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Vibrational spectra, gas phase structure and conformational properties of perfluorodimethyl trithiocarbonate, (CF₃S)₂C=S

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Dedicated to Professor Lou Allinger in recognition of his significant contributions to the field of molecular mechanics

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Abstract

The molecular structure and conformational properties of perfluorodimethyl trithiocarbonate, (CF₃S)₂C=S, were studied by gas electron diffraction (GED), vibrational spectroscopy and quantum chemical calculations (HF, MP2 and B3PW91 with 6-31G* basis sets). From Raman spectra a composition of 60(10)% (*syn,syn*) and 40(10)% (*syn,anti*) conformers ($\Delta G^0 = 0.2(2)$ kcal mol^{-1}) was derived for the liquid state. *Syn/anti* describes the orientation of the S–CF₃ bonds relative to the C=S bond. The GED investigation resulted in a mixture of 84(12)% (*syn,syn*) and 16(12)% (*syn,anti*) conformers for the gas phase ($\Delta G^0 = 1.0(5)$ kcal mol^{-1}). The calculations predict energy differences between the two conformers from 0.4 (B3PW91) to 0.9 (HF) kcal mol^{-1}. The predominant (*syn,syn*) form possesses a non-planar sulfur–carbon skeleton of C_2 symmetry with the S–CF₃ bonds rotated out of the CS₃ plane (ϕ(S=C–S–C) = 32(4)°). The theoretical calculations predict a planar or nearly planar skeleton for the (*syn,anti*) conformer. All three computational methods reproduce bond lengths and bond angles very well. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Trithiocarbonate; Molecular structure; Conformational properties; Gas electron diffraction; Quantum chemical calculations
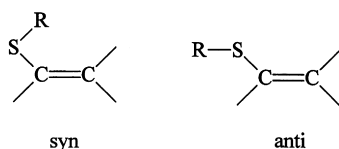
1. Introduction

The structural and conformational properties of compounds of the type RS–C(Y)=X depend primarily on the strength of conjugation between the p-shaped

sulfur electron lone pair and the π-bond, 1p(S) → π*(C=C). In ethenethiol, HS–C(H)=CH₂, this interaction stabilizes *syn*periplanar (ϕ(C=C–S–H) = 0°) and *anti*periplanar (ϕ(C=C–S–H) ≈ 180°) conformations [1]. In methyl vinyl thioether, CH₃S–C(H)=CH₂, *syn*periplanar and anticlinal (ϕ(C=C–S–C) ≈ 140°) conformations were observed [2,3]. In both compounds, the *syn* form is preferred. In these compounds, the p-shaped sulfur electron lone pair is parallel or nearly parallel to the C=C π-bond, which

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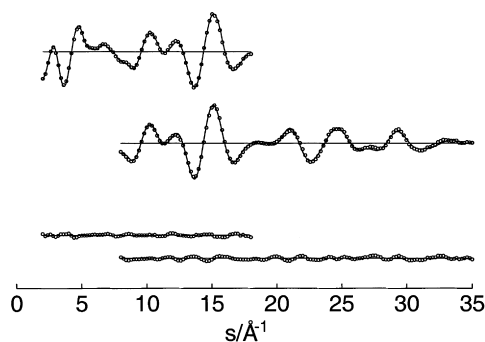*E-mail address:* heinz.oberhammer@uni-tuebingen.de (H. Oberhammer).

Scheme 1.

Fig. 1. Experimental (dots) and calculated (full line) molecular intensities for long (above) and short (below) nozzle-to-plate distances and residuals.

allows a maximum interaction with the $\pi*(C=C)$ orbital (Scheme 1). Fluorination of the methyl group in methyl vinyl thioether or perfluorination of this compound leads to a drastic change of the conformational properties. In $CF_3S–C(H)=CH_2$ and $CF_3S–C(F)=CF_2$ the CF_3 group is oriented anticlinal or nearly perpendicular to the plane of the vinyl group ($\phi(C=C–S–C) = 129.4(39)°$ [4] and $96.9(12)°$ [5], respectively). This indicates a strong decrease of the $1p(S) \rightarrow \pi^*(C=C)$ interaction upon fluorination.

Similar to ethenethiol, thioformic acid HSC(O)H exists as a mixture of planar *syn* and *anti* conformers [6]. Only a *syn*periplanar conformation was observed for *S*-methylthioformate, $CH_3SC(O)H$ [7], for trifluorothioacetic acid, $HSC(O)CF_3$ [8] for trifluorothioacetate chloride, $ClSC(O)CF_3$ [8], and for methyl trifluorothioacetate, $CH_3SC(O)CF_3$ [8]. In these carbonyl compounds, the conjugation $1p(S) \rightarrow \pi^*(C=O)$ stabilizes the sterically unfavorable planar structures and fluorination does not lead to a drastic change of the conformational properties. Also, $CF_3SC(O)F$ and $CF_3SC(O)Cl$ possess planar molecular skeletons. A mixture of *syn* and *anti* conformers exists in the case of $CF_3SC(O)F$ and only the *syn* form was observed in the case of $CF_3SC(O)Cl$ [9]. These results indicate, that the $1p(S) \rightarrow \pi^*(C=O)$ interaction does not change upon fluorination or the decrease is not strong enough to cause a conformational change as was observed in the case of $1p(S) \rightarrow \pi^*(C=C)$ interactions.

In the present investigation, we were interested in the effect of fluorination on the $1p(S) \rightarrow \pi^*(C=S)$ interaction. Dithioformic acid, HSC(S)H [10], and dimethyltrithiocarbonate, $(CH_3S)_2C=S$ [11,12] possess planar structures. In the former compound, the S–H bond is oriented *syn*- or *anti*periplanar. An electron diffraction study of the trithiocarbonate resulted for the gas phase in a planar structure with both methyl groups *syn* with respect to the C=S bond

[11]. The presence of a small amount of a (*syn,anti*) conformer could not be excluded. IR (liquid) spectra, however, show clearly a mixture of two conformers [12]. Thus, in the non-fluorinated species the conjugation between the sulfur lone pair and the C=S π-bond leads to planar structures. To obtain information about the effect of fluorination on this interaction we studied the structure and conformational properties of perfluorodimethyl trithiocarbonate using vibrational spectroscopy, gas electron diffraction (GED) and quantum chemical calculations.

2. Experimental

The first synthesis of $(CF_3S)_2C=S$ was reported by Haszeldine and Kidd in 1953 by trimerization of $F_3C=S$ [13]. This synthesis resulted in a mixture of the trimer $(CF_3S)_2C=S$ and the dimer $CF_3SC(F)=S$, which had to be separated by distillation. For our investigation, we prepared $(CF_3S)_2C=S$ by the reaction of thiophosgene, $Cl_2C=S$, with $AgSCF_3$, which resulted in a pure compound in nearly quantitative yield.

IR (gas) spectra were recorded with a Bruker IFS-66v FTIR spectrometer in a cell with 10 cm optical path length and Si windows. Raman (liquid) spectra were obtained with the Raman accessory of the same spectrometer using the 1064 nm exciting line of a narrow-band Nd-YAG Laser. The Raman measurements were performed in a glass capillary tube with a diameter of 6 mm.

The GED intensities were recorded with a

(syn,syn) (syn,anti)
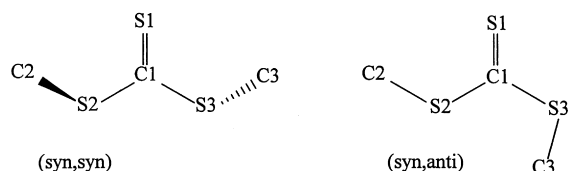
Scheme 2.

Gasdiffraktograph KD-G2 [14] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. The sample and gas nozzle were at room temperature. The photographic plates were analyzed with the usual methods [15] and averaged molecular intensities in the s-ranges 2–18 and 8–35 Å^{-1}, in intervals of $\Delta s = 0.2 \text{ Å}^{-1}$, are presented in Fig. 1.

3. Quantum chemical calculations

Geometry optimizations were performed with HF, MP2 and B3PW91 methods and 6-31G* basis sets, using the GAUSSIAN 94 [16] and GAUSSIAN 98 [17] program systems. Depending on the starting values for the two dihedral angles ϕ_1(S1=C1–S2–C2) and ϕ_2(S1=C1 − S3–C3), two minima on the energy surface were obtained for (*syn,syn*) and (*syn,anti*) conformations (see Scheme 2). The (*anti,-anti*) structure does not correspond to a minimum. The HF and B3PW91 approximations predict an exactly planar skeleton for the (*syn,anti*) conformer ($\phi_1 = 0°$, $\phi_2 = 180°$), whereas the MP2 method results in a slightly non-planar structure. All three computational methods predict the preferred (*syn,syn*) form to possess C_2 symmetry with a non-planar molecular skeleton and dihedral angles $\phi_1 = \phi_2$ between 16 and 24°. The geometric parameters and relative energies are listed together with the experimental values.

Vibrational frequencies were derived for both conformers with the three methods. The B3PW91 method reproduced the experimental values closest. This force field was used to calculate vibrational amplitudes with the program ASYM40 [18].

4. Vibrational spectra

The IR (gas) and Raman (liquid) spectra are shown in Fig. 2. The fundamental frequencies are listed
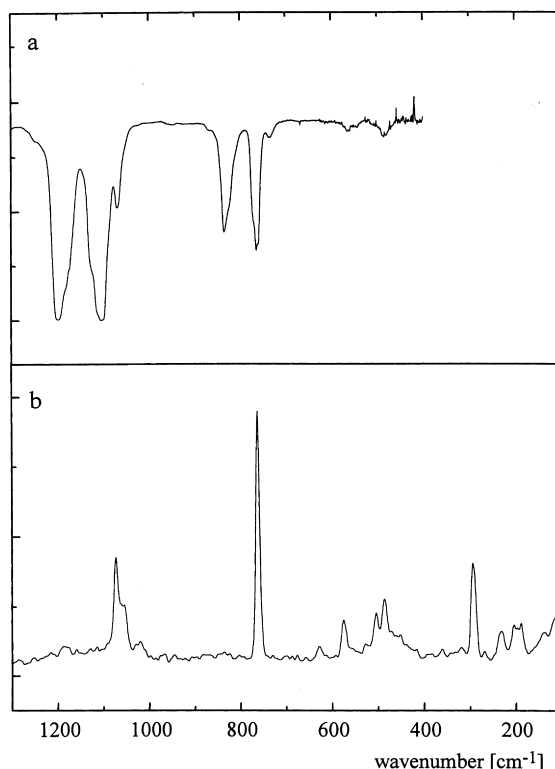

Fig. 2. Vibrational spectra of $(CF_3S)_2C=S$: (a) IR (gas) spectrum, pressure 4 mbar, resolution 1 cm^{-1}; (b) Raman (liquid) spectrum at room temperature, resolution 4 cm^{-1}.

together with their intensities and the calculated values in Table 1. The assignment is based on the potential energy distribution calculated from the theoretical force field and on comparison between experimental and calculated relative intensities.

In the Raman spectrum the C=S vibration around 1070 cm^{-1} possesses a shoulder at lower frequency, indicating the presence of two conformers. Comparison of experimental ν(C=S) Raman frequencies (1074 and 1056 cm^{-1}) with the respective calculated values (1079 and 1062 cm^{-1}) indicates very strongly that the higher frequency belongs to the (*syn,syn*) and the lower one to the (*syn, anti*) form. Deconvolution of this Raman band results in an intensity ratio $I(syn, syn) : I(syn, anti) = 1.30$. The ratio of the calculated Raman activities for these two vibrations is 0.86 (HF) and 0.90 (B3PW91). Using the mean of these two values a ratio of the two conformers of 60(10)% (*syn,syn*) and 40(10)% (*syn,anti*) is obtained for the

Table 1
Experimental and calculated vibrational frequencies of $(CF_3S)_2C=S$

		IR (gas)		Raman (liquid)			B3PW91/6-31G* [c]	Assignment
		$\tilde{\nu}(cm^{-1})$	I	$\tilde{\nu}(cm^{-1})$	I^{a}	ρ^{b}		
A	ν_1	1199	vs				1235	$\nu_{as}(CF_3)$
	ν_2	1182	sh				1224	$\nu_{as}(CF_3)$
	ν_3	1126	sh				1150	$\nu_s(CF_3)/\nu(C=S)$
	ν_4			1074	42	p	1079	$\nu(C=S)/\nu_s(CF_3)$
	ν_4' [d]	1070	m	1056	24	p	1062	$\nu(C=S)$
	ν_5	765	s	764	100	p	757	$\delta_s(CF_3)/\nu_s(CF_3)$
	ν_6			576	11	p	579	$\delta_{as}(CF_3)/\nu_s(CS_2)$
	ν_7			529	7	p	539	$\delta_{as}(CF_3)$
	ν_8			506	20	p	512	$\nu_s(CS_2)$
	ν_9			487	26	p	488	$\nu_s(S-CF_3)/\delta_{as}(CF_3)$
	ν_{10}			320	6	?	322	$\rho_{as}(CF_3)$
	ν_{11}			294	40	p	287	$\rho_s(CF_3)$
	ν_{12}'			205	15	?	206	$\delta(S=C-S)$
	ν_{12}			189	16	p	185	$\delta(S=C-S)$
	ν_{13}			100	11	p	94	$\delta(C-S-C)$
	ν_{14}						71	$\tau(S-CF_3)$
	ν_{15}						45	$\tau(C-S)$
B	ν_{16}	1199	vs				1228	$\nu_{as}(CF_3)$
	ν_{17}	1174	sh				1206	$\nu_{as}(CF_3)$
	ν_{18}	1105	vs				1092	$\nu_s(CF_3)$
	ν_{19}	836	s	836	4	?	790	$\nu_{as}(CS_2)$
	ν_{20}	762	sh				755	$\delta_s(CF_3)/\nu_s(CF_3)$
	ν_{21}	565	vw				559	$\delta_{as}(CF_3)$
	ν_{22}						539	$\delta_{as}(CF_3)$
	ν_{23}	485	vw				489	$oop(CS_3)$
	ν_{24}						441	$\nu_{as}(S-CF_3)$
	ν_{25}						384	$\rho_s(CF_3)$
	ν_{25}'			361	6	?	361	$\rho_s(CF_3)$
	ν_{26}						315	$\rho_{as}(CF_3)$
	ν_{27}			232	13	dp	240	$\delta(S=C-S)$
	ν_{28}						152	$\delta(C-S-C)$
	ν_{28}'			139	12	?	134	$\delta(C-S-C)$
	ν_{29}						81	$\tau(S-CF_3)$
	ν_{30}						31	$\tau(C-S)$

[a] Relative intensities; $I(\nu_5) \equiv 100$.
[b] p = polarised, dp = depolarised.
[c] The wavenumbers of the CF_3 stretching modes are scaled by a factor of 0.96.
[d] $\nu_i = (syn, syn)$ conformer, $\nu_i' = (syn, anti)$ conformer.

liquid phase. The error limit is estimated from uncertainties in the measurement of the relative areas and in calculated Raman activities. A splitting due to the presence of two conformers is also observed for the S–C–S deformation around 200 cm^{-1}.

In the IR (gas) spectrum only one band at 1070 cm^{-1} is observed in the C=S stretching region. The calculated IR intensities (square of transition moment) of ν(C=S) for the two conformers differ by a factor of almost 20, with the intensity for the (syn,syn) form being very weak. On the basis of these theoretical results, the IR (gas) band at 1070 cm^{-1} is assigned to ν(C=S) of the (syn,anti) conformer. This vibration for the (syn,syn) conformer, which should occur at a higher frequency, is expected to be weaker and is covered by the very strong CF stretches at 1105 cm^{-1}. Thus, the IR
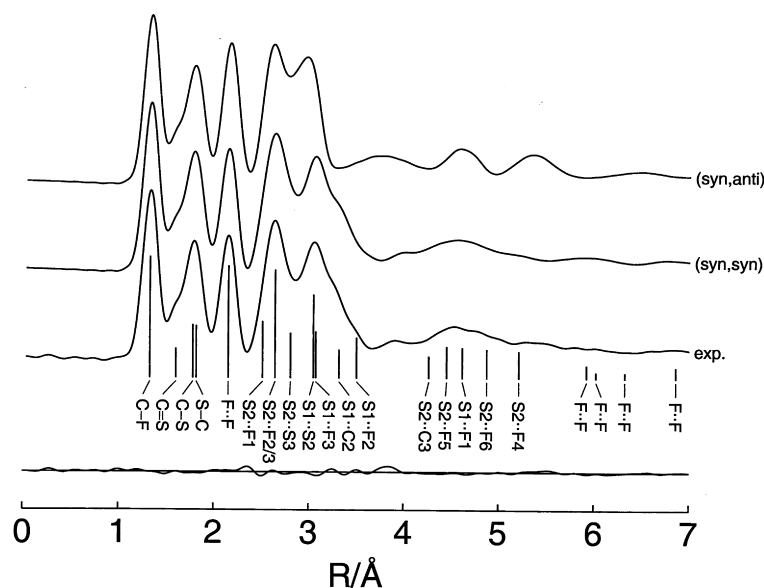
Fig. 3. Experimental and calculated radial distribution functions and difference curve for mixture. Important interatomic distances of the (*syn,syn*) conformer are shown by vertical bars.

spectra do not provide any information about the conformational properties in the gas phase.

5. Electron diffraction analysis

The radial distribution function (RDF) was derived by Fourier transformation of the molecular intensities applying an artificial damping function $\exp(-0.0019\,s^2)$. Comparison between experimental and calculated RDFs (Fig. 3) demonstrates, that the main conformer is (*syn,syn*). A preliminary structural model derived from the RDF was refined by least squares fitting of the molecular intensities. The intensities were multiplied with a diagonal weight matrix. The overall symmetry of the (*syn,syn*) conformer was constrained to C_2. Local C_{3v} symmetry was assumed for the CF_3 groups with a tilt angle between the C_3 axis and the S–C bond. The difference between the two closely spaced bond lengths $C(sp^2)$–S and S–$C(sp^3)$ was fixed to the MP2 value. Vibrational amplitudes were collected in groups and those amplitudes, which either caused high correlations with other parameters or which were badly determined by the GED experiment,

were set to the calculated (B3PW91) values. With these assumptions nine geometric parameters (p) and twelve vibrational amplitudes (l) were refined simultaneously. The following correlation coefficients had values larger than $|0.5|$: $p1/p4 = -0.52$, $p3/p6 = 0.59$, $p5/p8 = -0.74$, $p5/p9 = 0.50$, $p7/l4 = -0.66$, $p8/p9 = -0.57$, $l4/l5 = 0.76$ and $l9/l10 = 0.52$.

Slight improvement of the fit was obtained by addition of a small amount of (*syn,anti*) conformer. Bond lengths and bond angles for this conformer were tied to those of the (*syn,syn*) structure using the calculated (MP2) differences. The largest difference occurs for the S1=C1–S3 angle, which decreases from 127.7° for the (*syn,syn*) form to 116.0° for the (*syn,anti*) form. The two dihedral angles ϕ_1(S1=C1–S2–C2) and ϕ_2(S1=C1–S3–C3) were set to the MP2 values. All vibrational amplitudes for this conformer were fixed to the calculated values. Least squares analyses with different contributions were performed. The best fit was obtained for 16(12)% contribution of the (*syn,anti*) form. The uncertainty was derived with the Hamilton test [19] at a 1% significance level. The final results of the GED analysis are listed together with those of the quantum chemical

Table 2
Experimental and calculated geometric parameters of the (*syn,syn*) conformer of $(CF_3S)_2C=S$ and conformational properties

	GED[a]		HF/6-31G*	MP2/6-31G*	B3PW91/6-31G*
C=S	1.605(8)	p1	1.605	1.618	1.621
$C(sp^2)$–S	1.784(3)	p2	1.776	1.779	1.781
S–$C(sp^3)$	1.820(3)[b]		1.814	1.816	1.838
(C–F)$_{mean}$	1.329(2)	p3	1.310	1.340	1.332
S=C–S	128.1(3)	p4	127.5	127.7	128.1
C–S–C	102.7(7)	p5	104.8	102.1	103.8
(F–C–F)$_{mean}$	108.4(2)	p6	108.5	108.4	108.8
tilt (CF_3)	5.7(4)	p7	5.7	5.3	5.5
ϕ(S=C–S–C)	31.8(33)	p8	16.5	23.1	19.8
τ(CF_3)[c]	−0.2(25)	p9	−6.4	−9.2	−7.7
ϕ_1(S=C–S2–C2)[d]	8.6[e]		0.0	8.6	0.0
ϕ_2(S=C–S3–C3)[d]	−167.7[e]		180.0	−167.7	180.0
%(*syn,syn*)	84(12)		82	79	66
$\Delta G^0/\Delta E$ (gas)[f]	1.0(5)		0.9	0.8	0.4
ΔG^0 (liquid)[g]	0.2(2)				

[a] r_a distances and $\angle_a$ angles (°). Error limits are 3σ values. For atom numbering see Fig. 4.
[b] Difference $(S–C(sp^3))–(C(sp^2)–S)$ constrained to 0.036 Å (MP2 value).
[c] Torsion of the CF_3 groups from exactly staggered orientation.
[d] Dihedral angles for the (*syn,anti*) conformer. Different sign implies that both CF_3 groups lie on the same side of the CS_3 plane.
[e] Not refined.
[f] $\Delta G^0 = G^0(syn, anti) − G^0(syn, syn)$ from GED and $\Delta E = E(syn, anti) − E(syn, syn)$ from quantum chemical calculations in kcal mol^{-1}.
[g] ΔG^0 from the Raman spectrum of the liquid.

calculations in Table 2 (geometric parameters and conformational properties) and Table 3 (vibrational amplitudes). Molecular models of the two conformers are shown in Fig. 4.

6. Discussion

The electron diffraction analysis for gaseous perfluorodimethyl trithiocarbonate results in a mixture of 84(12)% (*syn,syn*) and 16(12)% (*syn,anti*) conformers. From Raman spectra, a composition of 60(10)% (*syn,syn*) and 40(10)% (*syn,anti*) was derived for the liquid state. Similar conformational properties have previously been reported for the non-fluorinated derivative $(CH_3S)_2C=S$. According to a GED experiment [11] the (*syn,syn*) form is present in the gas phase and a small amount of the (*syn,anti*) conformer could not be ruled out. IR spectra of the liquid and of solutions indicate a considerable contribution of the (*syn,anti*) form, which increases with increasing polarity of the solvent [12]. Thus, fluorination has no strong influence on the conformational properties of dimethyl trithiocarbonate. A strict

comparison between the experimental ΔG^0 and the calculated ΔE values is difficult in this case. HF and B3PW91 calculations predict the (*syn,anti*) conformer to possess a planar skeleton, whereas the MP2 method predicts a slightly non-planar structure. In the latter case we certainly expect non-rigid behavior with large amplitude vibrations. On the other hand, the (*syn,syn*) conformer is non-planar but the barrier to planarity is expected to be small. This may also lead to non-rigid behavior. Thus, a reliable calculation of entropies and temperature corrections is not possible for this molecule. If we assume the two minima for the (*syn,syn*) conformer ($\phi = \pm32(4)°$) to represent separate structures, the multiplicity of (*syn,syn*) and (*syn,anti*) conformers would be equal. Thus, roughly we can compare ΔG^0 with the calculated ΔE values.
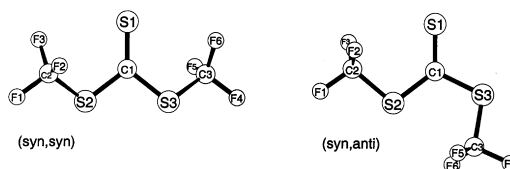

Fig. 4. Molecular models with atom numbering.

Table 3
Interatomic distances and vibrational amplitudes for the (*syn*,*syn*) conformer of $(CF_3S)_2C=S$ (values in Å; error limits are 3σ values. For atom numbering see Fig. 4)

	Distance	Ampl. GED		Ampl. B3PW91/6-31G* [a]
C–F	1.33	0.044(2)	l1	0.044
C–S	1.61	0.044(2)	l1	0.042
C–S	1.78	0.057(4)	l2	0.053
S–C	1.82	0.057(4)	l2	0.053
F···F	2.16	0.057(3)	l3	0.056
S2···F1	2.51	0.062(8)	l4	0.071
S2···F2/3	2.64	0.062(8)	l4	0.067
S2···S3	2.81	0.075(12)	l5	0.073
C1···C2	2.81	0.075(12)	l5	0.081
S1···S2	3.05	0.080(6)	l6	0.060
S1···F3/2	3.07–3.50	0.195[b]		0.195
C1···F2/3	3.16–3.17	0.141[b]		0.141
S1···C2	3.32	0.084(20)	l7	0.116
C1···F1	3.96	0.104(36)	l8	0.077
S2···C3	4.26	0.180(47)	l9	0.104
S2···F5	4.45	0.233[b]		0.233
S1···F1	4.61	0.180(47)	l9	0.111
S2···F6/4	4.88–5.21	0.181(50)	l10	0.121
C2···C3/F4	5.62–6.69	0.166(88)	l11	0.101
C2···F5/6	5.84–5.89	0.275(93)	l12	0.207
F2···F6	5.92	0.334[b]		0.334
F3···F6	6.02	0.221[b]		0.221
F1···F5	6.86	0.221[b]		0.221
F2···F5	6.32	0.200[b]		0.200
F1···F6	7.10	0.200[b]		0.200
F1···F4	7.68	0.166(88)	l11	0.120

[a] Mean values are given for amplitudes, which are not unique.
[b] Not refined.

Considering the large uncertainty for ΔG^0(gas) this value is reproduced very well by the three computational methods (see Table 2).

Fluorination, however, has some influence on the structural properties. Whereas the molecular skeleton of the (*syn*,*syn*) conformer of $(CH_3S)_2C=S$ is planar (C_{2v} symmetry), the fluorinated derivative possesses C_2 symmetry with the CF_3 groups above or below the CS_3 plane and $\phi_1(S1=C1–S2–C2) = \phi_2(S1=C1–S3–C3) = 32(4)°$. This deviation from planarity suggests that conjugation between sulfur lone pairs and the π-bond, $1p(S) \rightarrow \pi^*(C=S)$, decreases upon
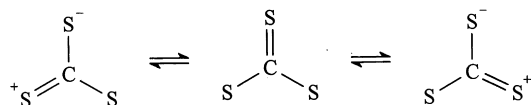
Scheme 3.

fluorination. Such a decrease of conjugation also shows up in the bond lengths. Loss of conjugation causes shortening of the C=S bond and lengthening of the $C(sp^2)$–S single bonds (see Scheme 3). The trends observed for the experimental bond lengths upon fluorination, i.e. shortening of the double bond from 1.634(5) to 1.605(8) Å and lengthening of the single bonds from 1.752(4) to 1.784(3) Å demonstrate such a loss of conjugation.

Table 2 compares experimental and calculated geometric parameters of $(CF_3S)_2C=S$. All three computational methods reproduce the bond lengths better than ± 0.02 Å and the bond angles better than $\pm 2°$. The experimental dihedral angle $\phi(S=C–S–C)$ is about 10° larger than the predicted values. To some extent this difference may be due to large amplitude torsional vibrations, which make the vibrationally averaged dihedral angle different from the

equilibrium value. The same applies to the torsional angle of the CF_3 groups.

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