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Vibrational spectra and structures of halogencarbonyl alkyldisulfanes XC(O)SSR with X = F, Cl and R = CF_3, CH_3

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Abstract

The disulfides $FC(O)SSCF_3$, $ClC(O)SSCF_3$ and $ClC(O)SSCH_3$ have been prepared by new synthetic routes. Infrared and Raman spectra have been recorded and assigned. From the vibrational spectra and from the gas electron diffraction experiment it was concluded that $FC(O)SSCF_3$ exists as a mixture of syn- and anti-conformers (C=O synperiplanar/antiperiplanar to S–S bond). The main conformer (83(5)% and $\Delta G^\circ = G^\circ(\text{anti}) - G^\circ(\text{syn}) = 0.95(28)$ kcal mol^{-1}) possesses syn-structure. The vibrational spectra of the chlorocarbonyl disulfanes are interpreted in terms of a single conformer, but small amounts (<5%) of a second conformer cannot be excluded. Quantum chemical calculations (HF, MP2, B3PW91 with 6-31G* basis sets) reproduce the experimental results (conformational properties, geometric structure and vibrational frequencies) satisfactorily. The predicted difference in Gibbs free energy, ΔG°, for $FC(O)SSCF_3$ varies between 0.8 and 1.5 kcal mol^{-1}, those for the chlorine derivatives are larger than 2.6 kcal mol^{-1}.

Keywords: Halogencarbonyl alkyldisulfanes; Vibrational spectra; Gas electron diffraction; Quantum chemical calculations

1. Introduction

The tertiary structure of many biological compounds is determined to a large extent by the structural properties of disulfane bridges. The most important structural property of disulfanes RSSR′ is the dihedral angle around the S–S bond (ϕ(R–S–S–R′)). The ''ideal'' value for this angle is 90°. In this case the p-shaped lone pairs of the two sulfur atoms are perpendicular to each other and this orientation allows maximum orbital interaction between these lone pairs and the opposite S–R bond (anomeric effect, lp(S) → σ*(S–R)). In many compounds these dihedral angles are indeed close to 90°, e.g. 90.76(6)° in HSSH [1], 87.7(4)° in FSSF [2], 85.2(2)° in ClSSCl [3] and 85.3(37)° in CH_3SSCH_3 [4]. Steric repulsion between the substituents may lead to larger dihedral angles such as 104.4(40)° in CF_3SSCF_3 [5] or 128.3(27)° in Bu^tSSBu^t [6]. The smallest dihedral angle for a gaseous disulfane was observed for bis(fluorocarbonyl)disulfane, FC(O)SSC(O)F (82.2(19)° [7]).

In the present study we report syntheses and the characterization of some halogencarbonyl alkyldisulfanes of the type XC(O)SSR with X = F or Cl and R = CH_3 or CF_3. These compounds can exist in two different conformeric forms, syn or anti (see Scheme 1), in which the C=O bond is syn- or antiperiplanar relative to the S–S bond. $FC(O)SSCF_3$ has been prepared by two synthetic routes, its vibrational spectra (IR (gas) and Raman (liquid)) were recorded and its geometric structure and conformational properties were determined by gas electron diffraction (GED). Syntheses and vibrational spectra are reported for $ClC(O)SSCF_3$ and $ClC(O)SSCH_3$. For these three compounds and for $FC(O)SSCH_3$ quantum chemical calculations have been performed. Vibrational [8] and microwave spectra [9] for the latter compound have been reported previously.

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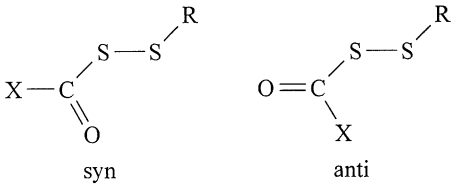

Scheme 1.

2. Experimental

2.1. Preparation of $FC(O)SSCF_3$

$FC(O)SSCF_3$ has previously been obtained by reaction of FC(O)SCl with $Hg(SCF_3)_2$ [10–12] and by treatment of FC(O)Cl or FC(O)F with CF_3SSH at the presence of an alkalimetal fluoride (CsF, KF) [13,14]. For our investigation we prepared $FC(O)SSCF_3$ by the reaction of FC(O)SCl with $AgSCF_3$ at room temperature or with CF_3SH in a temperature range from −13 to 5 °C. In both cases the purification was performed by trap-to-trap distillation.

2.2. Preparation of $ClC(O)SSR$ ($R = CF_3$, CH_3)

Haas et al. prepared $ClC(O)SSCF_3$ analogous to $FC(O)SSCF_3$ by reaction of ClC(O)SCl and $Hg(SCF_3)_2$ [10–12]. The synthesis of $ClC(O)SSCH_3$ is described in two patents of A.G. Bayer. The first patent is based on the reaction of ClC(O)SCl with CH_3SH [15]. In the second patent $ClC(O)SSCH_3$ was obtained by heating ClC(O)SCl with $H_2NC(O)SCH_3$ [16]. In our synthesis we used the fluorocarbonyl derivatives FC(O)SSR ($R = CF_3$, CH_3) as starting materials and treated them with BCl_3. This halogen exchange with BCl_3 was described in the literature for similar molecules [12]. The product was purified again by fractional distillation at reduced pressure.

2.3. Vibrational spectra

IR spectra were recorded with a Bruker IFS-113v FT-IR spectrometer (resolution 1 cm^{-1}). The spectra of the gas ($FC(O)SSCF_3$, $ClC(O)SSCF_3$) were measured in a cell with 10 cm optical path length and Si windows, the spectrum of liquid $ClC(O)SSCF_3$ was measured as a film between AgCl plates. Raman spectra of the liquid were obtained with a Spex Ramalog spectrometer (resolution 5 cm^{-1}). Radiation of 514.5 nm from a Spectra Physics Model 165 argon ion laser was used for excitation. The Raman measurements were performed in glass capillary tubes with a diameter of 6 mm.

2.4. Gas electron diffraction

The GED intensities of $FC(O)SSCF_3$ were recorded with a Gasdiffraktograph KD-G2 [17] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. The sample reservoir was kept at −13 °C, and the inlet system and nozzle were at room temperature. The photographic plates were analyzed with the usual methods [18]. Averaged molecular intensities in the *s*-ranges 2–18

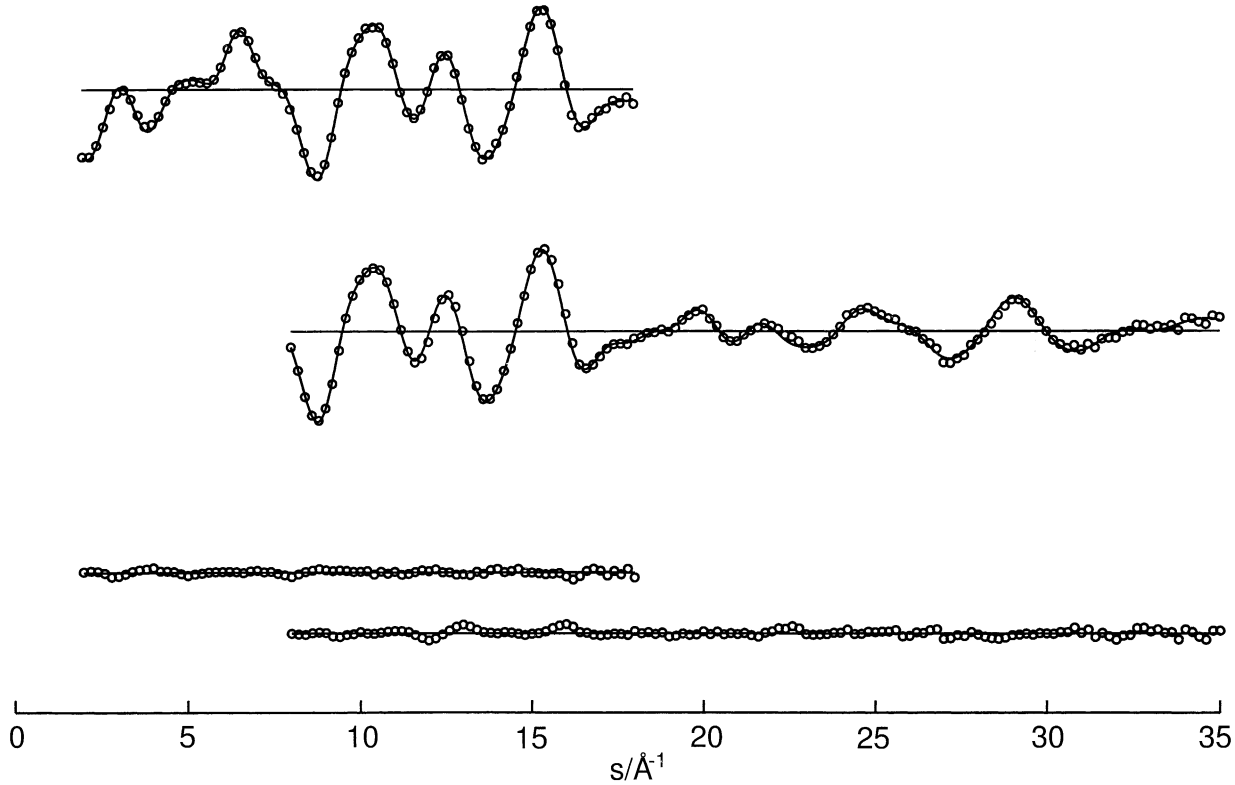

Fig. 1. Experimental (circled curve) and calculated (full line) molecular intensities and differences for $FC(O)SSCF_3$.

Table 1
Calculated relative Gibbs free energies $\Delta G^\circ = G^\circ(\text{anti}) - G^\circ(\text{syn})$ for the compounds XC(O)SSR with X = F, Cl and R = CF_3, CH_3 (kcal mol^{-1}).

	$FC(O)SSCF_3$	$FC(O)SSCH_3$	$ClC(O)SSCF_3$	$ClC(O)SSCH_3$
HF/6-31G*	1.20	1.55	3.39	3.39
MP2/6-31G*	1.49	1.71	3.11	2.97
B3PW91/6-31G*	0.82	1.09	2.55	2.55

and 8–35 $Å^{-1}$ in intervals of $\Delta s = 0.2$ $Å^{-1}$ are presented in Fig. 1 ($s = (4\pi/\lambda)\sin(\theta/2)$), λ is the electron wavelength and θ is scattering angle.

3. Quantum chemical calculations

The geometries of the syn- and anti-conformers of the four compounds XC(O)SSR with X = F, Cl and R = CF_3, CH_3 were optimized with ab initio techniques (HF and MP2) and with the hybrid method B3PW91. 6-31G* basis sets were used for the three methods. Frequency calculations indicate that both conformers represent stable structures. In all cases the syn-form is predicted to be lower in energy. The Gibbs free energy differences ΔG° which are more relevant for comparison with experiments than the relative energies ΔE are listed in Table 1. The differences between ΔE and ΔG° are in all cases smaller than 0.2 kcal mol^{-1}.

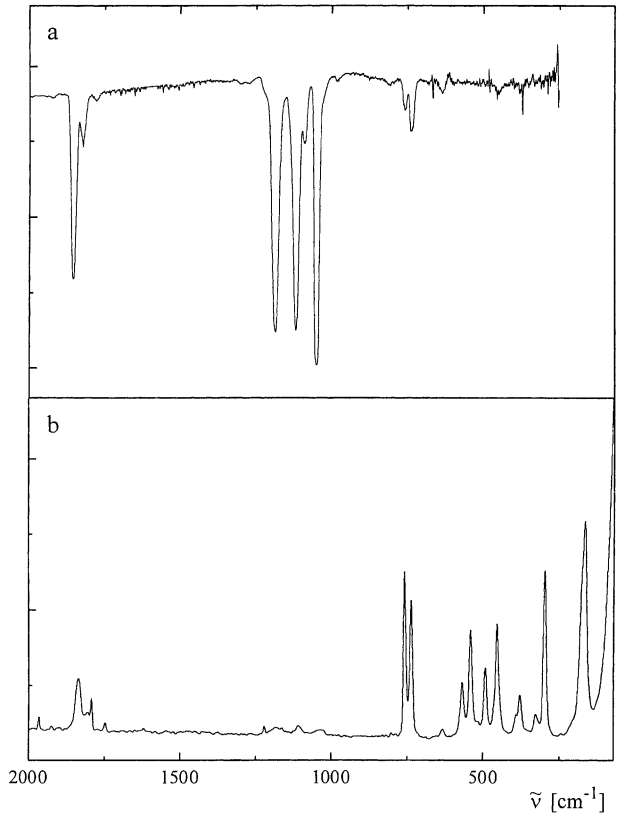

Fig. 2. Vibrational spectra of $FC(O)SSCF_3$: (a) IR (gas) spectrum, pressure 3.1 mbar, resolution 1 cm^{-1}; (b) Raman (liquid) spectrum at room temperature, resolution 5 cm^{-1}.

The dihedral angles in the two $XC(O)SSCF_3$ compounds are around 90° or slightly smaller and those in the CH_3 derivatives around 80° or slightly smaller. The calculated barriers to internal rotation around the S–S bonds are for all four compounds about 6 kcal mol^{-1} in the *trans*-configuration (ϕ(C–S–S–C) = 180°) and 10–13 kcal mol^{-1} in the *cis* (ϕ(C–S–S–C) = 0°) configuration.

The Cartesian force constants for $FC(O)SSCF_3$ (MP2 values) were transformed to a symmetry force field which was used to derive vibrational amplitudes. All quantum chemical calculations were performed with the GAUSSIAN 94 program suite [19] and the vibrational amplitudes were calculated with the program ASYM40 [20].

4. Vibrational spectra

IR (gas) and Raman (liquid) spectra for $FC(O)SSCF_3$ are shown in Fig. 2. The vibrational frequencies and intensities for this compound and for the other two disulfanes $ClC(O)SSCF_3$ and $ClC(O)SSCH_3$ are listed together with the calculated frequencies in Tables 2–4. The vibrations were assigned by comparison with similar molecules such as $FC(O)SSCH_3$ [8], FC(O)SSC(O)F [21], CF_3SSX (X = F, Cl, Br) [22], ClC(O)SSC(O)Cl [23], ClC(O)SBr [24] and $ClC(O)SSCH_3$ [25], and by comparison with calculated frequencies and intensities. The assignments in Tables 2–4 are based on the potential energy distributions which were derived from the calculated Cartesian force fields with the program ASYM40 [20]. In carbonyl compounds ν(C=O) is known to be very sensitive to conformational properties. The presence of two C=O bands in the IR and Raman spectra of $FC(O)SSCF_3$ indicates the existence of two conformers. Splitting is also observed for the $C(sp^2)$–F stretch (ν_5) and for the F–C=O rocking vibration (ν_{14}). Comparison with the calculated frequencies allows an assignment of these bands to the syn- and anti-conformers. The conformational composition was derived from the intensities of the C=O vibrations. Deconvolution results in a ratio of the areas $A_{syn}/A_{anti} = 3.57$. The ratio of the calculated intensities (square of transition moments) of the C=O vibrations in the two conformers is 0.74 (average of HF, MP2 and B3PW91). This analysis leads to a composition of 83(5)% syn and 17(5)% anti. The estimated error limit includes uncertainties in the measured areas and in the calculated intensities.

No splitting of the C=O vibration is observed in the spectra of $ClC(O)SSCF_3$ and $ClC(O)SSCH_3$. According to the calculations (B3PW91) which predict differences of

Table 2
Experimental and calculated vibrational frequencies of $FC(O)SSCF_3$

	IR (gas)		Raman (liquid)		B3PW91/6-31G*[b]	Assignment
	$\tilde{\nu}$ (cm^{-1})	I	$\tilde{\nu}$ (cm^{-1})	I[a]		
ν_1	1854	s	1834	31	1847	ν(C=O)
ν_1'[c]	1824	w	1793	20	1820	ν(C=O)
ν_2	1187	vs	1185	6	1194	$\nu_{as}(CF_3)$
ν_3			1164	5	1185	$\nu_{as}(CF_3)$
ν_4	1119	vs	1109	6	1138	$\nu_s(CF_3)/\delta_s(CF_3)$
ν_5'	1090	w			1069	$\nu(C(sp^2)–F)$
ν_5	1051	vs	1037	4	1057	$\nu(C(sp^2)–F)$
ν_6	759	w	758	99	765	$\delta_s(CF_3)/\nu_s(CF_3)$
ν_7	740	w	736	82	750	δ(F–C=O)/$\nu(C(sp^2)–S)$
ν_8	636	vw	633	5	642	oop(FC(O)S)
ν_9			567	34	572	ν(S–S)/$\delta_{as}(CF_3)$
ν_{10}			539	64	542	$\delta_{as}(CF_3)/\nu$(S–S)
ν_{11}					536	$\delta_{as}(CF_3)$
ν_{12}			491	42	492	$\nu(C(sp^2)–S)/\delta$(F–C=O)
ν_{13}	456	vw	452	68	453	$\nu(S–C(sp^3))$
ν_{14}'			391	14	393	ρ(F–C=O)
ν_{14}			377	26	380	ρ(F–C=O)
ν_{15}			326	14	326	$\rho_{as}(CF_3)$
ν_{16}			295	100	292	$\rho_s(CF_3)$
ν_{17}			165		170	$\delta(C(sp^2)–S–S)$
ν_{18}					156	$\delta(S–S–C(sp^3))$
ν_{19}					71	τ(FC(O)–S)
ν_{20}					57	τ(S–S)
ν_{21}					39	$\tau(S–CF_3)$

[a] Relative intensities: $I(\nu_{16}) \equiv 100$.
[b] The calculated wave-numbers of the C=O, the $C(sp^2)$–F and the asymmetric CF_3 stretching modes are scaled by a factor of 0.95.
[c] ν_i: syn-conformer; ν_i': anti-conformer.

Table 3
Experimental and calculated vibrational frequencies of $ClC(O)SSCF_3$

	IR (gas)		Raman (liquid)		B3PW91/6-31G*[a]	Assignment
	$\tilde{\nu}$ (cm^{-1})	I	$\tilde{\nu}$ (cm^{-1})	I[b]		
ν_1	1815	s	1799	13	1804	ν(C=O)
ν_2	1189	vs	1170	2	1194	$\nu_{as}(CF_3)$
ν_3					1186	$\nu_{as}(CF_3)$
ν_4	1116	vs	1087	7	1131	$\nu_s(CF_3)/\delta_s(CF_3)$
ν_5'[c]	856	vw			872	ν_{as}(Cl–C–S)/δ(Cl–C=O)
ν_5	810	vs			828	ν_{as}(Cl–C–S)/δ(Cl–C=O)
ν_6	759	w	755	52	764	$\delta_s(CF_3)/\nu_s(CF_3)$
ν_7			574	100	585	ν_s(Cl–C–S)
ν_8	569	vw			573	oop(ClC(O)S)
ν_9					565	$\delta_{as}(CF_3)/\nu$(S–S)
ν_{10}			530	13	536	$\delta_{as}(CF_3)$
ν_{11}					530	ν(S–S)/$\delta_{as}(CF_3)$
ν_{12}	457	vw	450	34	452	$\nu(S–C(sp^3))$
ν_{13}	426	vw	424	49	428	δ(Cl–C=O)/ν_{as}(Cl–C–S)
ν_{14}			338	9	340	$\rho_s(CF_3)/\rho_{as}(CF_3)$
ν_{15}			321	12	323	$\rho_{as}(CF_3)$
ν_{16}			241	77	239	ρ(Cl–C=O)/$\rho_s(CF_3)$
ν_{17}			156	74	158	$\delta(S–S–C(sp^3))$
ν_{18}					152	$\delta(C(sp^2)–S–S)$
ν_{19}					58	τ(ClC(O)–S)
ν_{20}					50	τ(S–S)
ν_{21}					42	$\tau(S–CF_3)$

[a] The calculated wave-numbers of the C=O and the asymmetric CF_3 stretching modes are scaled by a factor of 0.95.
[b] Relative intensities: $I(\nu_7) \equiv 100$.
[c] ν_i: syn-conformer; ν_i': anti-conformer.

Table 4
Experimental and calculated vibrational frequencies of $ClC(O)SSCH_3$

	IR (liquid)		Raman (liquid)		B3PW91/6-31G*[a]	Assignment
	$\tilde{\nu}$ (cm^{-1})	I	$\tilde{\nu}$ (cm^{-1})	I[b]		
ν_1	2997	w	2995	14	3032	$\nu_{as}(CH_3)$
ν_2					3015	$\nu_{as}(CH_3)$
ν_3	2922	w	2924	97	2925	$\nu_s(CH_3)$
ν_4	1774	vs	1772	12	1788	ν(C=O)
ν_5	1428	w	1429	5	1502	$\delta_{as}(CH_3)$
ν_6	1416	w	1415	6	1483	$\delta_{as}(CH_3)$
ν_7	1311	w	1311	3	1383	$\delta_s(CH_3)$
ν_8	960	w	959	3	1003	$\rho_s(CH_3)$
ν_9					997	$\rho_{as}(CH_3)$
$\nu_{10}{}'$[c]	846	w			861	ν_{as}(Cl–C–S)/δ(Cl–C=O)
ν_{10}	797	vs	795	3	827	ν_{as}(Cl–C–S)/δ(Cl–C=O)
ν_{11}	692	vw	691	48	709	ν(S–C(sp^3))
ν_{12}	570	w	567	100	582	ν_s(Cl–C–S)
ν_{13}					575	oop(ClC(O)S)
ν_{14}	522	w	518	17	522	ν(S–S)
ν_{15}	420	w	418	51	426	δ(Cl–C=O)/ν_{as}(Cl–C–S)
ν_{16}			285	30	282	δ(S–S–C(sp^3))/ρ(Cl–C=O)
ν_{17}			235	78	226	δ(S–S–C(sp^3))/ρ(Cl–C=O)
ν_{18}			164	28	187	τ(S–CH_3)
ν_{19}					150	δ(C(sp^2)–S–S)/τ(S–CH_3)
ν_{20}					73	τ(ClC(O)–S)
ν_{21}					65	τ(S–S)

[a] The calculated wave-numbers of the C=O and the CH_3 stretching modes are scaled by a factor of 0.95.
[b] Relative intensities: $I(\nu_{12}) \equiv 100$.
[c] ν_i: syn-conformer; ν_i': anti-conformer.

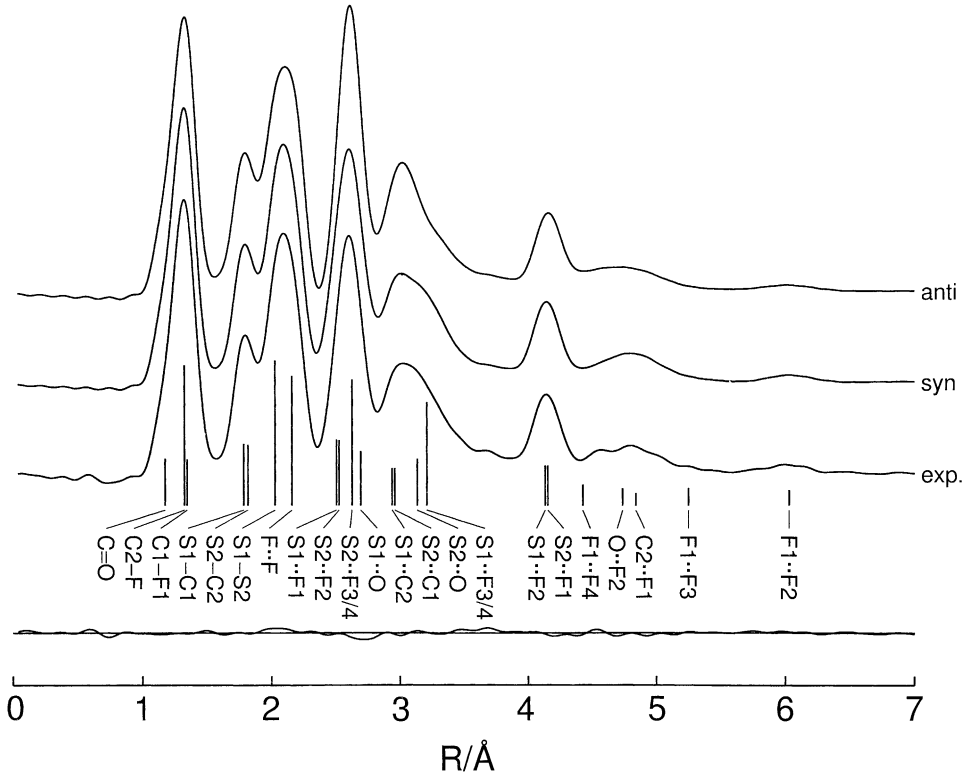

Fig. 3. Calculated and experimental radial distribution functions for $FC(O)SSCF_3$ and difference curve for the mixture. Important interatomic distances of the syn-conformer are shown by vertical bars.

the C=O vibrations for the syn- and anti-conformer of 37 and 22 cm^{-1}, respectively, the presence of a second conformer should show up in this region. On the other hand, very weak satellites or shoulders for other vibrations occur in the IR (gas) spectrum of $ClC(O)SSCF_3$ (ν_5) and in the IR (liquid) spectrum of $ClC(O)SSCH_3$ (ν_{10}). These features of the spectra could indicate the presence of a second conformer, but in any case it would be very small (<5%).

5. Structure analysis for $FC(O)SSCF_3$

The experimental radial distribution function (RDF) was obtained by Fourier transformation of the molecular intensities (Fig. 3). The RDF's which were calculated for the two conformers differ mainly in the region 2.5–3.5 Å. These differences are due to different S1–C1=O and S1–C1–F1 angles in the syn- and anti-conformer (for atom numbering see Fig. 4). According to the calculations (MP2) the

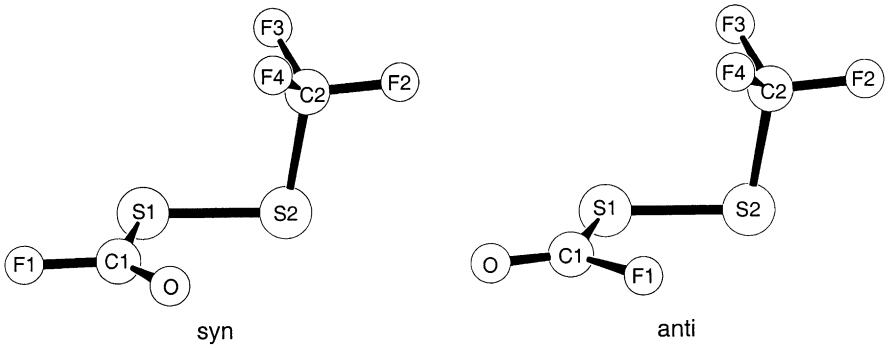

Fig. 4. Molecular models of the syn- and anti-conformers of $FC(O)SSCF_3$ with atom numbering.

Table 5
Experimental and calculated geometric parameters for the syn-conformer of $FC(O)SSCF_3$ and conformational properties

	EB[a]		HF/6-31G*	MP2/6-31G*	B3PW91/6-31G*
C=O	1.176(7)	p_1	1.160	1.193	1.183
C1–F1	1.342(2)	p_2	1.313	1.356	1.342
C2–F	1.329(2)[b]		1.312	1.343	1.334
S1–C1	1.785(5)	p_3	1.780	1.783	1.794
S2–C2	1.817(5)[c]		1.812	1.815	1.837
S–S	2.027(4)	p_4	2.040	2.046	2.051
S–C=O	129.9(16)	p_5	129.7	130.3	130.2
S1–C1–F1	105.7(3)	p_6	106.9	106.0	105.9
$(S2–C2–F)_{mean}$	110.3(3)[d]		110.6	110.6	110.2
$(F–C–F)_{mean}$	108.6(3)		108.3	108.3	108.7
S2–S1–C1	101.4(4)	p_7	102.3	100.6	102.0
S1–S2–C2	100.0(4)[e]		101.0	99.1	100.9
$Tilt(CF_3)$[f]	4.4(9)	p_8	3.9	3.9	4.4
ϕ(S2–S1–C1=O)[g]	2.3[h]		2.3	2.3	2.7
ϕ(S1–S2–C2–F2)[g]	180.0[h]		180.7	180.7	180.5
ϕ(C–S–S–C)	95.0(27)	p_9	89.3	86.3	90.7
Percentage syn	85(13)[i]				
	83(5)[j]		88[l]	92[l]	80[l]
ΔG°[k]	1.02(88)[i]				
	0.95(28)[j]		1.20	1.49	0.82

[a] r_a values in (Å) and (°), error limits are 3σ values. For atom numbering see Fig. 4.
[b] $\Delta CF = (C1–F1) - (C2–F) = 0.013$ Å (MP2 value).
[c] $\Delta SC = (S2–C2) - (S1–C1) = 0.032$ Å (MP2 value).
[d] $\Delta SCF = (S2–C2–F)_{mean} - (S1–C1–F1) = 4.6°$ (MP2 value).
[e] $\Delta SSC = (S2–S1–C1) - (S1–S2–C2) = 1.5°$ (MP2 value).
[f] Tilt angle between the C_3 axis of the CF_3 group and the S2–C2 bond, away from S–S bond.
[g] Torsion of the FC(O) and CF_3 groups around the S1–C1 and S2–C2 bonds, respectively. Positive values lead to a decrease of the $O\cdots F_2$ distance.
[h] Not refined.
[i] Value from GED.
[j] Value from the IR spectrum of the gas.
[k] $\Delta G^{\circ} = G^{\circ}(anti) - G^{\circ}(syn)$ in kcal mol^{-1}.
[l] Estimated values from ΔG° values.

S1–C1=O angle changes by 8.3° from 130.3° (syn) to 122.0° (anti) and the S1–C1–F1 angle changes by 8.5° from 106.0° (syn) to 114.5° (anti). Comparison between calculated and experimental RDF's reveals that the syn-conformer is present or is at least the prevailing form. Its geometric parameters were refined by least squares fitting of the molecular intensities. The following assumptions were made in this refinement: (1) C_{3v} symmetry of the CF_3 group with a possible tilt angle between the C_3 axis and the S2–C2 bond and exact staggered orientation relative to the S–S bond (ϕ(S1–S2–C2–F2) = 180°); (2) the differences between C–F distances ($\Delta CF = (C1–F1) - (C2–F)$) and S–C distances ($\Delta SC = (S2–C2) - (S1–C1)$) were set to the calculated (MP2) values; (3) the differences between the SSC bond angles ($\Delta SSC = (S2–S1–C1) - (S1–S2–C2)$) and between the S–C–F angles ($\Delta SCF = (S2–C2–F)_{mean} - (S1–C1–F1)$) were constrained to calculated differences; (4) the FC(O)S moiety was assumed to be planar and the MP2 result was used for the torsional angle around the S–C bond (ϕ(S2–S1–C1=O)=2.3°); (5) vibrational amplitudes were refined in groups and amplitudes which either caused large correlations with other parameters or which were poorly determined in the GED experiment were set to calculated values. With these assumptions nine geometric parameters (p_1–p_9) and 10 vibrational amplitudes (l_1–l_{10}) were refined simultaneously. The following correlation coefficients had values larger than |0.5|: $p_3/p_6 = -0.53$, $p_2/l_5 = 0.54$, $p_5/l_4 = 0.68$, $p_8/l_6 = -0.72$, $p_8/l_7 = -0.52$, $l_3/l_4 = 0.79$ and $l_6/l_7 = 0.63$.

The fit of the experimental intensities improved slightly, if a small amount of the anti-conformer was added. The geometric parameters of this form were tied to those of the syn-conformer, using the calculated (MP2) differences. Vibrational amplitudes derived from the theoretical force field were used. The best fit was obtained for a contribution of 15(13)%. The uncertainty was derived with the Hamilton test at a significance level of 1% [26]. The results are collected in Table 5 (geometric parameters) and Table 6 (vibrational amplitudes).

Table 6
Interatomic distances and vibrational amplitudes for the syn-conformer of $FC(O)SSCF_3$[a]

	Distance	Amplitude GED		Amplitude (theoretical)[b]
C=O	1.18	0.036[c]		0.036
C2–F	1.33	0.045(2)	l_1	0.045
C1–F1	1.34	0.045(2)	l_1	0.045
S1–C1	1.79	0.057(5)	l_2	0.050
S2–C2	1.82	0.057(5)	l_2	0.050
S1–S2	2.03	0.050(6)	l_3	0.047
F2···F3	2.16	0.054(8)	l_4	0.056
F2···F4	2.16	0.054(8)	l_4	0.056
F3···F4	2.16	0.054(8)	l_4	0.056
O···F1	2.23	0.069(12)	l_5	0.054
S1···O	2.70	0.069(12)	l_5	0.054
S1···F1	2.51	0.077(9)	l_6	0.068
S2···F2	2.53	0.077(9)	l_6	0.068
S2···F3	2.63	0.061(9)	l_7	0.063
S2···F4	2.63	0.061(9)	l_7	0.063
S1···C2	2.95	0.081(11)	l_8	0.083
S2···C1	2.95	0.081(11)	l_8	0.083
S2···O	3.14	0.121[c]		0.121
S1···F3	3.21	0.175(23)	l_9	0.177
S1···F4	3.21	0.175(23)	l_9	0.177
O···F4	3.37	0.290[c]		0.290
F1···F4	4.46	0.290[c]		0.290
F1···F3	5.27	0.290[c]		0.290
C1···F4	3.43	0.231[c]		0.231
C1···F3	4.39	0.231[c]		0.231
C1···C2	3.75	0.148[c]		0.148
O···C2	3.86	0.2090.148		0.209
S1···F2	4.14	0.078(7)	l_{10}	0.074
S2···F1	4.15	0.078(7)	l_{10}	0.074
O···F2	4.73	0.257[c]		0.257
O···F3	4.78	0.257[c]		0.257
C2···F1	4.86	0.175[c]		0.175
C1···F2	4.85	0.175[c]		0.175
F1···F2	6.05	0.175[c]		0.175

[a] Values in Å, error limits are 3σ values. For atom numbering see Fig. 4.
[b] Mean values are given for amplitudes which are not unique.
[c] Not refined.

6. Discussion

According to vibrational spectroscopy and GED $FC(O)SSCF_3$ exists at room temperature as a mixture of two conformers. The GED analysis demonstrates that the syn-conformer is prevailing. From IR (gas) spectra a contribution of 83(5)% of this conformer is obtained. A similar contribution with a larger uncertainty (85(13)%) is derived from the GED intensities. The relative Gibbs free energy ΔG° derived from the IR (gas) spectrum (0.95(28) kcal mol^{-1}) is reproduced correctly by the B3PW91 (0.82 kcal mol^{-1}) and HF (1.20 kcal mol^{-1}) calculations. The MP2 value is slightly larger (1.49 kcal mol^{-1}). The IR gas and matrix spectra of $FC(O)SSCH_3$ also indicate the presence of a mixture of two conformers [8]. These spectra were not analyzed quantitatively, but from the relative intensities of the C=O vibrations it is estimated that the contribution of the second conformer is similar or slightly smaller than that in $FC(O)SSCF_3$. This result is in agreement with our calculations, which predict ΔG° to be about 0.3 kcal mol^{-1} larger in $FC(O)SSCH_3$ than that in $FC(O)SSCF_3$ (see Table 1). The second conformer of $FC(O)SSCH_3$ was not observed in the microwave spectra [9]. The vibrational spectra of the analogous chlorocarbonyl compounds $ClC(O)SSCF_3$ (IR (gas)) and $ClC(O)SSCH_3$ (IR (liquid)) do not demonstrate unambiguously the presence of a second conformer, but small contributions (<5%) can not be excluded. This observation is in agreement with our quantum chemical calculations, which predict ΔG° values between 2.6 and 3.4 kcal mol^{-1}. Again, the syn-conformer is predicted to be more stable.

The vibrational frequencies are reproduced very well with the hybrid method B3PW91. Only the frequencies of uncoupled stretching vibrations (ν_1–ν_3, ν_5 in $FC(O)SSCF_3$, ν_1–ν_3 in $ClC(O)SSCF_3$ and ν_1–ν_4 in $ClC(O)SSCH_3$) are

Table 7
S–S bond lengths (Å) and dihedral angles ϕ(R–S–S–R) (°) of some symmetrically substituted disulfanes R–S–S–R

	S–S	ϕ(R–S–S–R)
F–S–S–F[a]	1.890(2)	87.7(4)
Cl–S–S–Cl[b]	1.950(3)	85.2(2)
FC(O)–S–S–C(O)F[c]	2.028(4)	82.2(19)
CF_3–S–S–CF_3[d]	2.030(5)	104.4(40)
H–S–S–H[e]	2.0610(3)	90.76(6)
CH_3–S–S–CH_3[f]	2.029(3)	85.3(37)
(Bu^t–S–S–Bu^t)[g]	2.018(4)	128.3(27)

[a] [2].
[b] [3].
[c] [7].
[d] [5].
[e] [1].
[f] [4].
[g] [6].

predicted slightly too high and were scaled with a factor of 0.95 (see Tables 2–4). A similarly good agreement is obtained with the MP2 method.

All three quantum chemical methods reproduce the experimental bond lengths better than 0.03 Å and bond angles better than 2° for $FC(O)SSCF_3$. A larger difference exists for the dihedral angle ϕ(C–S–S–C), where the experimental value is about 4–8° larger than the calculated values. This difference between the experimental r_a value and the calculated equilibrium values can be attributed to vibrational effects. The calculated torsional frequency around the S–S bond is 57 cm^{-1} (B3PW91).

S–S bond lengths and RSSR dihedral angles for some symmetrically substituted disulfanes are listed in Table 7. The rather large variation of this bond length from 1.890(2) Å in FSSF to 2.0610(3) Å in HSSH can be explained qualitatively by the orbital interaction between the p-shaped electron lone pair of sulfur and the opposite S–R bond ($lp(S) \rightarrow \sigma^*$ (S–R), anomeric effect). This interaction which can be represented by the no-bond-double-bond mesomeric structure (1) is expected to be strongest for R = F and weakest for R = H:

$$R{-}S{-}S{-}R \rightleftharpoons R{-}\overset{+}{S}{=}S \quad R^- \qquad (1)$$

in agreement with the observed S–S bond lengths. In all disulfanes in which R contains carbon (R = FC(O), CF_3, CH_3, Bu^t) the S–S bond lengths are similar (between 2.018(4) Å in Bu^tSSBu^t and 2.030(5) Å in CF_3SSCF_3) indicating similar $lp(S) \rightarrow \sigma^*$(S–C) anomeric interactions in these compounds. The S–S bond in the mixed disulfane $FC(O)SSCF_3$ (2.027(4) Å) is equal to those in FC(O)SSC(O)F and in CF_3SSCF_3. The predicted S–S bond lengths in $FC(O)SSCH_3$, $ClC(O)SSCF_3$ and $ClC(O)SSCH_3$ differ by less than 0.01 Å from those in $FC(O)SSCF_3$.

As mentioned in Section 1, the dihedral angles adopt values around 90°, with the exceptions of CF_3SSCF_3 (104.4(40)°) and Bu^tSSBu^t (128.3(27)°). The smallest experimental angle occurs in FC(O)SSC(O)F (82.2(19)°). The value in the mixed disulfane $FC(O)SSCF_3$ is exactly between those in FC(O)SSC(O)F and CF_3SSCF_3.

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