle$	0·814	0·798	0·886
$\lvert E\rvert>3$ (%)	0·3	0·3	0·01
$\lvert E\rvert>2$ (%)	4·5	5·0	1·8
$\lvert E\rvert>1$ (%)	31·3	32·0	37·0

Phases were determined for 241 reflexions with $|E|\geq 1{\cdot}5$ by the iterative application of Sayre's equation with the program *REL*. A trial solution was chosen for an E map which exhibited features similar to the geometry of two crystallographically independent CF_3SO_3 groups. The structural model was refined by full-matrix least-squares techniques with the program *UPALS*. The function minimized was $\sum w(|F_o|-|F_c|)^2$ where $w^{-1}=\sigma^2(F)=\sigma_c^2(F^2)/4F^2+(0{\cdot}01F)^2$ with $\sigma_c(F^2)$ based on counting statistics. Reflexions with $F^2<3\sigma_c(F^2)$ were given zero weight. After two cycles of refinement with anisotropic temperature factors the hydrogen positions were obtained from a Fourier difference synthesis calculated using only data with $\sin\theta/\lambda<0{\cdot}4$ Å^{-1}.

In the final cycles of refinement, a total of 170 parameters were allowed to vary which included one overall scale factor, coordinates for all atoms, anisotropic thermal parameters for the non-hydrogen atoms, and isotropic temperature factors for the hydrogen atoms. In addition to those reflexions with $F^2<3\sigma_c(F^2)$, 17 reflexions with very unequal backgrounds were given zero weight. 1550 reflexions had non-zero weight. No appreciable effects of secondary extinction were observed in the intensity data. All parameter shifts were less than $0{\cdot}1\sigma$ in the last cycle of refinement. The final agreement indices are

$$R\ =(\sum \lvert|F_o|-|F_c|\rvert)/\sum |F_o|=0{\cdot}048\ (0{\cdot}059)$$

$$R_w=[\ \sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2]^{1/2}=0{\cdot}057\ .^*$$

The conventional R value given in parentheses includes reflexions given zero weight. The final atomic parameters are given in Tables 2 and 3. Atomic scattering factors for S, F, O and C were those given by Hanson, Herman, Lea & Skillman (1964). The spherical scattering factors of Stewart, Davidson & Simpson (1965) were used for hydrogen. An anomalous dispersion correction was included for the non-hydrogen atoms (Cromer & Liberman, 1970). The programs used for all computations with IBM 370/155 and IBM 1800 computers have been described by Lundgren (1974*b*).

Description of the structure

The overall crystal structure of $2CF_3SO_3H.H_2O$ is shown in Fig. 1; bond distances and angles are given

Table 2. *Atomic coordinates*

Hydrogen coordinates are $\times 10^4$, others $\times 10^5$.

	x	*y*	*z*
S(1)	34390 (4)	63655 (10)	34412 (9)
S(2)	15996 (4)	65360 (11)	8095 (10)
F(1)	44006 (12)	50374 (26)	41899 (31)
F(2)	42046 (11)	62794 (25)	59764 (25)
F(3)	46458 (11)	68366 (27)	39040 (31)
F(4)	9493 (14)	46737 (29)	1915 (37)
F(5)	6453 (13)	61509 (26)	87705 (29)
F(6)	4170 (12)	60481 (29)	11935 (34)
O(1)	32936 (13)	75569 (27)	38049 (29)
O(2)	35158 (13)	61069 (26)	18081 (27)
O(3)	30367 (11)	55064 (27)	41328 (27)
O(4)	13811 (15)	78068 (30)	7906 (33)
O(5)	17686 (16)	61934 (32)	23854 (33)
O(6)	20147 (13)	63128 (29)	95981 (32)
O(*w*)	26094 (18)	60042 (35)	68147 (37)
C(1)	42249 (19)	61255 (45)	44463 (46)
C(2)	8535 (20)	58078 (51)	2059 (52)
H(1)	1426 (27)	8180 (53)	9938 (69)
H(2)	2235 (34)	6365 (57)	6687 (75)
H(3)	2637 (29)	5567 (64)	7633 (75)
H(4)	2695 (28)	5665 (57)	5960 (80)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31033 (9 pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

in Table 4. All illustrations were prepared with the program *ORTEP* II. Bond lengths and angles were calculated with the program *ORFFE*. The standard deviations given in parentheses were estimated from the variance-covariance matrix from the final cycle of refinement.

The asymmetric unit in $2CF_3SO_3H.H_2O$ contains one oxonium ion, one trifluoromethanesulphonate ion and one trifluoromethanesulphonic acid molecule which gives the formulation $H_3O^+CF_3SO_3^-.CF_3SO_3H$. This model is substantiated by the location of all four hydrogen atoms in the difference Fourier synthesis; three peaks were found near the water oxygen in positions corresponding to the pyramidal geometry of an oxonium ion, and a fourth peak was 0·84 Å from the sulphonate oxygen O(4) near the line connecting O(4) and O(2).

The structure as a whole consists of layers containing both acid molecules and anions alternately separated by zones of hydrogen bonding and zones of van der Waals interactions parallel to the *bc* plane. This feature is similar to that found in trifluoromethane-

Table 3. *Anisotropic thermal parameters* ($\times 10^5$)

The form of the temperature factor is $\exp[-(\beta_{11}h^2+\ldots+2\beta_{12}hk+\ldots)]$. The r.m.s. components of thermal displacement of the atoms along the ellipsoid axis are also listed ($\times 10^3$ Å). Isotropic thermal parameters (B, Å^2) for the hydrogen atoms are H(1) 4·5 (1·4), H(2) 5·6 (1·7), H(3) 5·5 (1·6), H(4) 5·2 (1·5).

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
S(1)	108 (2)	271 (11)	426 (10)	6 (4)	17 (3)	−11 (8)	124 (2)	135 (3)	156 (3)
S(2)	129 (2)	460 (13)	548 (12)	32 (4)	48 (4)	122 (9)	131 (2)	162 (2)	189 (2)
F(1)	142 (6)	611 (34)	1454 (42)	66 (10)	−62 (12)	−120 (28)	162 (4)	199 (5)	247 (4)
F(2)	179 (6)	732 (32)	681 (30)	−38 (10)	−80 (10)	10 (24)	143 (4)	206 (4)	228 (4)
F(3)	146 (5)	764 (34)	1390 (41)	−120 (11)	76 (12)	136 (28)	150 (4)	223 (3)	248 (4)
F(4)	262 (8)	481 (36)	1930 (54)	−50 (13)	89 (16)	160 (33)	170 (7)	244 (4)	268 (4)
F(5)	199 (6)	763 (34)	1058 (37)	−38 (11)	−119 (12)	185 (27)	165 (4)	211 (4)	254 (4)
F(6)	164 (6)	1042 (40)	1623 (48)	29 (12)	225 (14)	241 (33)	162 (4)	237 (4)	283 (4)
O(1)	196 (7)	277 (31)	697 (34)	36 (12)	−24 (12)	−161 (26)	115 (8)	168 (4)	217 (4)
O(2)	183 (6)	335 (31)	419 (31)	0 (11)	36 (11)	−12 (23)	122 (5)	150 (7)	202 (4)
O(3)	102 (5)	420 (32)	576 (31)	−10 (10)	54 (10)	89 (24)	129 (5)	156 (4)	174 (6)
O(4)	258 (8)	327 (34)	664 (35)	53 (13)	129 (14)	73 (27)	138 (6)	151 (5)	246 (4)
O(5)	222 (8)	844 (42)	698 (38)	53 (14)	−21 (14)	308 (32)	135 (5)	224 (4)	252 (6)
O(6)	148 (6)	597 (36)	874 (38)	52 (12)	130 (12)	77 (30)	149 (4)	183 (5)	218 (5)
O(*w*)	254 (9)	573 (41)	684 (41)	165 (15)	155 (15)	152 (31)	143 (5)	159 (7)	269 (5)
C(1)	137 (9)	460 (53)	766 (51)	−62 (17)	2 (17)	−56 (40)	147 (8)	172 (6)	196 (8)
C(2)	159 (10)	505 (59)	1100 (64)	40 (19)	123 (20)	247 (45)	154 (9)	175 (7)	231 (6)

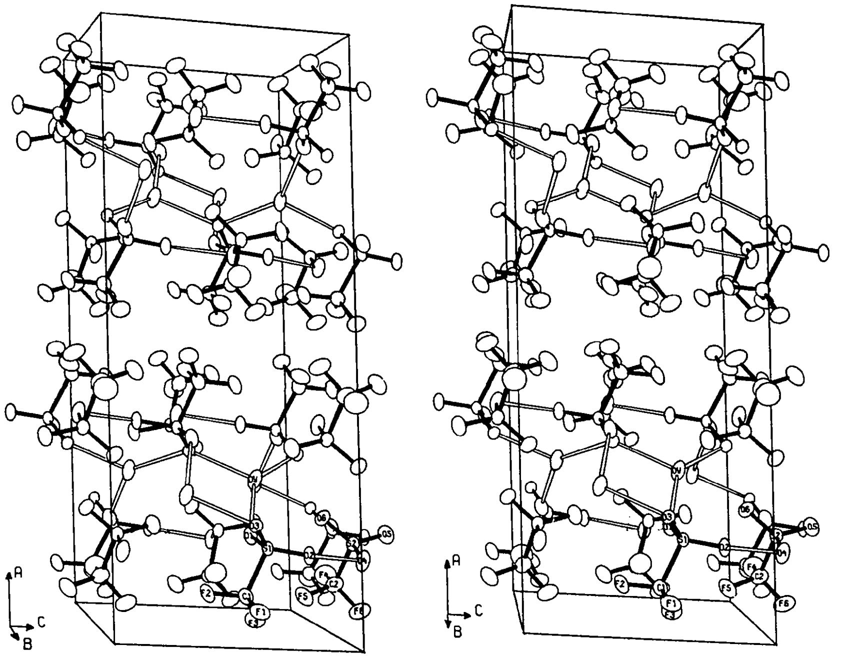

Fig. 1. Stereoscopic illustration of the crystal structure of $H_3O^+CF_3SO_3^-.CF_3SO_3H$ at 85 K. Covalent bonds are filled; hydrogen bonds are open. A unique set of atoms is labelled (see Fig. 2). Thermal ellipsoids enclose 50% probability.

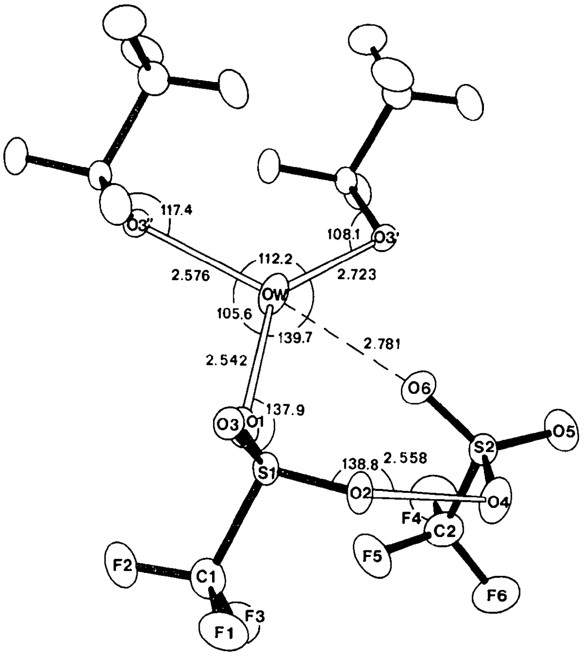

Fig. 2. Hydrogen-bond distances and angles at 85 K.

Table 4. *Interatomic distances* (Å) *and angles* (°)

(*a*) Covalent bonds within the trifluoromethanesulphonate ion

S(1)–O(1)	1·442 (3)	C(1)–F(1)	1·327 (5)
S(1)–O(2)	1·439 (2)	C(1)–F(2)	1·314 (4)
S(1)–O(3)	1·454 (3)	C(1)–F(3)	1·315 (5)
S(1)–C(1)	1·820 (4)		
O(1)–S(1)–O(2)	116·4 (2)	F(1)–C(1)–F(2)	108·7 (4)
O(1)–S(1)–O(3)	114·8 (2)	F(1)–C(1)–F(3)	109·0 (4)
O(2)–S(1)–O(3)	111·2 (2)	F(2)–C(1)–F(3)	109·7 (4)
C(1)–S(1)–O(1)	104·1 (2)	S(1)–C(1)–F(1)	108·7 (3)
C(1)–S(1)–O(2)	104·7 (2)	S(1)–C(1)–F(2)	110·1 (3)
C(1)–S(1)–O(3)	104·1 (2)	S(1)–C(1)–F(3)	110·7 (3)

(*b*) Covalent bonds within the trifluoromethanesulphonic acid molecule

S(2)–O(4)	1·531 (4)	C(2)–F(4)	1·320 (6)
S(2)–O(5)	1·412 (3)	C(2)–F(5)	1·322 (5)
S(2)–O(6)	1·424 (3)	C(2)–F(6)	1·320 (5)
S(2)–C(2)	1·817 (5)	O(4)–H(1)	0·85 (6)
O(4)–S(2)–O(5)	109·2 (2)	F(4)–C(2)–F(5)	109·0 (4)
O(4)–S(2)–O(6)	111·4 (2)	F(4)–C(2)–F(6)	109·1 (4)
O(5)–S(2)–O(6)	120·7 (2)	F(5)–C(2)–F(6)	109·0 (4)
C(2)–S(2)–O(4)	100·6 (2)	S(2)–C(2)–F(4)	109·2 (3)
C(2)–S(2)–O(5)	106·6 (2)	S(2)–C(2)–F(5)	109·8 (3)
C(2)–S(2)–O(6)	106·2 (2)	S(2)–C(2)–F(6)	110·7 (4)

sulphonic acid dihydrate (Delaplane, Lundgren & Olovsson, 1975).

The oxonium ion is hydrogen bonded to three oxygen atoms of three different sulphonate ions to form hydrogen-bonded zones at $x=\frac{1}{4},\frac{3}{4}$. There are no hydrogen bonds between the sulphonic acid molecules and the oxonium ions.

The CF_3 groups in both the acid molecule and the anion point away from the zone of hydrogen bonding in both the positive and negative **a** directions thus forming zones of van der Waals interactions at $x=0,\frac{1}{2}$. The shortest non-bonded contacts across this zone are 2·777(5), 2·908(5) and 2·934(5) Å, for the separations F(1)···F(1′), F(3)···F(3′) and F(6)···F(6′), respectively.

The H_3O^+ *ion*

The oxonium ion, H_3O^+, in solids typically is surrounded by three neighbours in a pyramidal arrangement; the average distance from the oxonium oxygen to oxygen acceptor atoms is 2·57 Å (Lundgren & Olovsson, 1975). In the present compound the situation is slightly more complicated, as shown in Fig. 2. The central atom O(*w*) has two close neighbours, O(1) and O(3″), at distances of 2·542 and 2·576 Å, respectively, and two more distant neighbours, O(3′) and O(6) at 2·723 and 2·781 Å. The refined hydrogen positions of the H_3O^+ ion are shown in Fig. 3. The H–O(*w*)–H angles are similar; the O–H distances (Table 4) as commonly found in X-ray diffraction investigations are more than 0·1 Å shorter than those expected using neutron diffraction. It is apparent that H(2) and H(4) participate in normal, slightly bent hydrogen bonds; the O···O distances are also close to the average distance found in other oxonium compounds. Atom H(3) on the other hand has two potential acceptor atoms, O(3′) and O(6). Even with the present low accuracy of the location of the hydrogen atoms it is clear that O(3′) is the principal hydrogen-bond acceptor. The contact H(3)···O(6) is 2·36 Å, only slightly less than the sum of van der Waals radii, and the O(*w*)–H(3)···O(6) angle is only 111°. Even with a true internuclear distance O(*w*)–H(3) which is slightly longer, the H(3)···O(6) distance would decrease only slightly because of the small O–H···O angle. (Empirical evidence suggests that the systematic discrepancy in the apparent hydrogen position as determined by

Table 4 (*cont.*)

(*c*) Hydrogen-bond system

X *Y* *Z*	*X–Y*	*Y–Z*	*X–Z*	*X–Y–Z*
O(4)–H(1)···(O2)	0·85 (6) Å	1·71 (6) Å	2·558 (4) Å	177 (6)°
O(*w*)–H(2)···(O1)	0·89 (7)	1·69 (7)	2·542 (5)	158 (6)
O(*w*)–H(4)···(O3″)	0·85 (7)	1·77 (7)	2·576 (4)	157 (6)
O(*w*)–H(3)···(O3′)	0·86 (7)	1·92 (7)	2·723 (4)	156 (6)

H(2)–O(*w*)–H(3)	113 (5)°	O(1)····O(*w*)···O(3″)	105·6 (1)°	S(1)—O(1)····O(*w*)	137·9 (2)°
H(2)–O(*w*)–H(4)	110 (5)	O(1)····O(*w*)···O(3′)	139·7 (2)	S(1″)–O(3″)···O(*w*)	117·4 (2)
H(3)–O(*w*)–H(4)	114 (6)	O(3″)···O(*w*)···O(3′)	112·2 (2)	S(1′)–O(3′)···O(*w*)	108·1 (1)
				S(1)—O(2)····O(4)	138·8 (2)

X-ray diffraction is predominantly along the bond direction O–H.) Thus we choose to describe the contact H(3)···O(3′) as a normal hydrogen bond, and H(3)···O(6) as an additional, weaker interaction. We prefer not to characterize the situation as a bifurcated hydrogen bond (Donohue, 1968). The longer contact to the acceptor of H(3) as compared with those of H(2) and H(4) is probably at least partly due to the situation just described. The angles between the bonds to the acceptors are 105·6, 112·2 and 139·7°. The large angle O(1)···O(*w*)···O(3′), (139·7°), also may be partially accounted for by the influence of O(6) which lies only 0·08(5) Å above the plane defined by the acceptors O(1), O(3′), and O(3″). In other oxonium compounds the average bond angle to the acceptors is 109° although the individual values can vary from 98 to 133° (Lundgren & Olovsson, 1975) which indicates that other crystal packing requirements probably play an important role also in the present case. The oxonium oxygen with the three oxygen acceptors form a flat pyramid. The perpendicular distance between O(*w*) at the apex and the base is 0·228(4) Å. The arrangement of acceptors about the H_3O^+ ion differs considerably from an ideal C_{3v} symmetry. The experimentally determined hydrogen positions suggest a more regular conformation of the H_3O^+ ion. However, the low accuracy of the positions of the hydrogen atoms as determined by X-ray diffraction methods does not permit a more detailed analysis. Even in the presence of an asymmetric environment of acceptors the oxonium ion tends to retain its ideal C_{3v} symmetry as was found in a neutron diffraction investigation of $CF_3SO_3H.H_2O$ (Lundgren, Tellgren & Olovsson, 1975).

The $CF_3SO_3^-$ *ion*

The geometry of the $CF_3SO_3^-$ ion here agrees well with that found for the same ion in both the monohydrate and dihydrate of trifluoromethanesulphonic acid (Spencer & Lundgren, 1973; Delaplane, Lundgren & Olovsson, 1975). In the present structure the $CF_3SO_3^-$ ion is also in a staggered conformation with C_{3v} symmetry. The sulphonate group has an average S–O bond distance of 1·445 Å, an average O–S–O bond angle of 114·1°, an average O–S–C bond angle of 104·3°, and a C–S bond distance of 1·820 Å. These values agree well with those found in other similar sulphonates as summarized by Arora & Sundaralingam (1971). The large difference (9·8°) between the O–S–O and O–S–C bond angles is typical for substituted sulphonate groups (Greenberg & Okaya, 1969). The distance S(1)–O(3) is slightly larger than the two corresponding distances involving O(1) and O(2) although this difference is only marginally significant. All three oxygen atoms are acceptors for hydrogen bonds of roughly equal strength. However, O(3) accepts an additional weaker hydrogen bond. The bonding arrangement around the carbon atom is tetrahedral with an average C–F bond distance of 1·319 Å. The F–C–S–O torsional angles for each O and F pair in the *trans* positions are 176·8(3), 179·5(3), and 178·6(3)°.

The CF_3SO_3H *molecule*

The existence of the CF_3SO_3H molecule and the $CF_3SO_3^-$ ion in the same structure presents the rare opportunity of comparing the geometry of an acid molecule with its corresponding anion under the same experimental conditions. The staggered conformation of the acid molecule is similar to that of the anion. The S–OH bond distance, where the hydrogen atom is covalently bonded to O(4), is 1·531(4) Å, which is about 0·1 Å longer than the two terminal S–O bonds (1·418 Å average). These terminal S–O distances are shorter than those (1·445 Å average) in the $CF_3SO_3^-$ ion. However, the average length of the S–OH and the two S–O bonds in the CF_3SO_3H molecule, 1·456 Å, is comparable to the average S–O distance in the $CF_3SO_3^-$ ion. This agrees with empirical evidence regarding average X–O distances in XO_4 tetrahedra containing Si, P, S or Cl (Cruickshank, 1961). The average O–S–O bond angle is 113·8°; however, the O(5)–S(2)–O(6) angle where both oxygen atoms are terminal is 120·7(2)° whereas the average O–S–OH angle is 110·3°. These same features have been observed in hydrogen sulphate ions (*cf.* Brown, 1973) and may be described as being due to O–O repulsion within the sulphate group or by variation of the strengths of the S–O bonds. The C–S–OH angle is 100·6(2)°, the average C–S–O (terminal) angle is 106·4(2)°, and the C–S bond distance is 1·817(5) Å. The –CF_3 group is also here tetrahedral with an average C–F bond distance

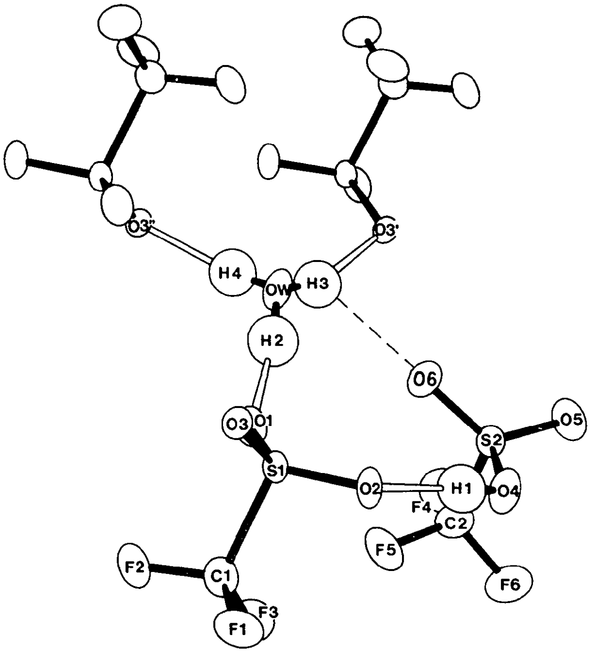

Fig. 3. Hydrogen atom positions as obtained from least-squares refinements. Thermal ellipsoids enclose 50% probability.

of 1·321 Å. The torsional angles for each *trans* O and F pair are 178·5(3), 175·9(3), and 174·6(3)°.

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Crystal and Molecular Structures of Dehydroeriolanin and Dehydroeriolangin in a Co-crystalline Mix

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The crystal and molecular structures of dehydroeriolanin, $C_{19}H_{24}O_6$, and dehydroeriolangin, $C_{20}H_{26}O_6$, oxidation products of the antileukemic *seco*-eudesmanolides eriolanin and eriolangin are described. The two compounds cocrystallize, randomly occupying equivalent sites in an orthorhombic unit cell having $a=8{\cdot}115$ (1), $b=10{\cdot}260$ (2), and $c=22{\cdot}857$ (3) Å, with space group $P2_12_12_1$ and $Z=4$. About 30% of the mix in the crystal studied is dehydroeriolangin which differs from its congener only in the substitution of an angelate for a methacrylate residue at C(6). The structure was solved by direct methods of phase determination, and refined by least-squares methods to $R=0{\cdot}063$ for 1293 reflections whose intensities were measured by counter diffractometry. Hydrogen atoms were located except in the C(6) ester group. The molecules contain a cyclohexane ring in a boat conformation, 7,8-*cis* fused to an α-methylene-γ-lactone ring having a near planar half-chair conformation. The mixed C(6) ester group is roughly planar and roughly parallel to the plane of the lactone ring. Several fairly close O···H and H···H interactions are involved in the overall molecular conformation. The molecules are joined in the crystal by hydrogen bonds involving the hydroxyl and aldehyde oxygen atoms so as to form chains extended along **a**.

Introduction

Eriolanin (I), $C_{19}H_{26}O_6$, and eriolangin (II), $C_{20}H_{28}O_6$, are sesquiterpene lactones isolated from *Eriophyllum lanatum* Forbes (Compositae) which show activity *in vivo* against P388-leukemia in the mouse and, *in vitro*, against cell cultures derived from human carcinoma of the nasopharynx (KB). Their isolation and structural characterization by n.m.r. and mass-spectral techniques, and by X-ray analysis of a mixed crystal of de-