Structures and Conformations of (Trifluoromethyl)thioacetic Acid, $CF_3C(O)SH$, and Derivatives $CF_3C(O)SCH_3$ and $CF_3C(O)SCl$

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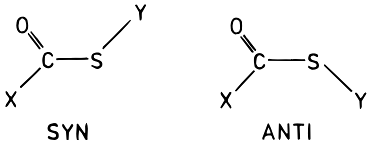
The geometric structures and conformations of (trifluoromethyl)thioacetic acid, $CF_3C(O)SH$, methyl trifluorothiolacetate, $CF_3C(O)SCH_3$, and trifluorothiolacetate chloride, $CF_3C(O)SCl$, were determined by gas electron diffraction and theoretical calculations (ab initio and density functional methods). In the cases of $CF_3C(O)SCH_3$ and $CF_3C(O)SCl$, the experimental scattering intensities are consistent only with the existence of a planar syn conformer (S−CH_3/S−Cl single bonds syn with respect to the C=O double bond) in the gas phase. The theoretically predicted energy differences ΔE between anti and syn forms are 4.2 kcal mol^{-1} (HF/3-21G* and HF/6-31G*) for $CF_3C(O)SCH_3$ and 3.2 (HF/3-21G*) or 5.6 kcal mol^{-1} (HF/6-31G*) for $CF_3C(O)SCl$. The conformational properties of $CF_3C(O)SH$ could not be determined unambiguously in the experiment. On the basis of the theoretical results ($\Delta E = 0.9-2.2$ kcal mol^{-1}), only a syn conformer was considered in the experimental structure analysis.

Introduction

Structural and conformational properties of thioacetyl compounds have attracted much interest because thioesters are essential components of coenzyme A, which plays a central role in metabolism.[1−5] This class of compounds can adopt two conformations, i.e., S−Y anti or syn with respect to C=O.



The relative stability of the two conformations depends on the substituents X and Y. In the parent compound, HC(O)SH, the syn form is preferred by 0.6613(17) kcal mol^{-1} relative to the anti structure.[6] Vibrational spectroscopy and gas electron diffraction (GED) of ClC(O)SCl[7,8] and FC(O)SCl[9−11] demonstrate that the predominant conformer possesses syn structure. According to GED studies, the difference in Gibbs free energy $\Delta G°$ between anti and syn is ≥1.6 kcal mol^{-1} in ClC(O)SCl and 1.2(3) kcal mol^{-1} in FC(O)SCl.

Ab initio calculations at various levels of theory predict for all thioacetyl compounds XC(O)SY with X, Y = H, F, Cl the predominance of the syn conformation, except for HC(O)SCl and HC(O)SF.[11] In the former compound the calculated energy difference is close to zero; in the latter the anti form is predicted to be lower in energy than the syn conformer by ca. 2 kcal mol^{-1}. Among the methyl substituted thioacetyls (X or Y = CH_3) the conformational properties of $HC(O)SCH_3$,[12] $CH_3C(O)SH$,[13] and $ClC(O)SCH_3$[14,15] have been studied experimentally. In the microwave (MW) spectrum of *S*-methyl thiolformate, $HC(O)SCH_3$,[12] only the syn form was observed. According to low-temperature NMR spectra, thioacetic acid, $CH_3C(O)SH$, exists in solution as a mixture of two conformers (ratio syn:anti of 3:1 at −150 °C).[13] MW[15] and GED[14] studies of *S*-methyl chlorothioformate, $ClC(O)SCH_3$, result in the syn structure only. To our knowledge, no experimental results have been reported for the structural and conformational properties of *S*-methyl thioacetate, $CH_3C(O)SCH_3$, where X = Y = CH_3.

In this paper we present GED investigations of the structures and conformational properties of (trifluoromethyl)thioacetic acid $CF_3C(O)SH$ and derivatives $CF_3C(O)SCH_3$ and $CF_3C(O)SCl$. In addition to the experimental studies, theoretical calculations using ab initio and density funtional theory (DFT) methods were performed. Vibrational spectra of $CF_3C(O)SH$ were interpreted in terms of the existence of a mixture of anti and syn conformers in the liquid state and of the presence of the anti form in the gas phase.[16]

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Table 1. Stable Structures of $CF_3C(O)SH$ As Obtained by Different Theoretical Methods

	HF/ 3-21G*	HF/ 6-31G**	MP2/ 6-31G*	LDFT[a]	NLDFT[b]
syn					
ϕ(O=C−S−H)	0.0	6.0	0.0	2.0	2.0
τ(O=C−C−F)	60.0	31.0	60.0	51.0	51.0
anti					
ϕ(O=C−S−H)	174.0	180.0	180.0	180.0	180.0
τ(O=C−C−F)	8.0	0.0	0.0	2.0	2.0
ΔE (kcal mol^{-1})					
E(anti) − E(syn)	2.2	1.0	2.2	0.9	1.0

[a] Local density functional approximation of Vosko, Wilk, and Nusair (VWN),[35] polarized triple ζ basis set. [b] VWN and nonlocal corrections of Becke (exchange)[36] and Perdew (correlation),[37] polarized triple ζ basis set.

Theoretical Calculations

All calculations were performed with the program systems Gaussian 92[17] and DGAUSS.[18] The main interest in these calculations were the following two conformational aspects: (1) relative stabilities of anti and syn conformations and (2) the rotational position of the CF_3 group. These two problems were studied by applying several theoretical methods in the case of the smallest compound $CF_3C(O)SH$. The results of ab initio (HF/3-21G*, HF/6-31G**, MP2/6-31G*) and local (LDFT) and nonlocal (NLDFT) density functional calculations are summarized in Table 1. The given conformations represent stable structures; i.e., they possess no imaginary frequencies. All computational approaches predict two minima on the energy hypersurface with the syn form lower in energy than the anti structure by 0.9−2.2 kcal mol^{-1}. HF/3-21G* and HF/6-31G** calculations result in a barrier to internal rotation around the C−S bond of 7.4 kcal mol^{-1}. The predictions for the rotational position of the CF_3 group depend on the theoretical method. According to the HF/3-21G* approximation the syn conformer possesses C_S symmetry and exactly staggered orientation of the CF_3 group with respect to the C=O double bond. The anti form deviates slightly from C_S symmetry (ϕ(O=C−S−H) = 174°), and one C−F bond is nearly eclipsed to the C=O bond. Calculations for an anti structure with exact C_S symmetry result in one imaginary frequency. The HF/6-31G** approach leads to a syn structure with ϕ(O=C−S−H) = 6° and an orientation of the CF_3 group which is intermediate between staggered and eclipsed (τ(O=C−C−F) = 31°), whereas the anti form possesses exact C_S symmetry and an eclipsed CF_3 group. In the MP2 approximation both minima are predicted to have C_S symmetry with staggered and eclipsed orientation of the CF_3 group in the syn and anti form, respectively. Both DFT methods result in slight deviations from C_S symmetry with nearly staggered (syn form) or nearly eclipsed orientations (anti form) of the CF_3 group. The calculated barrier to internal rotation of the CF_3 group amounts to 0.7 (HF/3-21G*) and 0.2 kcal mol^{-1} (HF/6-31G**). Theoretical geometric parameters are compared to the experimental values in Table 2. In the cases of $CF_3C(O)SCH_3$ and $CF_3C(O)SCl$ only HF/3-21G* and HF/6-31G* calculations were performed. In both compounds the anti structures are predicted to be higher in energy by 4.2 and 5.6 kcal mol^{-1} (HF/3-21G*) or 4.2 and 3.0 kcal mol^{-1} (HF/6-31G*). At the HF/3-21G* level the CF_3 group of the syn form is staggered to the C=O bond in both molecules. According to the HF/6-31G* method the CF_3 group in $CF_3C(O)SCH_3$ is rotated by τ(O=C−C−F) = 38°, whereas this group is exactly staggered in the chlorine derivative (τ(O=C−C−F) = 60°). Calculated geometric parameters (HF/3-21G* and HF/6-31G*) of the syn conformers are compared to the experimental data in Tables 3 ($CF_3C(O)SCH_3$) and 4 ($CF_3C(O)SCl$).

GED Analyses

Radial distribution functions (RDFs) were calculated by Fourier transform of the molecular scattering intensities which were multiplied with an artificial damping function $\exp(-\gamma s^2)$ (γ = 0.0019 Å^2). Preliminary geometric models derived from the RDFs were refined by least squares fitting of the molecular intensities. The intensities were modified by a diagonal weight matrix, and known complex scattering factors were used.[19] Planar skeletons and local C_{3v} symmetry for the CF_3 groups were assumed in the least squares refinements for all compounds. In all cases, refinements of tilt angles between the C_3 axis of the CF_3 group and the C−C bond direction resulted in values <1° with error limits in the same order of magnitude. Therefore, this tilt angle was set to zero in the final refinements. Vibrational amplitudes were collected in groups according to their distances, and further constraints are evident from the respective tables.

$CF_3C(O)SH$. Due to the low scattering power of hydrogen the GED intensities of this compound are not sensitive toward the orientation of the S−H bond, and the GED experiment cannot distinguish between anti and syn conformations. On the basis of the theoretical calculations (see above) a syn model was used in the structure refinement. Analysis of the RDF (Figure 1) results in an orientation of the CF_3 group which is intermediate between eclipsed and staggered with respect to the C=O double bond (τ(O=C−C−F) = 29.5(12)°). The calculated RDF is sensitive toward this torsional angle since it determines the nonbonded S···F distances, which contribute strongly to the scattering intensities. The S−H bond length and the C−S−H angle were tranferred from CH_3SH.[20] Eight geometric parameters and seven vibrational amplitudes were refined simultaneously, and one correlation was larger than |0.7| in the least squares analysis: p_2/p_7 = 0.75. The final results (geometric parameters p_i and vibrational amplitudes a_k) are collected in Table 2.

$CF_3C(O)SCH_3$. Comparison of RDFs calculated for anti and syn models with the experimental curve (Figure 2) clearly demonstrates that the syn form is present in the gas phase. As in the case of $CF_3C(O)SH$, the RDF in the range r > 2.5 Å is reproduced only with a rotated CF_3 group (τ(O=C−C−F) = 38.1(14)°). In addition to the geometric constraints described above, local C_{3v} symmetry was assumed for the CH_3 group. Vibrational amplitudes were collected in groups according to the type (dependent or independent of torsional motion) and to the length of the distance. Further constraints are evident from Table 3. With these assumptions eleven geometric parameters p_i and ten vibrational amplitudes a_k were refined simultaneously. The following correlation coefficients had values larger than |0.7|: p_4/p_5 = −0.95, p_4/p_7 = −0.78, p_5/p_7 = 0.76, p_4/p_8 = −0.70, p_4/a_3 = 0.93, p_5/a_3 = −0.94, p_7/a_3 = −0.75. These correlations cause large error limits for the two closely spaced S−C bond lengths (p_4 and p_5) and for the S−C=O bond angle (p_7). The final results (geometric parameters p_i and vibrational amplitudes a_k) are listed in Table 3.

Besides the structure analysis described above, a nonrigid model with large amplitude torsional motion of the CF_3 group was considered. Assuming free internal rotation, the fit between experimental and calculated intensities is markedly worse than that for the rigid model. No satisfactory fit can be obtained with a 3-fold potential, which has minima for staggered orientation and barriers between 0 and 1 kcal mol^{-1}. From this result we conclude that the experimentally determined dihedral angle, τ(O=C−C−F) = 38.1(14)°, corresponds to a torsional potential with minima between staggered and eclipsed orientation of the CF_3 group.

$CF_3C(O)SCl$. Comparison of calculated RDFs with the experimental curve (Figure 3) clearly demonstrates that the syn conformer is

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Table 2. Results of Electron Diffraction Analysis and Calculated Geometric Parameters for Syn $CF_3C(O)SH$]

Geometric Parameters

	GED[a]	HF/3-21G*	HF/6-31G**	MP2/6-31G*	LDFT[d]	NLDFT[e]
C=O	1.217(5) (p_1)	1.200	1.178	1.216	1.206	1.214
C—F	1.340(2) (p_2)	1.343	1.314	1.342	1.336	1.356
C—C	1.524(4) (p_3)	1.523	1.539	1.536	1.540	1.565
C—S	1.738(4) (p_4)	1.754	1.774	1.765	1.764	1.793
S—H	1.335[b]	1.325	1.325	1.342	1.366	1.362
S—C=O	127.6(10) (p_5)	126.2	125.2	126.2	127.0	126.6
S—C—C	115.7(9) (p_6)	114.0	114.9	114.5	112.8	113.2
C—C=O	116.7(14)	119.8	119.9	119.3	120.2	120.2
C—S—H	96.5[b]	93.7	93.9	92.1	92.5	93.1
F—C—F	107.4(2) (p_7)	108.4	108.8	108.6	108.6	108.4
τ(O=C—C—F)	29.5(12) (p_8)	60.0	31.0	60.0	51.0	51.0
ϕ(O=C—S—H)	0.0[c]	0.0	6.0	0.0	2.0	2.0

Interatomic Distances and Vibrational Amplitudes

	distances	amplitudes		distances	amplitudes
C=O	1.22	0.041(8) (a_1)	O···F1	2.61	0.179(22) (a_6)
C—F	1.34	0.047(2) (a_2)	S···F3	2.94	
C—C	1.52	0.045[c]	O···F2	3.02	
S—C	1.74	0.053(4) (a_3)	O···F3	3.41	0.164(10) (a_7)
F···F	2.16	0.053(2) (a_4)	S···F2	3.47	
O···C	2.32		S···F1	3.90	0.112(10) (a_8)
C···F	2.37				
S···O	2.66	0.083(11) (a_5)			
S···O	2.80				

[a] r_a distances in angstroms and $\angle_\alpha$ angles in degrees. Error limits are 3σ values. For atom numbering see Figure 1. [b] CH_3SH.[20] [c] Not refined. [d] See footnote *a* of Table 1. [e] See footnote *b* of Table 1.

Table 3. Results of Electron Diffraction Analysis and ab Initio Calculations for Syn $CF_3C(O)SCH_3$

Geometric Parameters

	GED[a]	HF/3-21G*	HF/6-31G*
C=O	1.206(6) (p_1)	1.204	1.182
C—F	1.335(2) (p_2)	1.345	1.318
C—C	1.527(5) (p_3)	1.522	1.540
C1—S	1.743(14) (p_4)	1.741	1.761
S—C3	1.807(16) (p_5)	1.810	1.811
C—H	1.095(13) (p_6)	1.079	1.080
S—C=O	127.2(19) (p_7)	125.8	125.3
S—C—C	116.0(8) (p_8)	114.6	115.6
C—C=O	116.8(21)	119.6	119.1
C—S—C	97.5(13) (p_9)	97.6	98.8
F—C—F	107.7(2) (p_{10})	108.3	108.2
H—C—H	109.0[b]	110.0	109.7
τ(O=C—C—F)	38.1(14) (p_{11})	60.0	37.5
ϕ(O=C—S—C)	0.0[b]	0.0	5.0
E(anti) − E(syn)[c]		4.2	4.2

Interatomic Distances and Vibrational Amplitudes

	distances	amplitudes		distances	amplitudes
C—H	1.09	0.070[b]	O···F1	2.70	0.155(19) (a_6)
C=O	1.21	0.045(11) (a_1)	S···F3	2.82	
C—F	1.34	0.046(2) (a_2)	O···F2	2.99	
C—C	1.53	0.040[b]	O···C3	2.83	0.110[b]
C1—S	1.74	0.057(8) (a_3)	O···F3	3.43	0.152(11) (a_7)
S—C3	1.81		S···F2	3.50	
F···F	2.16	0.059(2) (a_4)	S···F1	3.84	0.100(10) (a_8)
O···C2	2.35		C2···C3	4.14	0.100[b]
C1···F	2.36		C3···F3	4.50	0.10(3) (a_9)
S···O	2.64	0.064(10) (a_5)	C3···F2	4.80	0.13(4) (a_{10})
C1···C3	2.68		C3···F1	4.98	0.19(7) (a_{11})
S···C2	2.78				

[a] r_a distances in angstroms and $\angle_\alpha$ angles in degrees. Error limits are 3σ values. For atom numbering see Figure 2. [b] Not refined. [c] Calculated energy difference in kilocalories per mole.

present in the gas phase. Ten geometric parameters and eleven vibrational amplitudes were refined simultaneously. The following correlation coefficients had values larger than |0.7|: $p_3/p_9 = -0.77$ and $a_1/a_2 = 0.82$. The final results (geometric parameters p_i and vibrational amplitudes a_k) are collected in Table 4.

Discussion

The GED anlyses for $CF_3C(O)SCH_3$ and $CF_3C(O)SCl$ demonstrate that the syn conformations are clearly preferred in these two thioacetyl compounds and possible contributions of

Table 4. Results of Electron Diffraction Analysis and ab Initio Calculations for Syn $CF_3C(O)SCl$

Geometric Parameters

	GED[a]	HF/3-21G*	HF/6-31G*
C═O	1.224(5) (p_1)	1.195	1.173
C—F	1.340(2) (p_2)	1.343	1.312
C—C	1.546(5) (p_3)	1.524	1.540
C—S	1.765(5) (p_4)	1.765	1.783
S—Cl	2.013(3) (p_5)	2.005	2.009
S—C═O	126.4(8) (p_6)	126.8	126.2
S—C—C	112.5(6) (p_7)	112.1	113.6
C—C═O	121.1(10)	121.1	120.2
C—S—Cl	99.4(6) (p_8)	99.3	99.9
F—C—F	109.0(2) (p_9)	108.3	109.0
τ(O═C—C—F)	39.5(16) (p_{10})	60.0	60.0
ϕ(O═C—S—C)	0.0[b]	0.0	0.0
E(anti) − E(syn)[c]		5.6	3.0

Interatomic Distances and Vibrational Amplitudes

	distances	amplitudes		distances	amplitudes
C═O	1.22	0.042(9) (a_1)	Cl···O	2.99	0.119(22) (a_7)
C—F	1.34	0.044(3) (a_2)	S···F3	2.75	0.159(28) (a_8)
C—C	1.55	0.045[b]	O···F1	2.75	
C—S	1.76	0.055(5) (a_3)	O···F2	3.03	
S—Cl	2.01	0.055(2) (a_4)	S···F2	3.48	0.155(16) (a_9)
F···F	2.18	0.047(3) (a_5)	O···F3	3.48	
C···F	2.37		S···F1	3.82	0.100(12) (a_{10})
C2···O	2.42	0.070[b]	Cl···C2	4.34	0.093(18) (a_{11})
S···O	2.68	0.070(9) (a_6)	Cl···F3	4.66	0.098(13) (a_{12})
S···C2	2.76		Cl···F2	5.00	0.175(27) (a_{13})
C1···Cl	2.89		Cl···F1	5.17	

[a] r_a distances in angstroms and $\angle_\alpha$ angles in degrees. Error limits are 3σ values. For atom numbering see Figure 3. [b] Not refined. [c] Calculated energy difference in kilocalories per mole.

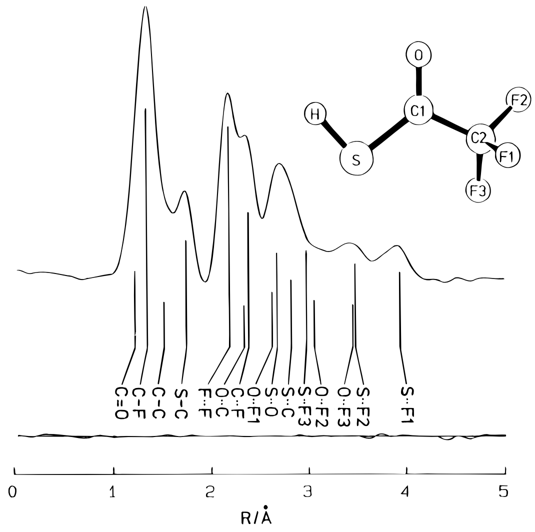

Figure 1. Experimental radial distribution curve, difference curve, and molecular model for syn $CF_3C(O)SH$. Interatomic distances are indicated by vertical bars.

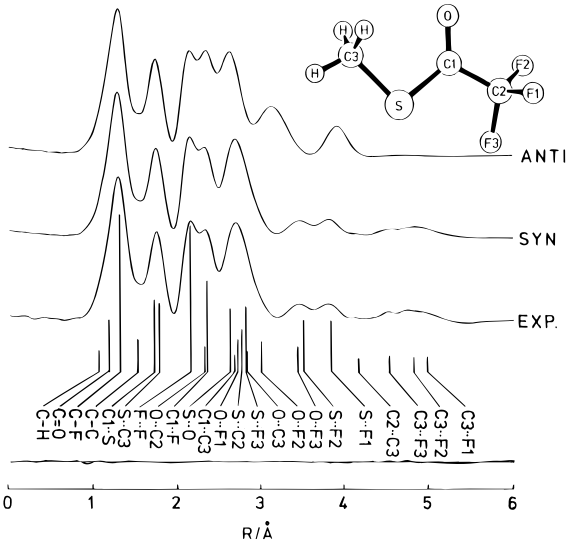

Figure 2. Calculated radial distribution functions for anti and syn forms, experimental curve and difference curve for $CF_3C(O)SCH_3$, and molecular model for the syn conformer. Interatomic distances are indicated by vertical bars.

anti forms are estimated to be <5%. In the IR spectra no splitting of the C═O vibration band is observed. Such a splitting, which is typical for the presence of two conformers in carbonyl compounds, was observed, for example, in the case of HC(O)SH,[6,21] FC(O)SCl,[11] and FC(O)SBr.[22] These experimental results for $CF_3C(O)SCH_3$ and $CF_3C(O)SCl$ are reproduced correctly by ab initio calculations, which predict the anti forms to be higher in energy by 4.2 and 3.0−5.6 kcal mol^{-1}, respectively.

The conformational properties of $CF_3C(O)SH$ cannot be determined in the GED experiment. All theoretical calculations (ab initio and DFT) predict the syn structure to be preferred by 0.9−2.2 kcal mol^{-1}. The infrared spectrum[16] exhibits a single C═O vibrational band at 1755(vs) cm^{-1} for the vapor, and two vibrations at 1739(s) and 1717(s) cm^{-1} are present in the liquid state. Crowder[16] interpreted this observation with the presence of a mixture of two conformers in the liquid and the presence of the anti form only in the gas phase. The preference of the anti conformation in the gas phase was rationalized by a stabilizing F···H interaction. Thereby, it was assumed that the CF_3 group staggers the C═O bond, allowing the formation of a planar $\overline{\mathrm{S{-}H{\cdots}F{-}C{-}C}}$ five-membered ring conformation with an estimated F···H contact of 2.4 Å. All of our theoretical

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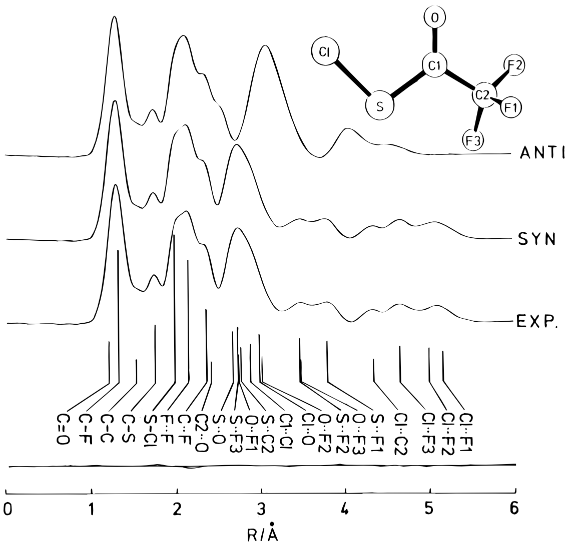

Figure 3. Calculated radial distribution functions for anti and syn forms, experimental curve and difference curve for $CF_3C(O)SCl$, and molecular model for the syn conformer. Interatomic distances are indicated by vertical bars.

calculations, however, predict an eclipsed orientation of this group for the anti structure (Table 1) with an F···H separation of ca 2.7 Å. This distance is definitely too long for F···H bonding, which occurs for distances between ca 1.56 Å in $(HF)_6$ [23] and ca 2.2 Å for weaker bonds. The GED result, i.e., a rotated CF_3 group ($\tau(O{=}C{-}C{-}F) = 29.5(12)°$) is also very unfavorable for the formation of a stabilizing F···H interaction. Thus, on the basis of the calculated relative energies and from the experimental orientation of the CF_3 group, we conclude that only the syn conformer is present in the gas phase. A detailed conformational analysis (IR matrix and low-temperature ^1H-NMR spectra) for this molecule is in progress.

The GED studies for all three thioacetyl compounds result in rotated CF_3 groups with torsional angles $\tau(O{=}C{-}C{-}F) = 29.5(12)°$ ($CF_3C(O)SH$); 38.1(14)° ($CF_3C(O)SCH_3$) and 39.5(16)° ($CF_3C(O)SCl$). A similar torsion of the CF_3 group ($\tau(O{=}C{-}C{-}F) = 17.3(9)°$) was reported for the trifluoroacetyl acid, $CF_3C(O)OH$.[24] This is in contrast to GED results for $CF_3C(O){-}X$ compounds (X = F[25] and Cl[26]), where the CF_3 group eclipses the C=O double bond ($\tau(O{=}C{-}C{-}F) = 0°$). The theoretical predictions for the orientation of the CF_3 group in the syn conformers are ambiguous. In $CF_3C(O)SH$ the result depends upon the calculational method (Table 1). The HF/3-21G* and MP2/6-31G* approximations lead to a staggered CF_3 group, whereas the HF/6-31G** and the DFT approaches predict a rotated CF_3 group with $\tau(O{=}C{-}C{-}F) = 31°$ and 51°, respectively. Similarly, the CF_3 group is calculated to be staggered (HF/3-21G*) or rotated ($\tau(O{=}C{-}C{-}F) = 37.5°$ (HF/6-31G*)) in $CF_3C(O)SCH_3$. On the other hand, both HF methods lead to a staggered CF_3 group in $CF_3C(O)SCl$, in contrast with the experimental result. Thus, only the HF/6-31G*^(*) approximations predict this structural feature correctly for $CF_3C(O)SH$ and $CF_3C(O)SCH_3$, but not for $CF_3C(O)SCl$. All other geometric parameters are reproduced reasonably well by the the theoretical calculations, i.e., distances within ±0.04 Å and bond angles within ±3°, except for the C−S bond in $CF_3C(O)SH$, which is predicted 0.06 Å too long by the NLDFT method.

Table 5 compares skeletal geometric parameters for some thioester compounds whose structures were studied in the gas phase. According to the GED analyses in all compounds, except for $CF_3C(O)SH$, the syn form represents unambiguously the most stable structure. Only in the case of FC(O)SCl the presence of the anti conformer (12(5)%) was clearly demonstrated.[11]

The C=O bond in all of these trifluoromethyl thioacetyls are remarkably longer than in other thioester compounds. All molecules in Table 5 possess similar $C(sp^2){-}S$ bond lengths of 1.750 ± 0.015 Å. $C(sp^3){-}S$ bond lengths in $CH_3{-}SX$ compounds (X = H, CH_3, and Cl) amount to 1.800 ± 0.015 Å (1.814(5) Å in CH_3SH,[20] 1.807(2) Å in CH_3SCH_3,[27] and 1.788(5) Å in CH_3SCl[28]). Since the covalent radii of sp^2 and sp^3 hybridized carbon atoms differ by 0.03 Å,[29] we expect $C(sp^2){-}S(II)$) bond lengths of ca. 1.77 Å. The experimental bond lengths are only slightly shorter than this value. Thus, the C−S bond lengths do not unambiguously prove the contribution of mesomeric structures of the type $O^-{-}C{=}S^+$ and $O^+{-}C{=}S^-$, as proposed by Baker and Harris.[2] Possibly, substituent effects compensate the expected shortening of the C−S bonds. On the other hand, the high barrier to internal rotation around the C−S bond calculated for $CF_3C(O)SH$ (7.4 kcal mol^{-1}) can be rationalized by some double bond character.

Conclusion

According to GED and ab initio calculations, $CF_3C(O)SCH_3$ and $CF_3C(O)SCl$ possess planar skeletal structures with the $S{-}CH_3$ and S−Cl bonds syn with respect to the C=O double bond. In the case of $CF_3C(O)SH$ the GED analysis is not conclusive about the conformational properties, but all of our theoretical calculations predict the preference of the syn form. The CF_3 group of all three compounds adopts an intermediate orientation between eclipsed and staggered with respect to the C=O bond. Most theoretical calculations of this study do not reproduce this structural feature correctly.

Experimental Section

$CF_3C(O)SH$ was obtained by the reaction between $CF_3C(O)Cl$ and H_2S according to ref 30.

$CF_3C(O)SCH_3$. The preparation of $CF_3C(O)SCH_3$ was performed by applying the method reported by ref 31. The synthesis was slightly modified. $CF_3C(O)Cl$ (instead of trifluoroacetic anhydride) and CH_3SH were condensed together at −100 °C. Warming slowly from −100 °C to room temperature resulted in the appearance of a colorless liquid.

$CF_3C(O)SCl$ was synthesized by condensing 0.02 mol of $CF_3C(O)SH$ and 0.025 mol of Cl_2 in a 420 ml Pyrex vessel.[32]

The compounds were purified by fractional condensation at reduced pressure, and their purities were checked by IR (gas), Raman (liquid), and ^1H- and ^{19}F-NMR spectroscopies. The electron diffraction intensities were recorded with the Balzers Gasdiffractograph KD-G2[33] at two camera (nozzle-to-plate) distances (25 and 50 cm) with an accelerating voltage of about 60 kV. The electron wavelength was calibrated with ZnO diffraction patterns. The sample reservoirs were kept at −35 ($CF_3C(O)SH$), −20 ($CF_3C(O)SCH_3$), and −30 °C ($CF_3C(O)SCl$). The

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Table 5. Skeletal Parameters of (Trifluoromethyl)thioacetic Acid and Some Derivatives of the Type X—C(O)S—Y

	$CF_3C(O)SH$[a]	$CF_3C(O)SCH_3$[a]	$CF_3C(O)SCl$[a]	FC(O)SCl[b]	ClC(O)SCl[c]	$ClC(O)SCH_3$[d]
C═O	1.217(5)	1.206(6)	1.224(5)	1.179(4)	1.183(5)	1.191(3)
C—X	1.524(4)	1.531(5)	1.546(5)	1.342(4)	1.789(8)	1.787(12)
C—S	1.738(4)	1.752(14)	1.765(5)	1.756(3)	1.752(9)	1.751(8)
S—C═O	127.6(10)	126.1(19)	126.4(8)	130.9(5)	129.6(20)	127.9(15)
X—C═O	116.7(14)	118.7(21)	121.1(10)	123.9(9)	124.2(20)	122.9(28)
C—S—Y	96.5[e]	98.1(13)	99.4(6)	100.3(5)	100.6(4)	99.0(3)

[a] r_a and $\angle_\alpha$ (this work). [b] r_a and $\angle_\alpha$.[11] [c] r_a and $\angle_\alpha$.[8] [d] r_g and $\angle_\alpha$.[14] [e] Not refined.

nozzle was maintained at room temperature, and the camera pressure did not exceed 2×10^{-5} Torr during the experiments. The exposure times for the long camera distance were 5−6 ($CF_3C(O)SH$), 6−8 ($CF_3C(O)SCH_3$), and 6−7 s ($CF_3C(O)SCl$) and 24−28 ($CF_3C(O)SH$), 20−28 ($CF_3C(O)SCH_3$), and 17−20 s ($CF_3C(O)SCl$) for the short distance. For all three compounds two plates of each camera distance were analyzed by the usual procedures.[34] The averaged molecular intensities for $CF_3C(O)SH$ in the scattering ranges 2−18 and 8−35 $Å^{-1}$, in steps of $\Delta s = 0.2$ $Å^{-1}$, are presented in Figure 4. The intensities for $CF_3C(O)SCH_3$ and $CF_3C(O)SCl$ are not shown. Numerical values for all of these compounds are included as Supporting Information.

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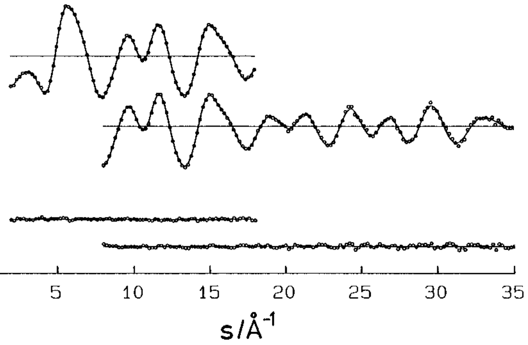

Figure 4. Experimental (dots) and calculated (full line) molecular scattering intensities and differences for $CF_3C(O)SH$.

Supporting Information Available: Tables of the total scattering intensities for $CF_3C(O)SH$, $CF_3C(O)SCH_3$, and $CF_3C(O)SCl$ (6 pages). Ordering information is given on any current masthead page.

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