The Gas-Phase Structure of Trifluoromethyl Vinyl Sulfide, $CF_3SC(H)=CH_2$☆

Max Lieb[a] **and Heinz Oberhammer***[b]

Lehrstuhl für Anorganische Chemie II, Ruhr-Universität[a],
D-44780 Bochum, Germany

Institut für Physikalische und Theoretische Chemie, Universität Tübingen[b],
D-72076 Tübingen, Germany

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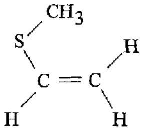
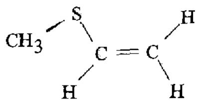
The geometric structure of trifluoromethyl vinyl sulfide, $CF_3SC(H)=CH_2$, was determined by gas electron diffraction and ab initio calculations (HF/3-21G* and MP2/6-31G*). A single conformer with a dihedral angle $\phi(C=C-S-C)$ = 129(4)° is present. The conformational properties are compared to those of the parent compound, $CH_3SC(H)=CH_2$, and of the perfluorinated species $CF_3SC(F)=CF_2$.

Previous gas-phase structure determinations of methyl vinyl sulfide, $CH_3SC(H)=CH_2$[1,2], and its perfluorinated derivative $CF_3SC(F)=CF_2$[3] demonstrated that fluorination has a drastic effect on the conformational properties of these compounds. The parent compound exists as a mixture of synperiplanar and anticlinal conformations, with the latter form being 1–2 kcal mol^{-1} higher in energy[2]. The potential curve for internal rotation around the $S-C(sp^2)$ bond possesses minima at $\phi(C=C-S-C) = 0°$ (synperiplanar) and 136(7)° (anticlinal) and a very small barrier at $\phi = 180°$ (antiperiplanar). In the perfluorinated species, however, only one single conformation is present and the minimum in the potential curve occurs at $\phi(C=C-S-C) = 96.9(12)°$, i.e. the SCF_3 group is nearly perpendicular to the plane of the vinyl group.



synperiplanar



anticlinal

In this context we were interested in the conformational properties of partially fluorinated methyl vinyl sulfides and in this work we report a gas-phase structure determination (GED) of $CF_3SC(H)=CH_2$, using gas-electron diffraction. The experimental study was supplemented by ab initio calculations at the HF/3-21G* and MP2/6-31G* level[4]. Geometries were optimized for various torsional angles $\phi(C=C-S-C)$ in steps of 30° with the HF/3-21G* approximation and the results of full geometry optimizations (HF/3-21G* and MP2/6-31G*) are included in Table 1. Vibrational amplitudes and perpendicular amplitudes were derived from calculated cartesian force constants (MP2/6-31G*) with the program ASYM40[5]. For this purpose the cartesian force constants were transformed to symmetry force constants and no scaling factors were used. The two lowest vibrational frequencies at 55 and 66 cm^{-1} correspond to the torsions around the $S-C(sp^2)$ and $S-C(sp^3)$ bonds, respectively. The calculated vibrational amplitudes are included in Table 2. The contributions of the two torsional vibrations were neglected for the perpendicular amplitudes of interatomic distances which do not depend on the torsional motions.

Table 1. Experimental and calculated geometric parameters of $CF_3SC(H)=CH_2$

	GED[a]		HF/ 3-21G*	MP2/ 6-31G*
$C-F$	1.337(3)	p_1	1.349	1.348
$C=C$	1.336[5][d]		1.314	1.336
$(S-C)_{mean}$	1.784(2)	p_2	1.772	1.782
$\Delta SC=(S-C3)-(S-C1)$	0.058(11)	p_3	0.002	0.027
$S-C1$	1.755(6)		1.771	1.767
$S-C2$	1.813(6)		1.773	1.796
$C-H$	1.084(14)	p_4	1.072	1.085
$C=C-S$	120.9(24)	p_5	122.5	122.1
$C-S-C$	100.4(14)	p_6	97.3	97.2
$F-C-F$	107.9(3)	p_7	107.5	107.6
$C=C-H$	121.5[e]		122.0	121.5
$tilt(CF_3)$[b]	2.4(18)	p_8	2.7	2.9
$\tau(CF_3)$[c]	3.4(38)	p_9	8.1	3.2
$\phi(C=C-S-C)$	129.4(39)	p_{10}	129.3	129.1

[a] r_a distances in Å and $\angle_\alpha$ angles in degrees; experimental uncertainties are 3σ values and include possible systematic errors; for atom numbering see Figure 3. – [b] Tilt angle between C_3 axis of CF_3 group and S–C3 bond direction, away from S–C1 bond. – [c] Torsional angle of CF_3 group; $\tau = 0°$ corresponds to the staggered orientation and a positive value leads to an increase of the C1···F2 distance. – [d] MP2/6-31G* value; the estimated uncertainty in square brackets is included in the experimental uncertainties of the refined parameters. – [e] Constrained to MP2/6-31G* value.

Both ab initio methods (Table 1) reproduce the experimental geometries within ±0.02 Å and ±3°, except for the $S-CF_3$ bond which is predicted too short by the HF/3-21G* method. The most relevant parameter of this study,

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Table 2. Interatomic distances and vibrational amplitudes[a]

	distance	ampl. (GED)		ampl. (ab initio)
C−H	1.09	0.074[b]		0.074
C−F	1.34	0.043(2)	l_1	0.044
C=C	1.34	0.041[b]		0.041
S−C	1.76−1.81	0.049[3][c]		0.049
F···F	2.16	0.054(3)	l_2	0.056
S···F	2.57−2.63	0.076(13)	l_3	0.065
S···C2	2.71			0.068
C1···C3	2.75	0.085[b]		0.085
C1···F3	3.03	0.146(18)	l_4	0.177
C1···F2	3.10			
C2···C3	3.84	0.188[b]		0.188
C1···F1	3.94	0.121(48)	l_5	0.076
C2···F2	3.98	0.146(38)	l_6	0.226
C2···F3	4.30			0.247
C2···F1	4.99	0.118(37)	l_7	0.167

[a] Values in Å, experimental uncertainties are 3σ values; for atom numbering see Figure 3. – [b] Fixed to ab initio value. – [c] See footnote[d] of Table 1.

the dihedral angle ϕ(C=C−S−C), is reproduced perfectly by both methods. The theoretical vibrational amplitudes for non-bonded interatomic distances which depend on torsional motions around the two S−C bonds (C2···F2 and C2···F3) are larger than the respective experimental values (Table 2). This indicates that the MP2/6-31G* method underestimates these torsional force constants.

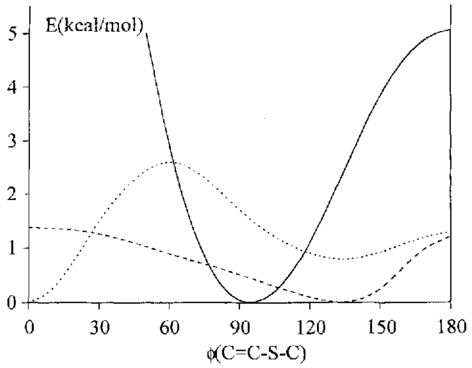
Table 3 compares the skeletal parameters of the three sulfides $CH_3SC(H)=CH_2$, $CF_3SC(H)=CH_2$, and $CF_3SC(F)=CF_2$. Fluorination of the methyl group causes slight lengthening of the $S-C(sp^3)$ bond while fluorination of the vinyl group leads to shortening of the $S-C(sp^2)$ and the C=C bond by 0.03 to 0.04 Å. The largest effect of fluorination is exerted on the dihedral angles and on the potential curves for internal rotation around the $S-C(sp^2)$ bond (Figure 1). The potential functions were calculated by ab initio methods and the gross shape of these curves, i.e. the number and position of the minima, is confirmed by the GED results. In the case of $CH_3SC(H)=CH_2$, the global minimum occurs for the synperiplanar conformation (ϕ = 0°). This orientation is stabilized by conjugation between the p-shaped sulfur lone pair, lp(S), and the vinyl π bond [S(lp)→π*]. A second and very flat minimum occurs for the anticlinal form with ϕ ≈ 130° (quasi-planar *anti* conformation) which allows reduced lp(S)→π* interaction. In both fluorinated species the synperiplanar structure corresponds to a maximum in the potential curves (transition state) and the curves posssess only one minimum for the anticlinal forms at ϕ ≈ 130° [$CF_3SC(H)=CH_2$] and ϕ ≈ 95° [$CF_3SC(F)=CF_2$]. Fluorination of the vinyl group causes a large increase of the barriers to internal rotation around the $S-C(sp^2)$ bond in $CF_3SC(F)=CF_2$. The shift of the minimum from the synperiplanar to anticlinal orientation upon fluorination indicates increased steric interactions between methyl and vinyl substituents and decreased lp(S)→π* interaction. The sulfur lone pair in $CF_3SC(F)=CF_2$ lies in the plane of the vinyl group and no such interaction occurs.

Table 3. Skeletal geometric parameters of methyl vinyl sulfide and fluorinated species

	$CH_3SC(H)=CH_2$[a] synperiplanar	anticlinal	CF_3SC-$(H)=CH_2$	CF_3SC-$(F)=CF_2$[b]
C=C	1.341(1)	1.341	1.336[c]	1.302(19)
$S-C(sp^2)$	1.759(8)	1.767	1.755(6)	1.719(9)
$S-C(sp^3)$	1.795(8)	1.795	1.813(6)	1.820(10)
C=C−S	127.5(7)	122.5	120.9(24)	120.0(9)
C−S−C	102.1(5)	98.9	100.4(14)	101.7(7)
ϕ(C=C−S−C)	0.0	135.8(65)	129.4(39)	96.9(12)

[a] Ref.[2]; the differences in bond lengths and bond angles between the synperiplanar and anticlinal conformer were fixed to ab initio values. – [b] Ref.[3]. – [c] Not refined.

Figure 1. Calculated (HF/3-21G*) potential functions for internal rotation around the $S-C(sp^2)$ bond; $CH_3SC(H)=CH_2$[10] (···), $CF_3SC(H)=CH_2$ (----), $CF_3SC(F)=CF_2$[3] (——)



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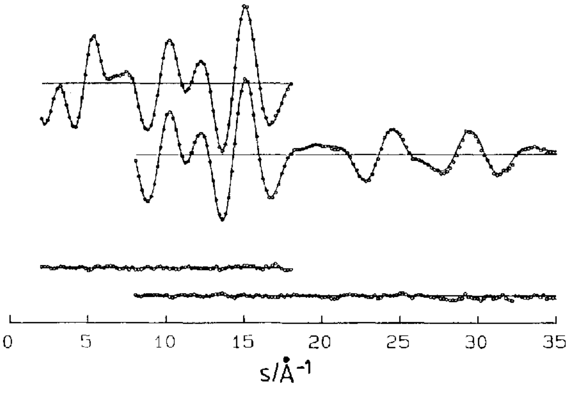
Experimental Section

Trifluoromethyl vinyl sulfide was prepared using a modification of a method published by Harris[6]. To a solution of 1 g of potassium hydroxide in 5 ml of absolute chinoline in a Teflon-stemmed Carius tube, 1.6 g (10 mmol) of 2-chloroethyltrifluoromethyl sulfide was added. The mixture was then heated for 16 h at 80°C. The contents of the tube were distilled, giving 1.0 g (83%) of trifluoromethyl vinyl sulfide. The compound was characterized by ^{19}F- and

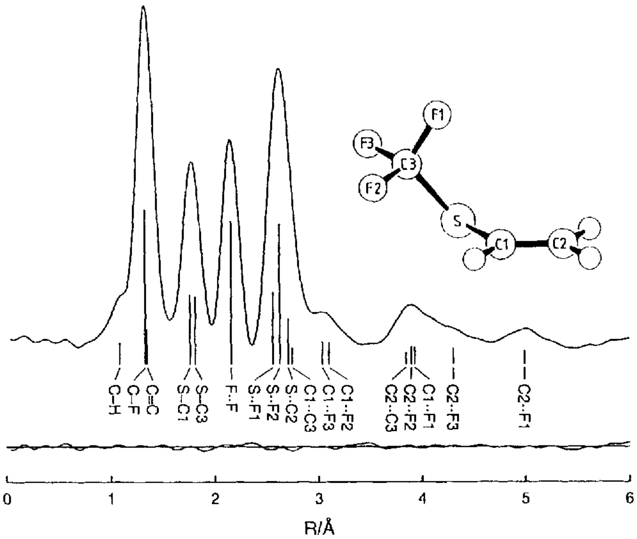
Figure 2. Experimental (dots) and calculated (full line) molecular intensities for the long (above) and short (below) nozzle-to-plate distances and differences



^{1}H-NMR, IR, and GC/MS spectroscopy and its purity was determined to be >98%. The electron-diffraction intensities were recorded with a Gasdiffractograph KD-G2[7] at two nozzle-to-plate distances (25 and 50 cm) with an accelerating voltage of ca. 60 kV. The sample reservoir was cooled to −55 °C (ca. 15 Torr vapor pressure) and the inlet system and gas nozzle were kept at room temperature. The photographic plates (Kodak Electron Image, 13 × 18 cm) were analyzed by the usual methods[8] and averaged molecular intensities in the s ranges [$s = (4\pi/\lambda)\sin\Theta/2$; λ: electron wavelength, Θ: scattering angle] 2−18 and 8−35 Å^{-1} at intervals of $\Delta s = 0.2$ Å^{-1} are shown in Figure 2.

Structure Analysis: The radial distribution function (RDF) was calculated by Fourier transformation of the molecular intensities with an artificial damping function $\exp(-\gamma s^2)$, $\gamma = 0.0019$ Å^2. The RDF (Figure 3) is reproduced very well with a single conformer possessing a dihedral angle $\phi(C{=}C{-}S{-}C) \approx 130°$. The preliminary structural parameters were refined by a least-squares analysis based on the molecular intensities. The intensities were modified with a diagonal weight matrix and known complex scattering factors were used[9]. The C=C bond length, which is very similar to the C−F bond lengths, was fixed at 1.336 Å (MP2/6-31G* value) with an estimated uncertainty of ±0.005 Å. The two closely spaced S−C distances are described by a mean value, $(S{-}C)_{mean} = 1/2[(S{-}C3) + (S{-}C1)]$, and by the difference $\Delta SC = (S{-}C3) - (S{-}C1)$. The CF_3 group was constrained to C_{3v} symmetry with a possible tilt angle between the C_3 axis and the S−C3 bond and with a possible torsional angle $\tau(CF_3)$ which describes the deviation from the exact staggered orientation. The C=C−H angles were fixed to the ab initio values. Some vibrational amplitudes which cause high correlations between geometric parameters or which are not well determined by the GED experiment, were fixed to the values derived from the ab initio force field. With these assumptions, ten geometric parameters p_i and seven vibrational amplitudes l_k were refined simultaneously. Four correlation coefficients had values larger than |0.6|: $p_1/p_7 = 0.75$, $p_5/p_9 = 0.76$, $p_5/l_3 = -0.88$ and $p_9/l_3 = -0.93$, causing large standard deviations for p_5 (C=C−S) and p_9 [tilt(CF_3)]. The final results are listed in Table 1 (geometric parameters p_i) and Table 2 (vibrational amplitudes l_k). The agreement factors for the two nozzle-to-plate distances were $R_{50} = 0.036$ and $R_{25} = 0.078$.

Figure 3. Experimental radial distribution function and difference curve; the positions of important interatomic distances are given by vertical bars



☆ Dedicated to Prof. Dr. mult. Dr. h.c. *Alois Haas* on the occasion of his 65th birthday.

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