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Preparation and Properties of Trifluorothioacetic Acid-*S*-(trifluoromethyl)ester, $CF_3C(O)SCF_3$

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Trifluorothioacetic acid-*S*-(trifluoromethyl)ester, $CF_3C(O)SCF_3$, was prepared by reacting $CF_3C(O)Cl$ and $AgSCF_3$ at 50 °C. The compound was characterized by ^{13}C-, ^{19}F-NMR, UV, and vibrational spectroscopy as well as by gas electron diffraction (GED) and quantum chemical calculations (HF, MP2, and B3LYP methods 6−31G(d) and 6−311+G(2df) basis sets). GED and vibrational spectroscopy result in the presence of a single conformer with C_1 symmetry and synperiplanar orientation of the S−CF_3 bond relative to the C═O bond. This result is in agreement with quantum chemical calculations which predict the anti conformer to be higher in energy by about 4 kcal/mol. An assignment of the IR (gas) and Raman (liquid) spectra is proposed, and the GED analysis results in the following skeletal geometric parameters (r_a and $\angle_a$ values with 3σ uncertainties; these parameters are thermal averages and are not inconsistent with calculated equilibrium values): C═O = 1.202(6) Å, C−C = 1.525(10) Å, S−C(sp^2) = 1.774(3) Å, S−C(sp^3) = 1.824 (3) Å. O═C−C = 118.7(21)°, O═C−S = 127.1(15)°, C−S−C = 99.8 (13)°.

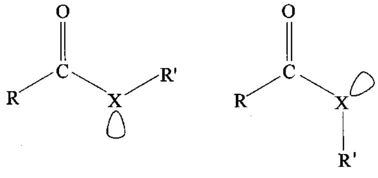
Introduction

Structural and conformational properties of thioesters of the type RC(O)SR′ are of great interest because of their close relation to many biomolecules. Thioesters present an important component of coenzyme A which play an essential role in metabolism.[1] They possess a very different reactivity in biochemical reactions compared to oxoesters. Esters of the type RC(O)OR′, with R,R′ = H, CH_3, F, Cl, CF_3 whose conformational properties have been determined in the gas phase, strongly prefer planar syn conformation (O−R′ bond synperiplanar with respect to the C═O bond, see Chart 1).[2]

Similarly, gas-phase structural studies of thioesters resulted in planar syn conformation. For the compounds $CH_3C(O)SCH_3$[3] and CF3C(O)SR′ with R′ = H,[4] CH_3,[4] and Cl,[4] only the syn form was observed. Relative small amounts of the anti form in addition to the syn conformer exist for thioformic acid HC(O)SH,[5] FC(O)SCl,[6] and ClC(O)SCl.[7]

In continuation of structural studies for $CH_3C(O)SCH_3$[3] and $CF_3C(O)SCH_3$,[4] we became interested in the structural and conformational properties of the perfluorinated derivative $CF_3C(O)SCF_3$. The first synthesis of this compound was reported by Man et al. in 1959 by reacting $CF_3C(O)Cl$ with $Hg(SCF_3)_2$ at 40 °C.[8] The compound was characterized only by its boiling point (24−26 °C). In 1978, Haas and Lieb claimed to have synthesized this compound by thermolysis of $CF_3SC(O)OC(O)CF_3$ at 150 °C. The thermolysis product was characterized by its boiling point of 35 °C and its ν(C═O) stretching frequency of 1868 cm^{-1}.[9] This frequency is much higher than those reported for other compounds which contain the $CF_3C(O)S$ moiety. IR (gas) frequencies near 1760 cm^{-1} have been measured for $CF_3C(O)SH$ and $CF_3C(O)SCl$[10] and for the $CF_3C(O)S$ entity in $CF_3C(O)SOC(O)CF_3$.[11] The discrepancy between the reported boiling points, the unreasonably high C═O vibrational frequency, and the lack of further characterization of the compound prompted us to synthesize $CF_3C(O)SCF_3$ by a novel route, to characterize the compound with ^{13}C- and ^{19}F-NMR and UV spectra, and to perform a vibrational and structural investigation applying IR (gas) and Raman (liquid) spectroscopy as well as gas electron diffraction (GED) and quantum chemical calculations.

CHART 1



syn (Z) anti (E)

Results

Quantum Chemical Calculations. Structural and conformational properties of $CF_3C(O)SCF_3$ have been investigated by quantum chemical calculations. HF and MP2 approximations and the density functional theory (DFT) method B3LYP with small (6−31G(d)) and large (6−311+G(2df)) basis sets have been applied. These calculations result in the existence of two stable conformers with the S−CF_3 bond synperiplanar (ϕ(O═C−S−C) = 0°) or antiperiplanar (ϕ(O═C−S−C ≈ 180°) with respect to the C═O bond. For the syn conformer, MP2 and B3LYP methods result in a geometry with planar molecular skeleton of C_S symmetry with the CF_3 group bonded to carbon

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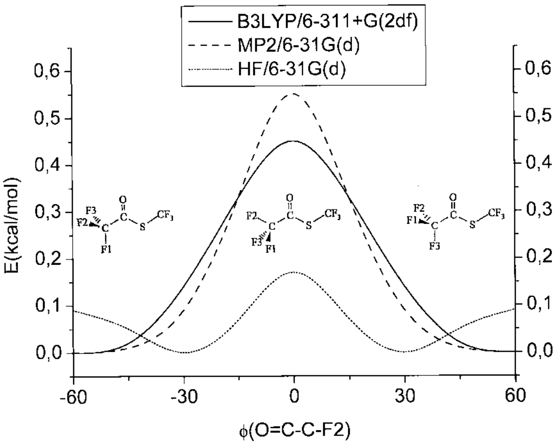

Figure 1. Calculated potential functions for internal rotation around the C(sp^2)−C bond.

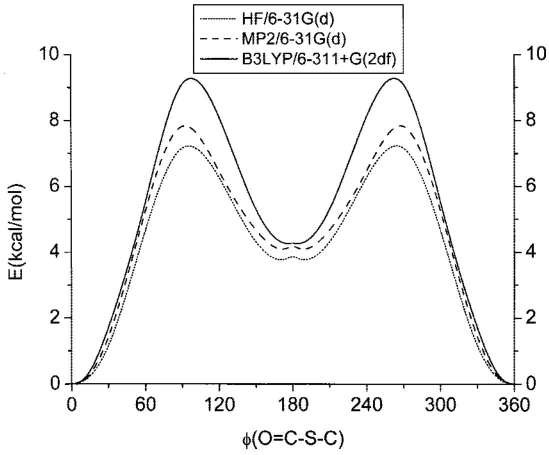

Figure 2. Calculated potential functions for internal rotation around the C(sp^2)−S bond.

staggering the C=O bond (ϕ(O=C−C−F) ≈ ±60°) and the CF_3 group bonded to sulfur staggering the C(sp^2)−S bond (ϕ(C−S−C−F) ≈ ±60°). On the other hand, the HF approximation predicts a structure possessing C_1 symmetry with slightly nonplanar molecular skeleton and the CF_3 group bonded to carbon between staggered and eclipsed orientation. Calculated potential functions for internal rotation of the CF_3 group around the C−C bond, which were derived by structure optimizations at fixed torsional angles, are shown in Figure 1. B3LYP and MP2 methods predict an equilibrium orientation with the CF_3 group exactly staggering the C=O bond, that is, one C−F bond exactly eclipsing the C(sp^2)−S bond. The potential function near the equilibrium orientation, however, is very shallow and the energy increases only by about 0.1 kcal/mol for rotation of ±30°. The calculated barriers to internal rotation are less than 0.6 kcal/mol. The HF approximation results in a potential function with its minima at intermediate orientation (ϕ(*O*=C−C−F) ≈ ±30°) and corresponding to almost free internal rotation.

All methods predict the anti conformer to possess C_1 symmetry with a slightly nonplanar skeleton (ϕ(O=C−S−C) between 173° and 177°) and the CF_3 group bonded to carbon eclipsing the C=O bond. Calculated potential functions for internal rotation around the C(sp^2)−S bond are shown in Figure 2. The anti conformer is predicted to be higher in energy by 3.9 kcal/mol (HF/6−31G(d)), 4.1 kcal/mol (MP2/6−31G(d)), 4.5 kcal/mol (MP2/6−311+G(2df)), and 4.3 kcal/mol (B3LYP/6−311+G(2df)). The Gibbs free energy is predicted to be even higher (5.8 kcal/mol from B3LYP calculation). Calculated barriers to internal rotation vary between about 7 and 9 kcal/mol.

Vibrational frequencies derived with the B3LYP/6−311+G(2df) method which were used in the analysis of the vibrational spectra are included in Table 1. Vibrational amplitudes were derived from a calculated force field (MP2/6−31G(d)) using the program ASYM40.[12] All quantum chemical calculations were performed with the GAUSSIAN03 program set.[13]

Vibrational Analysis. The IR (gas) and Raman (liquid) spectra of $CF_3C(O)SCF_3$ are shown in Figure 3. The observed and calculated (B3LYP/6−311+G(2df)) frequencies and their intensities as well as an approximate description of modes are listed in Table 1. The assignments in Table 1 are based on the potential energy distribution, which was derived from the calculated Cartesian force field using the program ASYM40[12] and by comparison between calculated and experimental intensities. The C=O vibrational frequency is known to be very sensitive to conformational properties. In the IR and Raman spectra of $CF_3C(O)SCF_3$, we observed only one band in the C=O spectral region at 1767 cm^{-1} (IR) and 1757 cm^{-1} (Raman), and this is in agreement with a single conformation present in gas and liquid phases.

UV Spectroscopy. The UV−vis spectrum of the vapor shows a band at $\lambda_{\max} = 226$ nm with medium absorption cross section ($\sigma_{\max} = 1.23 \times 10^{-18}$ cm^2) which is attributed to the $\pi \rightarrow \pi^*$ transition in the C(O)S chromophore taking into account the observed bands for $CF_3C(O)SH$ (226 nm),[14] $CF_3C(O)SCl$ (236 nm),[14] $CF_3C(O)SOC(O)CF_3$ (236 nm),[11] and $FC(O)SSC(O)CF_3$ (232 nm).[15]

NMR Spectroscopy. In the ^{13}C NMR spectrum of the sample at room temperature, three quartets at 176.9 (CO), 114.5 ($CF_3C(O)$), and 126.3 (CF_3S) ppm relative to TMS are observed. Table 2 summarizes the NMR data. The coupling constants are in good agreement with those of similar compounds containing the $CF_3C(O)$ group. In the ^{19}F NMR, two singlets with an intensity ratio of 1:1 at −78.3 ($CF_3C(O)$) and −41.8 (CF_3S) ppm relative to TFA were observed.

Structure Analysis. The radial distribution function (RDF) which was calculated by Fourier transform of the molecular intensities with an artificial damping function $\exp(-\gamma s^2)$ ($\gamma = 0.0019$ Å^2) is shown in Figure 4. This curve is well reproduced with the calculated geometry for the syn conformer. The preliminary molecular model (MP2/6−311+G(2df)) was refined by least-squares fitting of the experimental molecular intensities. Since different computational methods predict rather different and unreasonably low frequencies for the torsional vibration around the C−CF_3 bond ($\nu_{27} = 8$ cm^{-1} from B3LYP and 3 cm^{-1} from MP2) and since this vibration has a strong effect on calculated vibrational corrections for interatomic distances, such corrections are considered to be unreliable. Therefore, an r_a structure without any vibrational corrections was refined in the least-squares analyses. In the first analysis, the structure was constrained to C_S symmetry with the CF_3 group bonded to carbon (F_3C2, for atom numbering see Figure 4) exactly staggering the C=O bond (ϕ(O=C−C−F) = 60°) and the F_3C3 group staggering the C1−S bond (ϕ(C−S−C−F) = 60°). This model corresponds to the equilibrium structure predicted by B3LYP and MP2 methods. C_{3v} symmetry was assumed for both CF_3 groups with a tilt angle between the C_3 axis and the adjacent bond. Furthermore, a mean C−F bond distance was refined because calculated mean bond lengths of the two groups differ only by 0.003 Å (B3LYP) or by 0.002 Å (MP2). The difference

TABLE 1: Experimental and Calculated Vibrational Frequencies of $CF_3C(O)SCF_3$ and Tentative Assignment

	IR (gas)		Raman (liquid)			
	$\tilde{\nu}$ [cm^{-1}]	I	$\tilde{\nu}$ [cm^{-1}]	I[a]	B3LYP/6−311+G(2df)[b]	assignment[c]
ν_1	1767	s	1757	30	1819 (267)	ν(C=O)
ν_2	1284	s	1278	7	1254 (109)	ν(C−C)/δ_s(F_3C2)/ν_s(F_3C2)
ν_3	1222	vs, sh	1225	4	1188 (510)	ν_{as}(F_3C2)
ν_4	1205	s, sh	1206	5	1186 (162)	ν_{as}(F_3C3)
ν_5	1194	vs	1185	5	1179 (10)	ν_{as}(F_3C3)
ν_6			1176	11	1165 (263)	ν_{as}(F_3C2)
ν_7	1120	vs	1107	6	1098 (373)	ν_s(F_3C3)/δ_s(F_3C3)
ν_8	936	vs	928	3	924 (350)	ν_s(F_3C2)/ν(C1−S)/δ(*O*=C−S)
ν_9	766	w	765	100	760 (21)	ν_s(F_3C3)/δ_s(F_3C3)
ν_{10}	742	m	741	42	736 (83)	ν_s(F_3C2)/δ_s(F_3C2)
ν_{11}					695 (3)	oop(CC(O)S)
ν_{12}			615	25	613 (1)	δ(O=C−S)/δ(C−S−C)/ν(C1−S)
ν_{13}	560	vw	569	15	552 (8)	δ_{as}(F_3C2)
ν_{14}					542 (1)	δ_{as}(F_3C3)
ν_{15}			516	33	508 (2)	δ_{as}(F_3C3)
ν_{16}					503 (4)	δ_{as}(F_3C2)
ν_{17}	466	vw	464	25	451 (7)	ν(S−C3)
ν_{18}			406	11	403 (1)	δ_{as}(F_3C2)/ρ(O=C−S)
ν_{19}					323 (0)	ρ_{as}(F_3C3)
ν_{20}			316	11	303 (3)	δ(O=C−S)/ρ_s(F_3C3)
ν_{21}			287	74	276 (3)	ρ_s(F_3C3)
ν_{22}			235	13	243 (2)	ρ_{as}(F_3C2)/oop(CC(O)S)/ρ_s(F_3C2)
ν_{23}			180	49	175 (2)	ρ(O=C−S)
ν_{24}			111	30	109 (1)	δ(C−S−C)
ν_{25}			81	81	73 (1)	τ(F_3C3)
ν_{26}					55 (1)	τ(C1−S)
ν_{27}					8 (0)	τ(F_3C2)

[a] Intensities of the Raman lines are relative to strongest line (100%). [b] Calculated frequencies and IR intensities in km/mol in parentheses. [c] For atom numbering, see Figure 4.

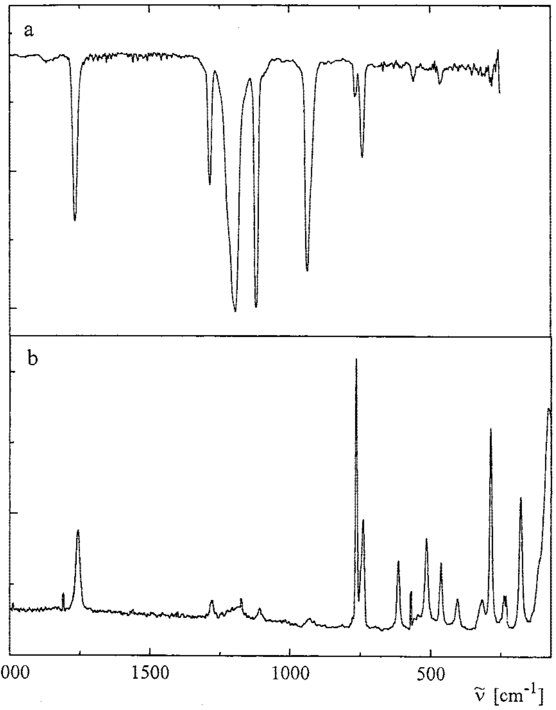

Figure 3. (a) IR (gas) 2 Torr, optical path 10 cm and (b) Raman (liquid) spectra of $CF_3C(O)SCF_3$.

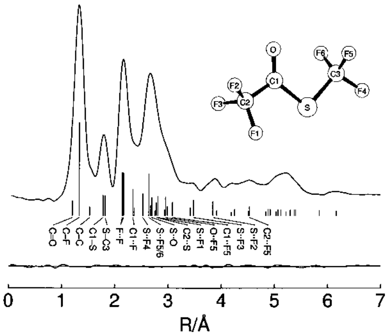

Figure 4. Experimental radial distribution function and difference curve. The positions of interatomic distances are indicated by vertical bars.

TABLE 2: NMR Data for $CF_3C(O)SCF_3$

	^{13}C NMR			^{19}F NMR	
	CO	$F_3\underline{C}$(CO)	CF_3−S	F_3C(CO)	CF_3−S
δ[a]	176.9	114.5	126.3	−78.3	−41.8
M[b]	(qq)	(qq)	(qq)	S	s
J[c]	$^2J_{CF} = 44$ $^3J_{CF} = 1.5$	$^1J_{CF} = 292$ $^4J_{CF} = 3$	$^1J_{CF} = 313$ $^4J_{CF} = 2$		

[a] δ (^{13}C) in ppm relative to TMS in $CDCl_3$. δ(^{19}F) in ppm relative to TFA as external reference. [b] Signal multiplicities: s = singlet, dq = double quartet. [c] Coupling constant values in Hz.

between the two C−S bond distances was constrained to 0.050 Å. The MP2 approximation predicts a difference of 0.049 Å, and the B3LYP method predicts a difference of 0.051 Å. Since the tilt angle of the F_3C2 group is badly determined in the GED analysis, with an uncertainty larger than its value, it was constrained to the calculated value of 1.4° (MP2). Vibrational amplitudes were collected in groups, and amplitudes which are not well determined in the GED experiment were set to calculated values. With this model, the RDF is not fitted satisfactorily in the distance range 3.3−4.5 Å. This distance range corresponds primarily to interatomic distances between sulfur and fluorine atoms of the F_3C2 group. In the subsequent least-squares analysis, the torsional angle of this CF_3 group (ϕ(O=C−C−F) was refined in addition to the bond distances

TABLE 3: Experimental and Calculated Geometric Parameters for the Syn Conformer of $CF_3C(O)SCF_3$

	EB[a]		HF/6−31G*	MP2/ 6−311+ G(2df)	B3LYP/ 6−311+ G(2df)
C=O	1.202(6)	p1	1.174	1.201	1.190
$(C-F)_{mean}$	1.327(1)	p2	1.312	1.329	1.334
C−C	1.525(10)	p3	1.539	1.545	1.559
C1−S	1.774(3)	p4	1.783	1.776	1.794
S−C3	1.824(3)[b]		1.812	1.825	1.845
S−C=O	127.1(15)	p5	125.8	127.1	127.0
S−C−C	114.2(14)	p6	113.7	112.6	112.5
C−C=O	118.7(21)[c]		120.5	120.3	120.5
C−S−C	99.8(13)	p7	99.0	97.0	98.7
F−C2−F	108.2(5)	p8	108.8	108.5	108.6
F−C3−F	108.5(5)	p9	108.5	108.6	108.6
tilt(F_3C2)[d]	1.4[f]		1.6	1.4	1.3
tilt(F_3C3)[e]	4.9(7)	p10	4.2	4.2	4.5
ϕ(O=C−C−F)	37(4)[g]	p11	29	60	60

[a] r_a distances in Å and angles in degrees. Estimated uncertainties are 3σ values. For atom numbering, see Figure 4. [b] ΔSC = (S−C3) − (C1−S) fixed to 0.050 Å. [c] Dependent parameter. [d] Tilt angle between C_3 axis of F_3C2 group and C1−C2 bond direction [e] Tilt angle between C_3 axis F_3C3 group and S−C3 bond direction. [f] Not refined. [g] Large-amplitude thermal average value.

TABLE 4: Interatomic Distances and Experimental and Calculated Vibrational Amplitudes for Syn Conformation of $CF_3C(O)SCF_3$[a]

	distance	amplitude GED		amplitude calcd[b]
C=O	1.20	0.035[c]		0.035
C−F	1.33	0.043(2)	l_1	0.042
C−C	1.53	0.047(4)	l_2	0.048
C1−S	1.78			
S−C3	1.82			
F1···F2	2.15	0.056(2)	l_3	0.053
F4···F5	2.16			
C1···F1	2.35	0.063(7)	l_4	0.064
C1···F2	2.35			
C1···F3	2.35			
S···F4	2.52			
S···F5	2.64			
S···F6	2.64			
S···C2	2.78			
O···C2	2.35	0.057[c]		0.057
O···S	2.68			
O···F2	2.68	0.140(37)	l_5	0.132
C1···F5	3.08			
C1···F6	3.08			
C1···C3	2.75	0.075[c]		0.075
C1···F4	3.92			
C2···C3	4.19			
S···F1	2.81	0.131(48)	l_6	0.178
O···F5	2.94			
O···F6	2.94			
O···C3	2.94	0.103(37)	l_7	0.112
O···F1	3.42			
O···F3	2.99	0.208(87)	l_8	0.273
S···F3	3.48			
C3···F3	4.84			
S···F2	3.85	0.113(24)	l_9	0.126
C3···F1	4.51			
C3···F2	5.04			
O···F4	4.25	0.103[c]		0.103
C2···F5	4.53	0.159[c]		0.159
C2···F6	4.53			
F3···F6	4.88	0.345(182)	l_{10}	0.300
F2···F5	5.07			
F3···F4	5.85			
F1···F5	4.92	0.173(59)	l_{11}	0.189
F1···F6	5.13			
F1···F4	5.30			
F2···F6	5.38			
C2···F4	5.22	0.081[c]		0.081
F3···F5	5.40	0.140[c]		0.140
F2···F4	6.17			

[a] Values in Å, estimated uncertainties are 3σ values. For atom numbering, see Figure 4. [b] Mean values are given for slightly differing amplitudes within each group. [c] Not refined.

and bond angles. Its value converged to 37(4)° corresponding to an intermediate orientation between staggering and eclipsing the C=O bond. The agreement factor decreased from 5.2% in the first analysis to 3.8% in the latter refinement. With this model, 11 geometric parameters (p1−p11) and 11 vibrational amplitudes (l1−l11) were refined simultaneously, and the following correlation coefficients had values larger than |0.7|: p2/p7 = 0.88, p8/p9 = −0.87, p2/l2 = −0.78, p6/l6 = 0.85, and p7/l6 = −0.74. The final results for geometric parameters and vibrational amplitudes are collected together with calculated values in Table 3 and Table 4. Attempts to refine a dynamical model with a large amplitude torsional motion around the C−CF_3 bond were not successful. It was not possible to determine the barrier to internal rotation, and a model with free rotation did not improve the fit of the experimental GED intensities.

Discussion

The above results (spectroscopic data and GED) unambiguously characterize this compound to be $CF_3C(O)SCF_3$. The boiling point of the compound reported by Man et al.[8] (24−26 °C) is reasonably close to our extrapolated boiling point (21 °C), and seems to demonstrate that this compound was also $CF_3C(O)SCF_3$. Boiling point (35 °C) and ν(C=O) vibrational frequency (1868 cm^{-1}) reported by Haas and Lieb[9] for the thermolysis product of $CF_3SC(O)OC(O)CF_3$, however, differ strongly from our values (21 °C and 1767 cm^{-1}) and clearly prove that this compound was not $CF_3C(O)SCF_3$.

In the GED analysis, only a single conformer with syn orientation of the SCF_3 moiety is observed in agreement with the IR (gas) and Raman (liquid) spectra. These spectra exhibit no splitting of the C=O band which would be expected for a mixture of conformers. This result is reproduced correctly by all quantum chemical calculations which predict the anti form to be higher in energy by 3.8−4.5 kcal/mol which implies a contribution of the anti form of much less than 1%. Considering experimental uncertainties and systematic differences between vibrationally averaged r_a values derived in the GED experiment and equilibrium r_e values obtained from calculations, the experimental bond lengths and angles are reproduced reasonable well by all computational methods except for C−C and C−S bond lengths, which are predicted somewhat too long by the B3LYP method. The experimental torsional orientation of the F_3C2 group (ϕ(O=C−C−F) = 37(4)°) seems to be reproduced satisfactorily only by the HF method (ϕ(O=C−C−F) = 29°), and a strong discrepancy between the GED experiment and high-level calculations appears to occur. Whereas the MP2 and B3LYP methods with small (6−31G(d)) and large (6−311+G(2df)) basis sets predict an exactly staggered orientation relative to the C=O bond (ϕ(O=C−C−F) = 60°), the vibrationally averaged orientation derived by GED is intermediate between staggered and eclipsed. This large discrepancy is almost certainly due to the use of a rigid model in the GED analysis. Considering the very flat minimum of the calculated potential functions at the staggered orientation (see Figure 1) and the extremely low frequency predicted for torsional vibration around the C−C bond

TABLE 5: Experimental Skeletal Geometric Parameters and Calculated (MP2/6−31G(d)) Syn−Anti Energy Differences (kcal/mol) of $CH_3C(O)SCH_3$, $CF_3C(O)SCH_3$, and $CF_3C(O)SCF_3$

	$CH_3C(O)SCH_3$[a]	$CF_3C(O)SCH_3$[b]	$CF_3C(O)SCF_3$
C=O	1.214 (3)	1.206(6)	1.202(6)
C−C	1.499(5)	1.527(5)	1.525(10)
S−C1	1.781(6)	1.743(14)	1.774(3)
S−C3	1.805(6)	1.807(16)	1.824(3)
O=C−C	123.4(8)	116.8(21)	118.7(21)
O=C−S	122.8(5)	127.2(19)	127.1(15)
C−S−C	99.2(9)	97.5(13)	99.8(13)
ΔE/kcal mol^{-1}[c]	5.3	5.0	4.1

[a] Reference 3. [b] Reference 4. [c] $\Delta E = E(\text{anti}) - E(\text{syn})$.

of 8 cm^{-1} (see Table 1), the experimental torsional angle derived for a rigid model is expected to deviate strongly from the equilibrium value. Thus, the experimental orientation is fully compatible with an exactly staggered equilibrium structure and a large amplitude torsional motion. A similar discrepancy between GED and high-level quantum chemical calculations was observed previously for the trifluoromethylthio compounds $CF_3C(O)SR'$ with R′ = H, CH_3, and Cl.[4] For these compounds, torsional angles ϕ(O=C−C−F) between 29° and 40° have been determined by GED, whereas MP2 calculations which were performed recently predict exactly staggered orientation in all three derivatives. For these three compounds as well, the torsional angles have to be interpreted as vibrationally averaged values which correspond to an exactly staggered equilibrium structure. Such a staggered orientation occurs only in $CF_3C(O)S$ moieties. In compounds of the type $CF_3C(O)X$ with X = F[16] and Cl[17] and of the type $CF_3C(O)OR$ with R = H[18] and SC(O)F,[19] the CF_3 group exactly eclipses the C=O bond.

Table 5 compares experimental skeletal geometric parameters and calculated syn/anti energy differences of $CH_3C(O)SCH_3$, $CF_3C(O)SCH_3$, and $CF_3C(O)SCF_3$. CH_3/CF_3 substitution at the sp^2-hybridized carbon atom in methyl thioacetate causes shortening of the C=O bond, lengthening of the C−C bond, and considerable shortening of the S−C(sp^2) bond from 1.781(6) Å to 1.743(14) Å. Furthermore, the O=C−C angle decreases by about 6° and the O=C−S angle increases by about the same amount, that is, the C=O bond is bent more strongly toward the CF_3 group. Additional CH_3/CF_3 substitution at sulfur lengthens both S−C bonds and causes no further changes of geometric parameters in $CF_3C(O)SCF_3$ larger than the experimental uncertainties. In all three thioesters, the syn conformer is strongly preferred and the syn/anti energy difference decreases slightly with increasing fluorination.

The preference of the syn structure in $CF_3C(O)SCF_3$ can be rationalized by orbital interactions between the two sulfur lone pairs (n_π and n_σ) and vicinal antibonding orbitals. According to a natural bond orbital (NBO) analysis, the anomeric orbital interaction $n_\sigma(S) \rightarrow \sigma^*(C{=}O)$ of 5.8 kcal/mol in the syn form is higher than the interaction energy $n_\sigma(S) \rightarrow \sigma^*(C{-}C)$ of 3.1 kcal/mol in the anti conformer (see Chart 1 for relative orientation of n_σ and vicinal bonds). This anomeric effect stabilizes the syn conformation. An even stronger stabilization of the syn structure arises from conjugation ($n_\pi \rightarrow \pi^*(C{=}O)$) which increases from 40.9 kcal/mol in the anti structure to 46.0 kcal/mol in the syn form. Thus, the combination of both orbital interactions strongly favors the syn conformation and overrides possible differences in steric repulsion.

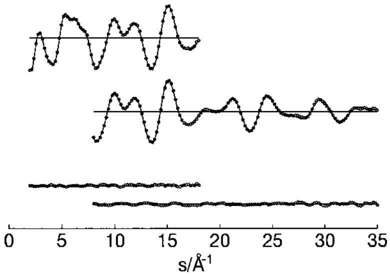

Figure 5. Experimental (dots) and calculated (full line) molecular intensities for long (above) and short (below) nozzle-to-plate distances and residuals.

Experimental Section

Synthesis. The synthesis of $CF_3C(O)SCF_3$ was previously reported by Man et al.[8] and by Haas and Lieb.[9] In this work, $CF_3C(O)SCF_3$ was obtained by condensing 1.4 mmol of $CF_3C(O)Cl$ and 1.5 mmol of $AgSCF_3$ in a Pyrex vessel at 50 °C within 72 h. The product was isolated by repeated fractional condensation in vacuo through a series of traps held at −78, −105, and −196 °C. The trap at −105 °C retained pure $CF_3C(O)SCF_3$ (45% yield). The purity was checked by IR and Raman spectroscopy. Further purity tests were made by using ^{19}F and ^{13}C NMR spectroscopy. $CF_3C(O)SCF_3$ is a colorless liquid and the vapor pressure in the temperature range between 230 and 278 K follows the equation $\ln p = 18.35 - 3445/T$ (p/Torr, T/K). The extrapolated boiling point is 21 °C.

Vibrational Spectra. Gas-phase infrared spectra were recorded in the range 4000−400 cm^{-1} on the Fourier transform infrared (FTIR) instrument Bruker IFS66 (resolution of 1 cm^{-1}) using a glass cell (10 cm optical path length, Si windows). Raman spectra between 3500 and 150 cm^{-1} were recorded using an FTBruker IFS85 spectrometer (spectral resolution 4 cm^{-1}). The 1064 nm radiation line of an Nd/YAG laser was used for excitation. The liquid sample was handled in Pyrex capillaries at room temperature.

UV Spectra. The gas-phase UV spectra of $CF_3C(O)SCF_3$ were obtained in a quartz cell (10 cm optical path length) with the UV/vis Hewlettt-Packard 8454-A diode array spectrometer (2 nm resolution).

NMR Spectra. ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AC 250 NMR spectrometer (62.9 and 235.2 MHz, respectively) at room temperature using 5 mm probes. $CDCl_3$ was used as solvent and was referenced internally to $(CH_3)_4Si$ for ^{13}C NMR, while for ^{19}F NMR the spectrum was compared with $CF_3C(O)OH$ (0.5% in $CDCl_3$) as external reference.

Electron Diffraction. The GED intensities were recorded with a Gasdiffractograph KD-G2[20] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of approximately 60 kV. The sample was kept at −40 °C during the experiment, and the inlet system and nozzle were at room temperature. The photographic plates were analyzed with the usual methods,[21] and averaged molecular intensities in the s-ranges 2−18 and 8−35 Å^{-1} in steps of $\Delta s = 0.2$ Å^{-1} are presented in Figure 5 ($s = (4\pi/\lambda)\sin\theta/2$, λ = electron wavelength, θ = scattering angle).

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