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Structures and conformations of trifluoromethanesulfonic anhydride, $(CF_3SO_2)_2O$, and bis(trifluoromethylsulfonyl)difluoromethane, $(CF_3SO_2)_2CF_2$

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Abstract

The geometric structures and conformational properties of trifluoromethanesulfonic anhydride, $(CF_3SO_2)_2O$, and bis(trifluoromethylsulfonyl)difluoromethane, $(CF_3SO_2)_2CF_2$ have been studied by gas electron diffraction (GED) and ab initio calculations (HF/3-21G*). The calculations predict for both systems two stable conformers with C_2 symmetry and one with C_1 symmetry. In both compounds structures with C_2 symmetry and dihedral angles SOSC $\approx 100°$ ($(CF_3SO_2)_2O$) and SCSC $\approx 150°$ ($(CF_3SO_2)_2CF_2$) are lowest in energy. According to the GED analyses the dominant conformer of $(CF_3SO_2)_2O$ possesses C_2 symmetry with SOSC dihedral angles of 99.1(14)°. The presence of up to 30% of the two other conformers cannot be excluded; for $(CF_3SO_2)_2CF_2$ only one conformer with C_2 symmetry and SCSC dihedral angles of 143(2)° is observed. A complete set of geometric parameters is given.

Keywords: Electron diffraction; Ab initio calculation; Trifluoromethanesulphonic anhydride; Bis(trifluoromethylsulphonyl)difluoromethane

1. Introduction

The high electronegativity and the chemical reactivity of the trifluoromethylsulfonyl group (CF_3SO_2) are well known [1–3]. There has been a rapid growth in the chemistry of triflic acid (CF_3SO_2OH) and its derivatives which include the corresponding anhydride, $(CF_3SO_2)_2O$. Very little is known about the structural and conformational properties of these compounds, particularly those systems which contain two adjacent CF_3SO_2 groups. Four different conformations have to be considered for these systems (see Scheme 1): both CF_3 groups trans to the opposite X–S bonds (C_{2v} symmetry), both CF_3 groups gauche, either on opposite sides of the SXS plane (C_2 symmetry) or on the same side (C_s symmetry) and one CF_3 group trans and the other gauche (C_1 symmetry).

Previous gas electron diffraction (GED) studies of bis(fluorosulfonyl)difluoromethane, $(FSO_2)_2CF_2$ [4], and pyrosulfuryl fluoride, $(FSO_2)_2O$ [5], the anhydride of fluorosulfonic acid, could not determine

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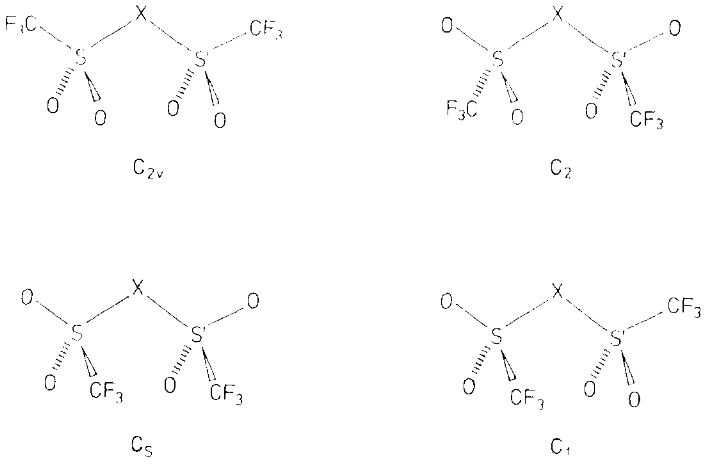

C_{2v} C_2 C_s C_1

Scheme 1.

the conformational properties of these compounds unambiguously. The reason for these difficulties in the GED analyses is the very similar scattering power of oxygen and fluorine atoms. This makes it difficult to distinguish between non-bonded distances involving oxygen or fluorine which determine the conformation. Therefore, we decided to investigate the analogous trifluoromethylsulfonyl compounds, where the scattering power of the CF_3 groups differ strongly from those of the oxygen atoms. The geometric structures of trifluoromethanesulfonic anhydride $(CF_3SO_2)_2O$, and bis(trifluoromethylsulfonyl)difluoromethane, $(CF_3SO_2)_2$ CF_2, and their conformational properties were determined by GED. Ab initio calculations were performed in order to determine possible minima in the energy hyperface and support the analyses of the GED intensities.

2. Experimental

$(CF_3SO_2)_2O$. A commercial sample (Merck) was purified by repeated distillation.

$(CF_3SO_2)_2CF_2$. This compound was prepared by fluorination of $(CF_3SO_2)_2CH_2$. To 11.2 g of $(CF_3SO_2)_2CH_2$ (40.0 mmol) and 10.9 g of NaF (260 mmol), which were thoroughly mixed and placed in a 500 ml stainless-steel cylinder, 2.1 g F_2 were added at a rate of about 0.4 g per day, while the reaction vessel was kept at 0°C. Fractionation of the products (−78°, −196°C) yielded 7.75 g colorless material in the dry-ice trap. Additional fractionation, after drying with P_4O_{10}, through −18, −78 and −196°C traps, gave 0.33 g $(CF_3SO_2)_2CHF$ in the −18°C trap, 2.8%, m.p. +8.5°C and 7.00 g $(CF_3SO_2)_2CF_2$ in the dry-ice trap, vapour pressure 8 mbar (0°C), 27 mbar (20°C). Treatment of the residual material in the reaction vessel with 1.3 g F_2 at ambient temperature afforded an additional 3.6 g $(CF_3SO_2)_2CF_2$; total yield 84%.

IR (*gas*): $\tilde{\nu}$ (cm^{-1}) = 1435 (s), 1247 (vs), 1208 (m), 1184 (w), 1120 (s), 905 (vw), 763 (vw), 673 (vw), 614 (w), 589 (m), 545 (w), 506 (m), 443 (vw). *Raman* (*liquid*): $\tilde{\nu}$ (cm^{-1}) = 1423 (vw), 1251 (m), 1203 (vw), 1102 (m), 902 (vw), 772 (vs), 669 (m), 556 (vw), 519 (vw), 439 (vw), 375 (vw), 334 (s), 312 (w), 271 (vw), 241 (vs), 216 (w), 136(s). *MS*: m/z (%) = 133 (2), 117 (16), 69 (100), 64 (6), 50 (7), 48 (18). ^{19}F *NMR*($CDCl_3$): $\delta_{CF_2} = -95.6$ (2F, sept.), $\delta_{CF_3} = -70.2$ (6F, t), $^4J_{F-F} = 7.9$ Hz, $^1J_{CF_3} = 332.1$ Hz, $^1J_{CF_2} = 350.7$ Hz. ^{13}C *NMR* ($CDCl_3$): $\delta_{C1} = 120.5$ (t, sept), $\delta_{C_2} = 119.15$ (q), $^1J_{C1} = 350.65$ Hz, $^3J_{C1} = 3.0$ Hz, $^1J_{C2} = 332.0$ Hz. (For atom numbering see Fig. 7.)

The electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2 [6] at two nozzle-to-plate distances (25 and 50 cm) and with an accelerating voltage of about 60 kV. The electron wavelength was determined from ZnO powder diffraction patterns. The sample reservoirs were

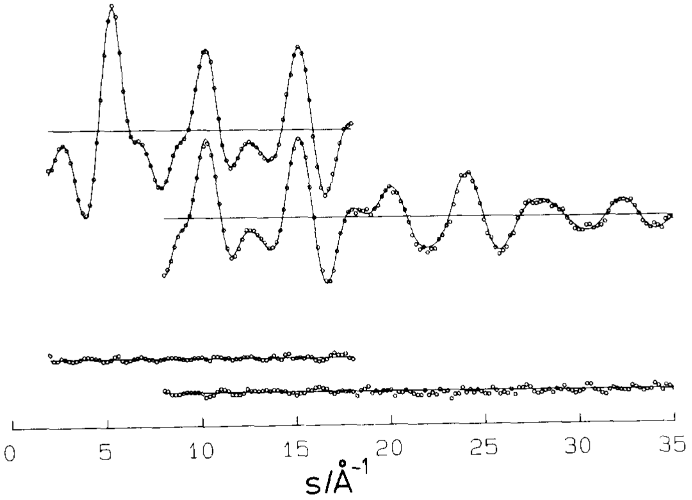

Fig. 1. Experimental (dots) and calculated (full line) molecular intensities and differences for $(CF_3SO_2)_2O$.

cooled to −15 ($(CF_3SO_2)_2O$) and 5°C ($(CF_3SO_2)_2CF_2$), respectively. The inlet nozzle was at room temperature. The camera pressure did not exceed 2×10^{-5} Torr during the experiment. The photographic plates were analysed by standard procedures [7] and averaged molecular intensities in the s-range 2–18 and 8–35 $Å^{-1}$ are shown in Figs. 1 and 2.

3. Ab initio calculations

The geometric parameters were optimized for various torsional angles around the X–S bonds (X=O or CF_2), $\Phi_1(SXS'C')$ and $\Phi_2(S'XSC)$ with the HF/3-21G* method [8]. The potential energy for C_2 structures ($\Phi_1 = \Phi_2$) of the anhydride is shown in Fig. 3. Since unreasonably short non-bonded contacts occur for $\Phi_1 = \Phi_2 < 80°$, no calculations were performed for such dihedral angles. The ab initio calculations for $(CF_3SO_2)_2O$ predict two stable conformers with C_2 symmetry and dihedral angles of 96 and 149°, with the former structure being slightly lower in energy (see Table 1). The structure with C_{2v} symmetry

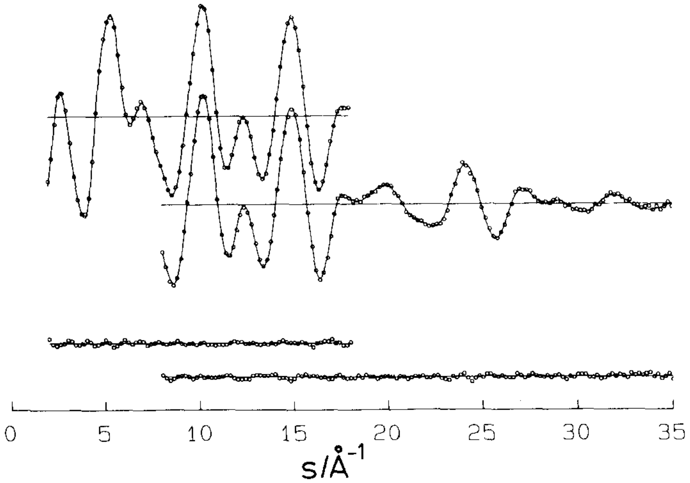

Fig. 2. Experimental (dots) and calculated (full line) molecular intensities and differences for $(CF_3SO_2)_2CF_2$.

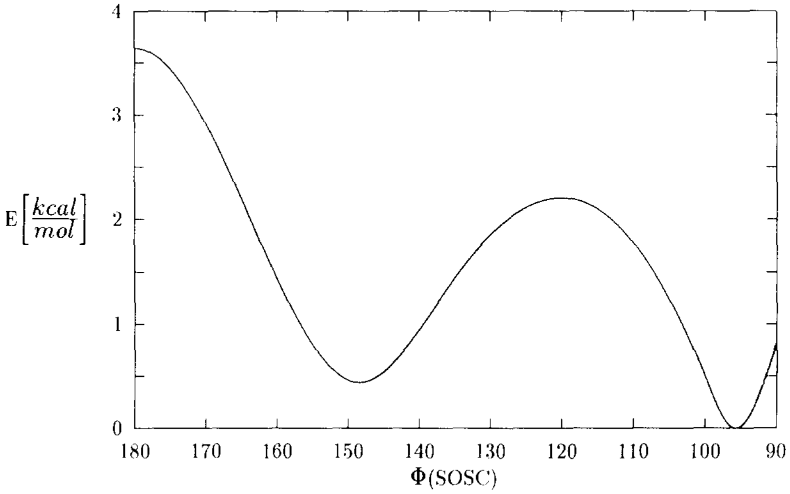

Fig. 3. Potential energy of $(CF_3SO_2)_2O$ for structures with C_2 symmetry, $\Phi_1(SOS'C') = \Phi_2(S'OSC)$.

($\Phi_1 = \Phi_2 = 180°$) does not correspond to a stable structure, but to a transition state. Model calculations demonstrate that conformations with C_s symmetry ($\Phi_1 = -\Phi_2$) are highly unfavorable, because of close contacts between oxygen atoms or CF_3 groups of the two CF_3SO_2 substituents. An additional minimum in the energy hyperface of $(CF_3SO_2)_2O$ occurs for a conformation with C_1 symmetry and dihedral angles $\Phi_1 = 175°$ and $\Phi_2 = 120°$ (see Table 1). In the case of $(CF_3SO_2)_2CF_2$ the geometries were optimized only for stable structures. The dihedral angles and energies are listed in Table 1. The conformational properties of this compound are qualitatively similar to those of the anhydride, i.e. two stable C_2 structures and one stable C_1 structure. In $(CF_3SO_2)_2CF_2$, however, the C_2 conformer with the large dihedral angles $\Phi_1 = \Phi_2 = 155°$ is lowest in energy. Furthermore, both CF_3 groups of the C_1 form lie on the same side of the SCS′ plane.

4. GED analyses

Radial distribution functions (RDFs) were derived by Fourier transform of the molecular intensities with an artificial damping function $\exp(-\gamma s^2)$ ($\gamma = 0.0019$ Å^2) and are shown in Figs. 4 and 5. The choice of molecular models was based on the ab initio predictions and on the agreement between calculated and experimental RDFs. The preliminary models were then refined by least squares fitting of the molecular intensities. The intensities were modified with a diagonal weight matrix and known scattering amplitudes and phases were used [9]. In all cases the CF_3 groups were constrained to C_{3v} symmetry. The geometry around the sulfur atoms was described by the X–S–C, X–S=O and C–S=O angles. The differences between the two X–S=O angles, ((X–S=O1) – (X–S=O2)), were set to the ab initio values with an estimated uncertainty of

Table 1
Dihedral angles S′–X–S–C (X=O or CF_2) and relative energies of the minima in the energy hyperface for $(CF_3SO_2)_2O$ and $(CF_3SO_2)_2CF_2$

	$(CF_3SO_2)_2O$			$(CF_3SO_2)_2CF_2$		
	Φ_1 (deg)	Φ_2 (deg)	E (kcal mol^{-1})	Φ_1 (deg)	Φ_2 (deg)	E (kcal mol^{-1})
C_2(I)	96	96	0.0	87	87	3.7
C_2(II)	149	149	0.4	155	155	0.0
C_1	175	120	0.4	196	96	2.3

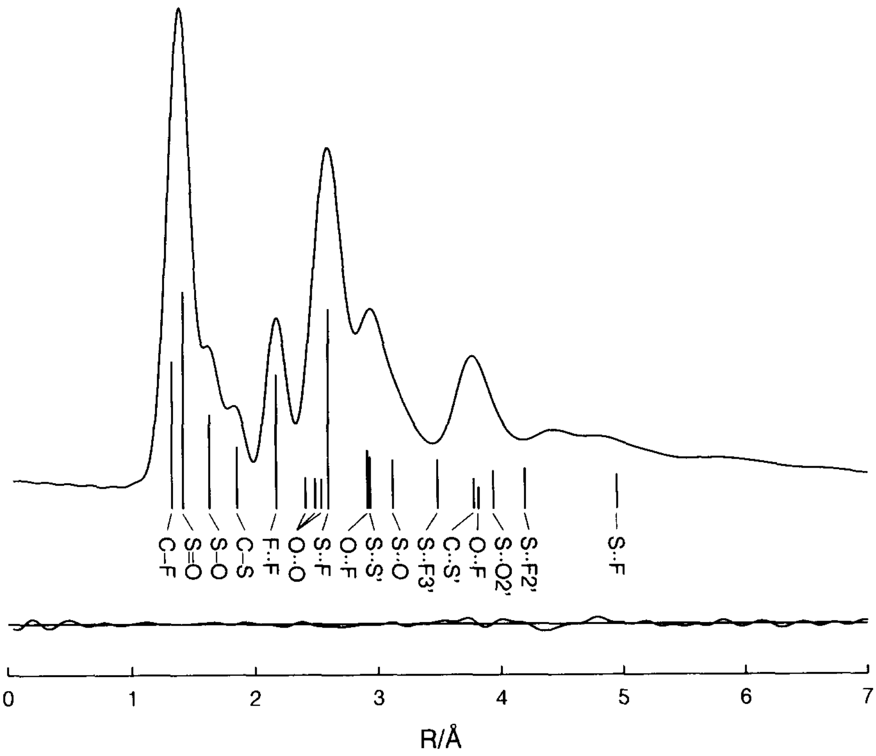

Fig. 4. Experimental radial distribution function and difference curve for $(CF_3SO_2)_2O$. The positions of important interatomic distances are indicated by vertical bars.

± 1°. The two C–S=O angles were assumed to be equal, since the respective differences in the ab initio structures are less than 1°. Vibrational amplitudes were collected in groups according to their distances. Further assumptions are evident from Tables 3 and 5.

4.1. $(CF_3SO_2)_2O$

The ab initio calculations predict three low-energy conformers, C_2(I), C_2(II) and C_1 (Table 1). When the different statistical weights (2, 2 and 4, respectively) of these three conformers are taken into account, a composition of 2 : 1 : 2 is estimated from the predicted relative energies. The RDFs for the three conformers are similar, and differ only in the range $r > 3.6$ Å. In the first step, least squares analyses were separately performed for each conformer. Only the R-factor for the intensities of the long nozzle-to-plate distance (R_{50}) is sensitive towards changes in this r-range. The best fit ($R_{50} = 0.031$) is obtained for the C_2(I) conformer and $\Phi_1 = \Phi_2 = 99°$. For the C_2(II) and C_1 forms, this R-factor increases to 0.083 and 0.076, respectively. From these refinements it is concluded that the C_2(I) conformer is the predominant form. With the above assumptions 10 geometric parameters p_i and 10 vibrational amplitudes a_k were refined simultaneously for this conformer. The following correlation coefficients had values larger than |0.7|: $p_4/p_9 = -0.77$, $p_1/p_9 = 0.79$, $p_1/a_2 = 0.75$, $p_2/a_1 = -0.87$ and $a_1/a_2 = 0.79$. Numbering of the geometric parameters and vibrational amplitudes and the results are listed in Tables 2 and 3.

In the second step, least squares refinements were performed for various mixtures of these three conformers. Bond lengths and bond angles were set equal in the three forms and the dihedral angles of the less abundant conformers were fixed to the values derived from the previous least squares refinements of the individual forms. In each case, R_{50} increases if a second conformer is added to the

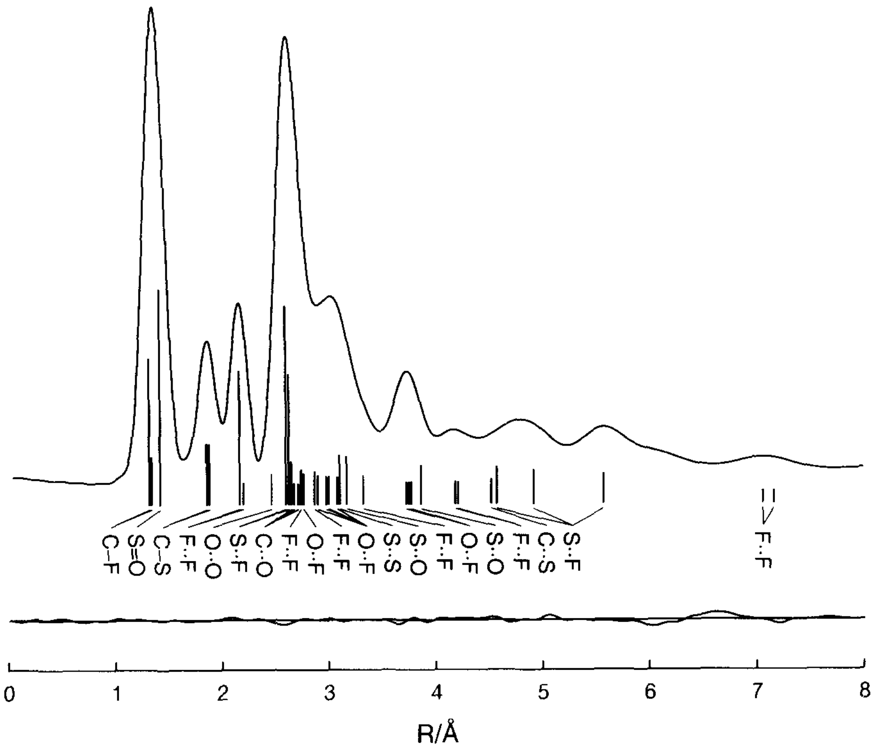

Fig. 5. Experimental radial distribution function and difference curve for $(CF_3SO_2)_2CF_2$. The positions of important interatomic distances are indicated by vertical bars.

Table 2
Geometric parameters from electron diffraction[a] and ab initio calculations for $(CF_3SO_2)_2O$

	GED		HF/3-21G*
C–F	1.318(3)	p_1	1.336
S=O	1.409(3)	p_2	1.407
S–O	1.623(5)	p_3	1.605
S–C	1.848(6)	p_4	1.775
S–O–S′	128.1(14)	p_5	129.5
$(O–S=O)_m$	107.1(9)	p_6	108.2
Δ(O–S=O) = (O–S=O1) – (O–S=O2)	5.0[10][b]		5.0
O–S=O1	109.6(11)		110.7
O–S=O2	104.6(11)		105.7
O=S=O	128.0(21)		123.8
$(C–S=O)_m$	105.9(11)	p_7	108.7
O–S–C	99.1(14)	p_8	95.5
F–C–F	110.4(4)	p_9	109.8
Φ(S′OSC)	99.1(14)	p_{10}	96.3

[a] r_a distances in Ångströms and bond angles in degrees. Error limits are 3σ values. For atom numbering see Fig. 6.
[b] Taken from ab initio calculation, estimated uncertainty in square brackets.

Table 3
Interatomic distances and vibrational amplitudes for $(CF_3SO_2)_2O$[a]

	Distance	Amplitude			Distance	Amplitude	
C–F	1.32	0.044(6)	a_1	O···F	3.98	0.30[b]	
S=O	1.41	0.036(4)	a_2	S···F2′	4.19		
S–O	1.62	0.054(5)	a_3	C···O	4.38	0.16[b]	
S–C	1.85	0.053(7)	a_4	O···O	4.39		
S···F	2.17	0.057(3)	a_5	O···F	4.44–4.61		
O···O	2.40–2.53	0.077[b]		O···O	4.78	0.14[b]	
S···F	2.59	0.086(5)	a_6	O···F	4.79		
C···O	2.61–2.64			S···F1′	4.94	0.17(5)	a_{10}
O···O	2.69	0.165(18)	a_7	C···F	5.14	0.16[b]	
O···F	2.86–3.06			C···C	5.16		
S···S′	2.92	0.066[b]		F···F	5.29		
S···O	3.11	0.155[b]		C···F	5.55	0.30[b]	
O···F	3.26			F···F	5.65–5.98		
S···F3′	3.47	0.19(6)	a_8	O···F	5.67		
O···F	3.71–3.81	0.09[b]		C···F	6.22	0.21[b]	
S···C′	3.77	0.16(3)	a_9	F···F	6.66–7.28		
C···O	3.83						
S···O2′	3.93						

[a] Values in Ångströms, error limits are 3σ values. For atom numbering see Fig. 6.
[b] Not refined.

C_2(I) form. R_{50} increases by more than 10% when (i) 30% C_1 conformer is present, (ii) 20% C_2(II) is present or (iii) 15% C_1 and 10% C_2(II) forms are present. From these analyses we conclude that the main conformer of the anhydride possesses C_2 symmetry with $\Phi_1 = \Phi_2 = 99°$ and contributions from other forms are less than 30%.

4.2. $(CF_3SO_2)_2CF_2$

According to the ab initio calculations only one conformer with C_2 symmetry and large SCSC dihedral angles is expected for this compound. In addition to the assumptions described above, the differences between the C–F bond lengths, $\Delta CF = (C1{-}F) - (C2{-}F)$, and between the S–C bond lengths, $\Delta SC = (S{-}C1) - (S{-}C2)$, and the central F–C1–F angle were constrained to the ab initio results. Only mean values for the C–F and S–C distances were determined. With these assumptions 10 geometric parameters p_i and 11 vibrational amplitudes a_k were refined. The following correlation coefficients had values larger than $|0.7|$: $p_1/p_8 = 0.75$, $p_4/p_5 = 0.74$, $p_4/p_{10} = 0.76$, $p_2/a_1 = -0.82$, $p_4/a_6 = -0.79$, $p_{10}/a_6 = -0.73$, and $a_1/a_2 = 0.83$. Numbering of the geometric parameters and vibrational amplitudes and their final values are listed in Tables 4 and 5. Structures with C_2 symmetry and small SCSC dihedral angles

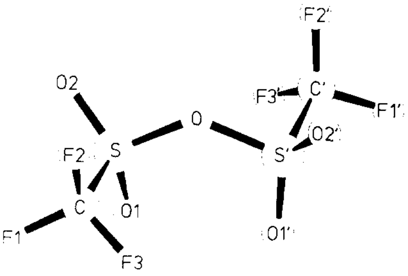

Fig. 6. Structural model of $(CF_3SO_2)_2O$.

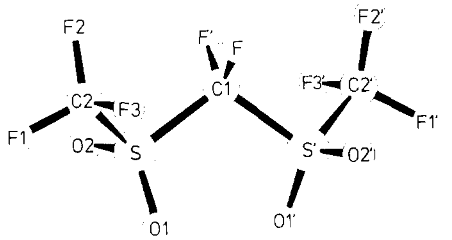

Fig. 7. Structural model of $(CF_3SO_2)_2CF_2$.

Table 4
Geometric parameters from electron diffraction[a] and ab initio calculations for $(CF_3SO_2)_2CF_2$

	GED		HF/3-21G*
$(C-F)_m$	1.323(2)	p_1	1.340
$\Delta CF = (C1-F) - (C2-F)$	0.021[5][b]		0.021
C1–F	1.339(5)		1.356
C2–F	1.318(3)		1.335
S=O	1.420(2)	p_2	1.417
$(S-C)_m$	1.869(3)	p_3	1.800
$\Delta SC = (S-C1) - (S-C2)$	0.014[5][b]		0.014
S–C1	1.876(4)		1.807
S–C2	1.862(4)		1.793
S–C–S	110.0(8)	p_4	111.6
F–C1–F	110.5[c]		110.5
C–S–C	103.8(7)	p_5	99.6
$(C1-S{=}O)_m$	109.1(8)	p_6	107.2
$\Delta CSO = (C1-S{=}O1) - (C1-S{=}O2)$	2.8[5][b]		2.8
C1–S=O1	110.5(9)		108.6
C1–S=O2	107.7(9)		105.8
C2–S=O	106.6(8)	p_7	107.8
O=S=O	120.3(22)		124.6
F–C2–F	110.4(3)	p_8	109.9
$\tau(CF_3)$[d]	8(3)	p_9	16.0
$\Phi(S'CSC)$	143(2)	p_{10}	154.8

[a] r_a distances in Ångströms and bond angles in degrees. Error limits are 3σ values. For atom numbering see Fig. 7.

[b] Taken from ab initio calculation, estimated uncertainty in square brackets.

[c] Not refined.

[d] Torsion of CF_3 groups, for $\tau = 0$ the CF_3 groups stagger the bonds around the sulfur atom.

(C_2(I) conformer) or C_1 symmetry poorly reproduce the experimental radial distribution function in the distance range $r > 3$ Å. From the comparison between calculated RDFs with the experimental curve we estimate that the contribution of such conformers is less than 10%.

5. Discussion

The most interesting aspects of these structural studies are the conformational properties of the two bis(trifluoromethylsulfonyl) derivatives. The GED analyses for both compounds demonstrate that no structures with C_{2v} symmetry occur. According to the ab initio calculations the C_{2v} forms correspond to transition states between two equivalent C_2 conformers with dihedral angles around 150°. The ab initio calculations predict for both compounds two stable C_2 conformers with dihedral angles around 100 and 150° and one stable C_1 form. The GED analysis for the anhydride, $(CF_3SO_2)_2O$, results in a C_2 structure with dihedral angles $\Phi(S'OSC)$ of 99.1(14)° with possible contributions of up to 30% of the two other conformers. This implies that the relative free enthalpies of the C_2(II) and C_1 forms are higher (>0.8 kcal mol^{-1}) than the relative energies predicted by the ab initio calculations (0.4 kcal mol^{-1}). For $(CF_3SO_2)_2CF_2$, the experimental analysis yields a structure with C_2 symmetry and dihedral angles $\Phi(S'CSC)$ of 143(2)°. Contributions of other conformers are estimated to be less than 10%, in agreement with the calculated relative energies of these forms (Table 1).

A possible explanation for the destabilization of the C_{2v} structure, where both CF_3 groups are furthest apart from each other, is repulsion between the doubly eclipsed S=O bonds. The shortest O···O contacts between the two CF_3SO_2 groups (about 3.2 Å) are longer than the respective van der Waals distance (2.80 Å).

Table 5
Interatomic distances and vibrational amplitudes for $(CF_3SO_2)_2CF_2$[a]

	Distance	Amplitude			Distance	Amplitude	
C–F	1.32	0.045(3)	a_1	Y···F^{d}	3.74–4.10	0.090^{c}	
S=O	1.42	0.035(3)	a_2	F···F	4.18–4.21	0.148(22)	a_8
S–C	1.87	0.053(3)	a_3	S···Z^{e}	4.52–4.57	0.26(5)	a_9
F···F	2.16–2.20	0.056(2)	a_4	O···F	4.57		
O···O	2.46			S···F	4.91	0.21(3)	a_{10}
S···F	2.60–2.63	0.075(2)	a_5	X···X^{b}	4.68–4.93		
C···O	2.65–2.67			C···O	4.90–4.91		
C···C	2.94			O···F	5.13		
X···F^{b}	2.74–3.26	0.140(18)	a_6	O···F	5.39–5.70	0.15(3)	a_{11}
F···F	2.87			S···F	5.57		
O···O	2.91			F···F	5.76–6.51	0.08^{c}	
S···O	3.17			C···C	5.88		
S···S	3.09	0.075^{c}		Y···F^{d}	5.93–6.06		
X···F^{b}	3.32–3.76	0.127(12)	a_7	C···F	7.00	0.09^{c}	
O···O	3.67			F···F	7.06–8.09		
S···O	3.86						

[a] Values in Ångströms, error limits are 3σ values. For atom numbering see Fig. 7.
[b] X = C, O or F.
[c] Not refined.
[d] Y = C or O.
[e] Z = C or F.

The dihedral angles which determine the conformational properties are similar to those reported recently for perfluoro-*n*-butane. For this compound, ab initio calculations [10,11] predict the existence of three conformers with dihedral angles around the central C–C bond, Φ(CCCC) of 165, 95 and 54°. Also, in perfluoro-*n*-butane the C_{2v} structure ($\Phi = 180°$) is destabilized by 1,3-substituent interactions. Interestingly, the conformations which correspond to the small torsional angle of 54° are not observed in the trifluoromethylsulfonyl compounds because of short 1,4-substituent contacts.

The experimental geometric parameters are reproduced reasonably well by the HF/3-21G* method, except for the S–C bond lengths in both derivatives and the S′CSC dihedral angle in $(CF_3SO_2)_2CF_2$. The HF/3-21G* method predicts shorter (≈ 0.07 Å) peripheral S–CF_3 bonds in both compounds and a shorter (≈ 0.07 Å) central S–C bond in $(CF_3SO_2)_2CF_2$. The failure of HF calculations with small split basis sets to reproduce experimental E–CF_3 bond distances (E = Si, P, S) has been pointed out previously [12,13].

A comparison of the skeletal parameters of the two bis(trifluoromethylsulfonyl) compounds with the analogous bis(fluorosulfonyl) derivatives, $(FSO_2)_2O$ [5] and $(FSO_2)_2CF_2$ [4], shows that the S–O bonds lengthen by about 0.01 Å and the S–C bonds by 0.03 Å when fluorine is substituted by CF_3. The central angles change in opposite directions, i.e. the S–O–S angle in the anhydrides increases by about 4°, whereas the S–C–S angle decreases by about 3° upon replacing F by CF_3.

Acknowledgments

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