The Gas-Phase Structure of 1-Trifluoromethylthio-1,2,2-trifluoroethene, $CF_3SC(F)=CF_2$

Adriana Olleta[a][+], **Alois Haas**[a], **and Heinz Oberhammer***[b]

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

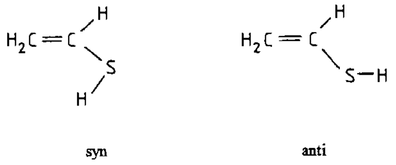
Institut für Physikalische und Theoretische Chemie, Universität Tübingen[b],
72076 Tübingen, Germany

Received April 25, 1995

Key Words: Trifluorotrifluoromethylthioethene / Gas-phase structure / Electron diffraction

The molecular structure of 1-trifluoromethylthio-1,2,2-trifluoroethene, $CF_3SC(F)=CF_2$, was determined by gas electron diffraction (GED) and ab initio calculations (HF/3-21G*). The $S-CF_3$ bond is oriented nearly perpendicular to the ethene plane with $\Phi(C=C-S-C) = 96.9(12)°$. This orientation implies that the p-shaped sulfur lone pair is perpendicular to the ethene π orbitals. The following skeletal bond lengths (r_a in Å) and angles ($\measuredangle_\alpha$ in °) were obtained (error limits are 3σ values): $C=C$ = 1.302(19) Å, $C(sp^2)-S$ = 1.719(9) Å, $S-C(sp^3)$ = 1.820(10) Å, $C=C-S$ = 120.0(9)°, and $C-S-C$ = 101.7(7)°. The experimental geometric parameters were reproduced reasonably well by the ab initio method.

The structure and conformational properties of ethenethiol, $H_2C=C(H)SH$, have been studied extensively by infrared and microwave spectroscopy (MW)[1-5] and by ab initio calculations[6]. The molecule exists in two conformations, planar *syn* and pseudoplanar *anti*. The potential function for internal rotation around the C–S bond which was derived from MW data, possesses its global minimum for the *syn* structure [$\Phi(CCSH) = 0°$] and a flat double minimum for the *anti* form. The *anti* conformer is 0.15(7) kcal/mol higher in energy. The barrier between *syn* and *anti* forms occurs for the perpendicular orientation of the S–H bond [$\Phi(CCSH) \approx 80°$] and is found to be ca. 2.5 kcal/mol above the global minimum. This demonstrates that parallel orientation of the p-shaped sulfur lone pair and the ethene π-orbitals is favored. The conformation with the S–H bond eclipsed to the C=C double bond (*syn*) is slightly lower in energy than that with the S–H bond eclipsed or nearly eclipsed to the C–H single bond (*anti*). Two independent gas electron diffraction (GED) studies of methyl vinyl sulfide, $CH_3SC(H)=CH_2$, provided somewhat different results for the conformational properties of this thioethene. Both investigations report a mixture of planar *syn* [$\Phi(CCSC) = 0°$] and nonplanar *gauche* [$\Phi(CCSC) \approx 140°$] forms. Derissen et al.[7] found that the major component is the planar *syn* conformer [84(5)% at 40 °C] and Samdal et al.[8] found the nonplanar gauche conformer [62(7)% at 200 °C] to be predominant. In the present study we are interested in the effect of fluorination on the conformational properties of methyl vinyl sufide and report on a GED investigation of the perfluorinated derivative, $CF_3SC(F)=CF_2$. This compound was tested as a precursor for fluorocarbon polymers, but found to be less suitable than the corresponding ether, $CF_3OC(F)=CF_2$. The experimental investigation is supplemented by ab initio calculations at the HF/3-21G* level. The calculations were performed with the GAUSSIAN 90 program[9].



Structure Analysis

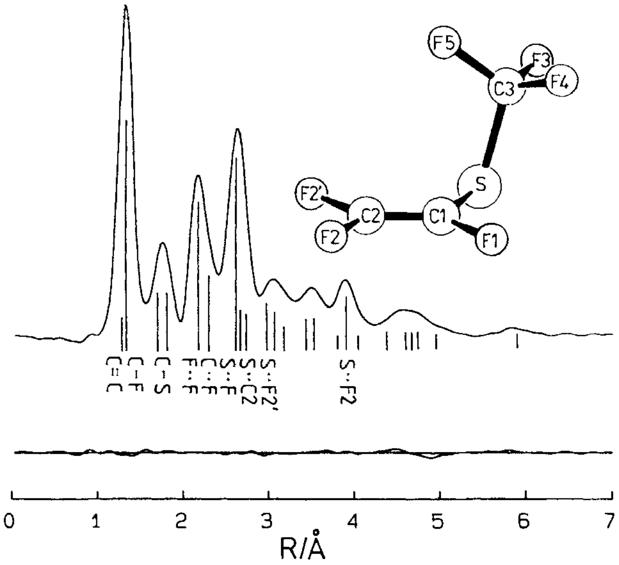
Model calculations with standard values for bond lengths and bond angles show that the planar *syn* structure in this molecule is highly unfavorable for steric reasons. Nonbonded F···F contacts between the CF_3 group and F2′ (see Figure 1 for atom numbering) are much shorter (2.10 Å) than the corresponding van der Waals distance (2.70 Å). Planar anti or gauche structures possess F···F contacts longer than 2.70 Å and are not excluded for steric reasons. The radial distribution function (Figure 1) which was obtained by Fourier transform of the molecular intensities with an artificial damping function $\exp(-\gamma s^2)$ ($\gamma = 0.0019$ Å^2), depends strongly on the torsion around the C–S bond in the range $r > 2.5$ Å. The experimental curve is reproduced only with approximately perpendicular orientation of the $S-CF_3$ group relative to the ethene plane, i.e. $\Phi(CCSC) \approx 95°$. In the least-squares refinement the molecular intensities were modified with a diagonal weight matrix, and known scattering amplitudes and phases were used[10]. The following assumptions were made in the structure analysis: (1) planarity of the $F_2C=C(F)S$ skeleton, (2)

[+] Present address: Instituto de Investigaciones en Fisicoquimica de Cordoba (INFIQC), Departamento de Fisica Quimica, Facultad de Ciencias Quimicas, Universidad National Cordoba, 5016 Cordoba (Argentina).

0009–2940/95/0808–0803 $ 10.00+.25/0

C_{3v} symmetry of the CF_3 group with a possible tilt angle between the C_3 axis and the S−C bond direction. (3) The differences between the C−F bond lengths in the CF_3 group and in the trifluorovinyl group and the difference between the C2C1F1 and C1C2F2 angles were equated with the ab initio values. The estimated uncertainties for these differences of 0.015 Å and 1°, respectively, are used to include possible systematic errors in the refined parameters. (4) The assumptions C2−F2 = C2−F2′ and C1C2F2 = C1C2F2′ are justified by the ab initio calculations which predict these differences to be 0.000 Å and 0.6°, respectively. Vibrational amplitudes were collected in groups according to their type (dependent on or independent of torsional motions) and distances. Further assumptions are evident from Table 1. With these assumptions ten geometric parameters and eight vibrational amplitudes were refined simultaneously. The following correlation coefficients had values larger than $|0.6|$: $p_1/p_2 = -0.72$, $p_3/p_4 = -0.64$, $p_3/a_2 = 0.76$, $p_4/a_2 = -0.78$, $p_5/a_5 = 0.68$. The numbering of the geometric parameters p_i and vibrational amplitudes a_k and the results of the GED analysis and the ab initio calculations are given in Table 1.

Figure 1. Experimental radial distribution function and difference curve RDF(expt)−RDF(calcd) for $CF_3SC(F)=CF_2$. Interatomic distances are indicated by vertical bars



Results and Discussion

Perfluorination of $CH_3SC(H)=CH_2$ has a strong effect on the conformational properties of this thioethene. In the parent compound and in ethenethiol the potential curve for internal rotation around the C1−S bond possesses two minima corresponding to a planar *syn* and to a *gauche* or near planar *anti* conformation. Both structures allow conjugation between the sulfur lone pair and the π-orbitals of the C=C bond. In the fluorinated derivative $CF_3SC(F)=CF_2$, however, only one stable conformation exists with the $S-CF_3$ bond nearly perpendicular to the ethene plane. In this structure no overlap between the sulfur lone pair and the π-orbitals occurs. The potential curve for internal rotation around the C1−S bond was calculated by the ab initio method for torsional angles between 60 and 180° (Figure 2). For Φ(CCSC) <60° unreasonably short F···F contacts occur [≈1.75 Å for Φ(CCSC) = 30°]. The minimum in the calculated curve lies near 90°, in good agreement with the experiment result [96.9(12)°], which is an effective value due to the large amplitude torsional motion. The planar *anti* form is predicted to be ca. 5 kcal/mol higher in energy than the ground state structure.

Table 1. Results of GED analysis and ab initio calculations for $CF_3SC(F)=CF_2$

Geometric parameters

	GED[a]		HF/3-21G*
C=C	1.302 (19)	p_1	1.305
C3-F3	1.331 (2)	p_2	1.345
(C1-F1) - (C3-F3)	0.017.[5][b]		0.017
(C2-F2) - (C3-F3)	-0.023 [5][b]		-0.023
C1-F1	1.354 (6)		1.362
C2-F2=C2-F2′	1.314 (6)		1.322
S-C1	1.719 (9)	p_3	1.732
S-C3	1.820 (10)	p_4	1.783
C2=C1-S	120.0 (9)	p_5	123.5
C2=C1-F1	119.5 (4)	p_6	118.2
(C1=C2-F2) - (C2=C1-F1)	6.0 [10][b]		6.0
(C1=C2-F2)=(C1=C2-F′)	125.5 (11)		124.2
C1-S-C3	101.7 (7)	p_7	98.1
F3-C-F4	108.9 (4)	p_8	108.2
tilt(CF_3)	3.9 (8)	p_9	3.2
Φ(C2=C1-S-C3)	96.9 (12)	p_{10}	90.2

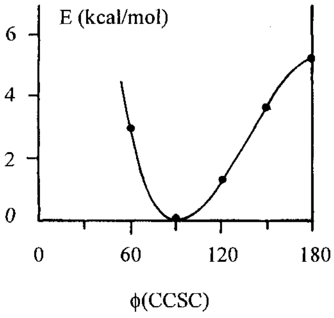
Interatomic distances and vibrational amplitudes

C=C	1.30	0.040		C1··F4	3.08	0.150[c]	
C−F	1.31 - 1.35	0.047(2)	a_1	F1··F5	3.21		
S−C	1.72 - 1.82	0.051(12)	a_2	C··F	3.40 - 3.42	0.13(2)	a_6
F··F	2.14 - 2.17	0.057(4)	a_3	C2··C4	3.54		
C··F	2.31 - 2.34	0.054(7)	a_4	C··F	3.81 - 4.06	0.16(2)	a_7
S··F	2.54 - 2.67	0.069(7)	a_5	F1··F4	3.91		
S··C2	2.64			F1··F2'	3.54	0.070[c]	
C1··C3	2.74			S··F2	3.90		
F1··F2	2.74	0.075[c]		C··F	4.66 - 4.69	0.25(3)	a_8
S··F2'	2.97			F··F	4.39 - 4.97		
				F2··F3	5.89	0.17[c]	

[a] r_a distances in Å and α angles in degree. Error limits are 3σ values and include possible systematic errors (see text). — [b] Constrained to the ab initio value with estimated uncertainty in brakkets. — [c] Not refined.

Fluorination also affects the skeletal bond lengths. The C=C bond is shortened from 1.343(1) Å in $CH_3SC(H)=CH_2$[8] to 1.302(19) Å in $CF_3SC(F)=CF_2$. The latter value agrees within experimental uncertainties with the bond length in tetrafluoroethene [1.311(7) Å[11]]. The two S−C bonds are affected differently by fluorination. The $C(sp^2)-S$ bond is shortened from 1.759(8) Å to 1.719(9) Å and the $S-C(sp^3)$ bond is lengthened from 1.795(8) Å to 1.820(10) Å upon fluorination. The ab initio calculation at the HF/3-21G* level reproduces the experimental geometric parameters reasonably well. The difference between the two S−C bond lengths is underestimated by the calculation and the discrepancy between the calculated and experimental dihedral angles Φ is partly due to a large amplitude torsional motion. Because of the large asymmetry of the torsional potential near the minimum (see Figure 2), the average torsional angle is expected to be larger than the equilibrium value.

Figure 2. Calculated (HF/3-21G*) potential curve for internal rotation around the C(sp^2)–S bond in $CF_3SC(F)=CF_2$



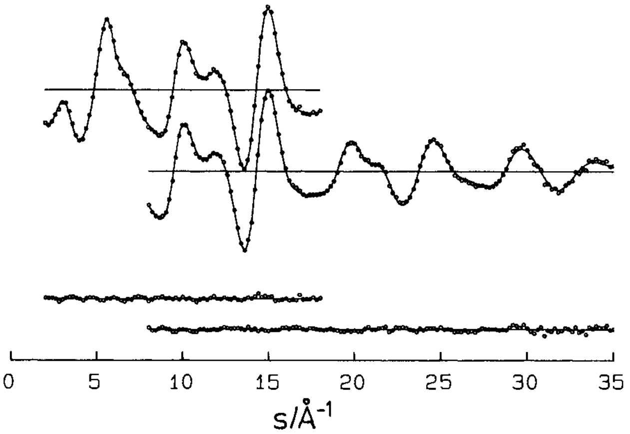
We gratefully acknowledge financial support by the *Fondacion Antorchas* and the *Deutsche Akademische Austauschdienst*. A. O. is grateful for a *Heinrich Hertz* fellowship.

Experimental

Synthesis of $CF_3SC(F)=CF_2$: 70 ml of freshly distilled ethanol, dried with CaO, was heated with 50 g of activated Zn up to reflux temperature with vigorous stirring[12]. A mixture (16 g) of the isomers $CF_3S-CFCl-CF_2Cl$ (80%) and $CF_3S-CF_2-CFCl_2$ (20%) was added and the mixture was allowed to react for 60 min. Only the former isomer reacted to give the expected product[13]. The volatile substances were trapped at −78 °C. The pure product was obtained by fractional condensation (20, −20, −78 and −196 °C) in the trap cooled to −78 °C as colorless liquid. The yield was 5 g (27 mmol) of $CF_3SC(F)=CF_2$ (theoretical yield 58% of starting mixture or 9.2 g). The product was identified by IR (Bruker IFS 85), ^{19}F-NMR (Bruker WP 80 PFT) and GC-MS spectroscopy. – IR (gas): $\tilde{\nu}$ [cm^{-1}] = 1746.4 (s) [ν(C=C)], 1337.1 (s), 1185.7 (vs), 1122.0 (s), 1054.5 (s), 759.2 (m), 606.5 (w). – ^{19}F-NMR ($CFCl_3$); $CF_3SC(F_X)=CF_AF_B$ (F_A *cis* to F_X and F_B *trans* to F_X): $\delta(CF_3) = -42.05$ (m), $\delta(F_A) = -81.05$, $\delta(F_B) = -100.25$, $\delta(F_X) = -151.80$; $J^2(F_AF_B) = 122.07$ Hz, $J^3(F_AF_X) = 26.40$, $J^3(F_BF_X) = 40.50$, $J^4(F_XCF_3) = 2.90$, $J^5(F_ACF_3) = 2.40$, $J^5(F_BCF_3) = 2.30$. – MS (70 eV) *m/z* (%): 182 (44) [M$^+$]; 163 (3.3) [M$^+$ − F]; 94 (63.2) [SC(F)=CF$^+$]; 69 (83.5) [CF_3^+]; 63 (100) [SCF$^+$].

Gas Electron Diffraction: The GED intensities were recorded with a Gasdiffractograph KD-G2[14] at two camera distances (25 and 50 cm) and with an accelerating voltage of ca. 60 kV. The electron wavelength was calibrated by a ZnO powder diffraction analysis. The sample reservoir was cooled to −56 °C and the inlet system and nozzle were at room temperature. The camera pressure during the experiment was below 2×10^{-5} Torr. Exposure times were 5–7 and 18–25 s for the long and short camera distance, respectively. The photographic plates were analyzed with standard methods[15] 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 Δs = 0.2 Å^{-1} are presented in Figure 3.

Figure 3. Experimental (dots) and calculated (full line) molecular intensities for the long (above) and short (below) nozzle-to-plate-distances and differences



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