Inorg. Chem. **2002**, *41*, 5699–5705

Inorganic Chemistry
Article

Trifluoroacetylsulfenyl Trifluoroacetate, $\mathrm{CF_3C(O){-}S{-}O{-}C(O)CF_3}$, a Novel Compound with a Symmetrically Substituted S–O Bond: Synthesis, Spectroscopic Characterization, and Quantum Chemical Calculations

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Received April 17, 2002

The new compound trifluoroacetylsulfenyl trifluoroacetate, $\mathrm{CF_3C(O)SOC(O)CF_3}$, which possesses two identical carbonyl substituents attached to the S–O bond, has been synthesized. The IR and UV spectra of the gas phase as well as the ^{13}C NMR spectrum of the solution in $\mathrm{CDCl_3}$ were recorded and assigned. Quantum chemical calculations were performed with the ab initio methods HF and MP2 and the density functional approach B3LYP. The 6-31G* basis set was chosen in all calculations. The molecule possesses a skew structure, and according to all computational methods, the syn–syn structure (C═O bonds of both $\mathrm{C(O)CF_3}$ groups synperiplanar to S–O bond) represents the most stable conformer. In agreement with the quantum chemical calculations, the presence of small amounts ($\leq$5%) of a second conformer (anti–syn) cannot be excluded on the basis of the IR spectrum. The calculated values for the torsional angle around the S–O bond (δ(C–S–O–C)) of the syn–syn form are smaller than 80° (72–78°). Comparison with theoretical results for the corresponding disulfide $\mathrm{CF_3C(O)SSC(O)CF_3}$ and peroxide $\mathrm{CF_3C(O)OOC(O)CF_3}$ indicates that the structural properties of sulfenyl compounds are more similar to those of disulfides than to those of peroxides.

Introduction

Coenzyme A, HSCoA, is one of the most important biological molecules, because it plays a central role in the metabolism.[1–5] Its active center is the SH group. Coenzyme A is bonded to acyl groups through a thioester bond. The hydrolysis of a thioester (XC(O)SY) is more favored than that of the corresponding ester (XC(O)OY) from a thermodynamical point of view: $\Delta G°$ at pH = 7 amounts to −7.5 kcal mol^{-1} (1 cal = 4.18 J) for the hydrolysis of acetyl-CoA. This implies a high transference potential for acetyl groups. The usual explanation is a more extended double bond character of the C−O single bond in esters than that of the C−S bond in thioesters.[6]

However, for a true comparison between conformational properties of thioesters and esters, a molecule containing both groups would be appropriate. Therefore, we became interested in a compound possessing a C(O)SOC(O) framework, which belongs to the class of sulfenic esters RSOR′. They are structurally more related to peroxides (ROOR′) and disulfides (RSSR′) with a linear connectivity.

Another requirement for such a comparison is the type of the substituents; that is, the molecule must be symmetric with exception of the S−O group (R = R′). However, many

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10.1021/ic025659f CCC: $22.00

sulfenic esters were found to be quite unstable because of their sensitivity to moisture and disproportionation.[7] Even more unstable are sulfenyl carboxylates containing the C(O)-SO group. It was observed that the stability of them correlates with the electron-withdrawing ability of the functional group attached to the sulfur atom.[8] Thus, the only compound with two acyl groups attached to the S−O group known so far is fluorocarbonylsulfenyl trifluoroacetate, $FC(O)SOC(O)CF_3$.[9] On the basis of these experimental findings, a good candidate, which possesses the necessary features, is the new compound trifluoroacetylsulfenyl trifluoroacetate, $CF_3C(O)SOC(O)CF_3$. In this work, we present the synthesis and the chemical and spectroscopic characterization (IR, UV, ^{13}C NMR) of this molecule. The structure and conformational properties were determined by quantum chemical calculations at various levels of theory.

In the study of sulfenic esters, another interesting point of view is the comparison with peroxides and disulfides. A computational study of Gregory and Jenks[10] showed that the S−O bond dissociation energy (64 kcal mol^{-1} for CH_3SOCH_3) is much closer to that of the S−S bond in disulfides (72 kcal mol^{-1} in the case of CH_3SSCH_3, experimental value) than to that of the O−O bond in peroxides (37 kcal mol^{-1} in CH_3OOCH_3, experimental value). This is attributed to the reduced lone pair repulsion and to the difference in electronegativity between S and O. Both effects increase the bond enthalpy of S−O relative to O−O.

A prominent structural parameter of interest in these compounds is the torsional angle around the S−O, S−S, or O−O bonds. In the gas phase, the geometric structures of noncyclic disulfides are characterized by torsional angles δ(X−S−S−X) close to 90°, for example, H_2S_2, 90.6(5)°;[11] F_2S_2, 87.7(4)°;[12] Cl_2S_2, 85.2(2)°;[13] and $(CH_3)_2S_2$, 85.3(37).[14] Exceptions are disulfides with very bulky substituents, such as *t*-Bu_2S_2, δ(C−S−S−C) = 128(3)°,[15] or $(CF_3)_2S_2$, δ(C−S−S−C) = 104.4(40)°,[16] which have torsional angles considerably larger than 90°, and FC(O)SSC(O)F, δ(C−S−S−C) = 82.2(19)°,[17] which possesses a torsional angle quite smaller than 90°. In the case of peroxides, the values for δ(X−O−O−X) show larger variations. In the parent compound, H_2O_2, this angle amounts to 120(5)°,[18] but in most other peroxides, it becomes larger, for example, in $(CF_3)_2O_2$, 123(4)°;[19] $(CH_3)_2O_2$, 135(5)°;[20] or *t*-Bu_2O_2, 166(3)°.[21] These torsional angles are vibrationally averaged values. Surprisingly small torsional angles possess the peroxides F_2O_2, δ(X−O−O−X) = 88.1(4)°,[22] and Cl_2O_2, δ(X−O−O−X) = 81.03(1),[23] as well as peroxides with two sp^2-hybridized substituents, that is, FC(O)OOC(O)F, 83.5(14)°,[24] and $CF_3C(O)OOC(O)CF_3$, 86.5(32)°.[25]

Unfortunately, there exist very few gas-phase structural data for sulfenic esters. The structure of CH_3SOH was studied by microwave spectroscopy (δ(C−S−O−H) = 93.9(1)°).[26] Gas-phase electron diffraction measurements were performed for $(CH_3O)_2S$ and $(CH_3O)_2S_2$ (δ(O−S−O−C) = 84(3)°[27] and δ(C−O−S−S) = 74(3)°[28]).

Experimental Section

Preparation. Trifluoroacetylsulfenyl trifluoroacetate, $CF_3C(O)SOC(O)CF_3$, was synthesized by reaction of 2.5 mmol of $CF_3C(O)SCl$ and 4.4 mmol of $AgOC(O)CF_3$. The reaction was carried out in a flame sealed glass tube (o.d. 6 mm) as reaction vessel at −80 °C. After warming up to −5 °C (about 24 h), the volatile products were separated by fractional condensation in vacuo. The product, $CF_3C(O)SOC(O)CF_3$, was purified by repeated trap-to-trap condensation. The title compound decomposes to give trifluoroacetic anhydride, $CF_3C(O)OC(O)CF_3$, and sulfur.

The volatile materials were manipulated in a glass vacuum line equipped with a capacitance pressure gauge (Setra Systems, INC., Acton, MA, model 280E, range 0−172 kPa) and valves with PTFE stems (Young, London). The product was stored in glass tubes in liquid nitrogen. Chemical analyses for C and S were also performed (Elemental Analyzer Mod. 1106, Carlo Erba). The results were C, 20.3 (theoretical 19.8); S, 12.5 (theoretical 13.2).

Instrumentation. (a) Vibrational Spectroscopy. Gas-phase infrared spectra were recorded in the range 4000−400 cm^{-1} on the FTIR Instrument Bruker IFS66 (resolution of 2 cm^{-1}), using a glass cell (10 cm optical path length, Si windows).

(b) UV Spectroscopy. The gas-phase UV spectra of $CF_3C(O)SOC(O)CF_3$, $CF_3C(O)SH$, $CF_3C(O)OH$, and $CF_3C(O)OC(O)CF_3$ were obtained in a quartz cell (10 cm optical path length) with the UV−vis Hewlett-Packard 8454-A diode array spectrometer (2 nm resolution).

(c) NMR Spectroscopy. ^{13}C NMR spectra were recorded at room temperature on a Bruker AC 250 NMR spectrometer using samples dissolved in $CDCl_3$ and referenced internally to $Si(CH_3)_4$.

Results

(a) Quantum Chemical Calculations. The calculations were performed with the Gaussian 94[29] and Gaussian 98[30] program packages applying the ab initio Hartree−Fock (HF)

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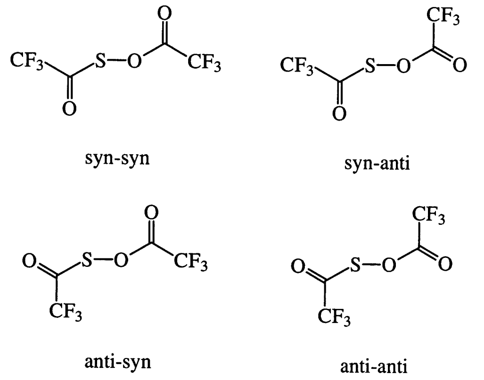
Chart 1



and MP2 methods as well as the density functional B3LYP approach, in which Becke's three parameter hybrid functional,[31] representing the exchange term, is combined with the correlation functional of Lee, Yang, and Parr.[32] The 6-31G* basis set was chosen for all calculations.

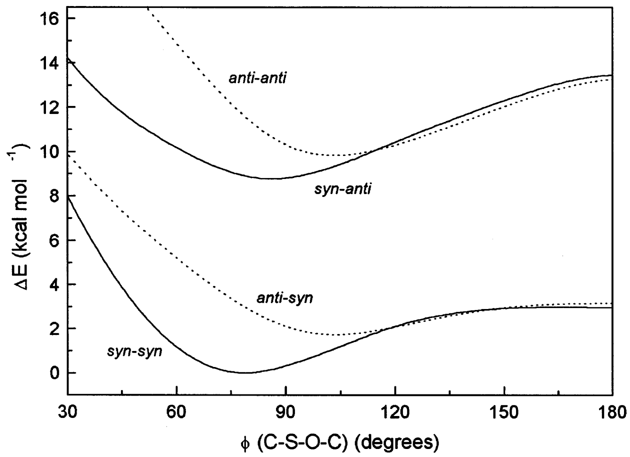


Figure 1. Calculated relative energies (HF/6-31G*) for various dihedral angles δ(C−S−O−C) for the syn−syn, syn−anti, anti−syn, and anti−anti conformers.

Table 1. Calculated Relative Energies ΔE (kcal mol^{-1}) of the Conformers of $CF_3C(O)SOC(O)CF_3$

	HF/6-31G*	MP2/6-31G*	B3LYP/6-31G*
syn−syn	0.00	0.00	0.00
syn−anti	8.78	7.40	6.00
anti−syn	1.73	2.36	2.36
anti−anti	9.83	9.26	7.89

Table 2. Calculated Torsional Angles δ(C−S−O−C) (deg) around the S−O Bond of the Conformers of $CF_3C(O)SOC(O)CF_3$

	HF/6-31G*	MP2/6-31G*	B3LYP/6-31G*
syn−syn	78	72	77
syn−anti	86	80	86
anti−syn	103	96	100
anti−anti	104	98	102

$CF_3C(O)SOC(O)CF_3$ can, in principle, exist in four different conformeric forms, in which the two C═O bonds are syn- or antiperiplanar relative to the S−O bond (see Chart 1). To determine the approximate values for the torsional angle δ(C−S−O−C), for which the four possible structures syn−syn, syn−anti, anti−syn, and anti−anti correspond to minima on the energy hypersurface, in a first step the potential functions for rotation around the S−O single bond were determined. The geometries were optimized with fixed values for the torsional angle δ(C−S−O−C) in steps of 30° using the HF/6-31G* approximation. The resulting potential curves for dihedral angles between 30° and 180° are shown in Figure 1. For smaller torsional angles, strong distortions of the $C(O)CF_3$ groups occur because of steric repulsions between these two groups. The four curves exhibit global minima near $\delta(C{-}S{-}O{-}C) = 90°$. Subsequently, the four conformations were fully optimized using HF, MP2, and B3LYP methods, and frequency calculations were performed with the HF and B3LYP methods. The relative energies of the four conformers are collected in Table 1. All three computational methods predict the syn−syn rotamer to be the most stable structure and the anti−anti conformer to be the highest in energy.

The potential functions for the four conformers are very flat for torsional angles around 180°. For this dihedral angle, all three computational methods result for the syn−syn conformer in structures without an imaginary frequency. However, the lowest frequency which corresponds to torsion around the S−O bond is predicted between 8 and 11 cm^{-1}. Furthermore, the depth of this minimum at $\delta = 180°$ is on the order of only 10 cal, that is, lower or on the order of the zero-point vibrational energy of the torsional modes. Thus, this structure with trans orientation of the two $C(O)CF_3$ groups does not correspond to a stable, observable conformer at room temperature. In the case of the anti−syn conformer, only the B3LYP method resulted in a trans structure without imaginary frequency. This method predicts imaginary frequencies for the syn−anti and anti−anti conformers of $\delta =$ 180°.

As is evident from Table 2, the smallest values (72−78°) of the torsional angle δ(C−S−O−C) were obtained for the syn−syn form. The corresponding values for the syn−anti conformation are larger by 8−9°. The torsional angles of the two conformers with anti orientation of the $CF_3C(O)S$ moiety (anti−syn and anti−anti) are nearly equal, and their

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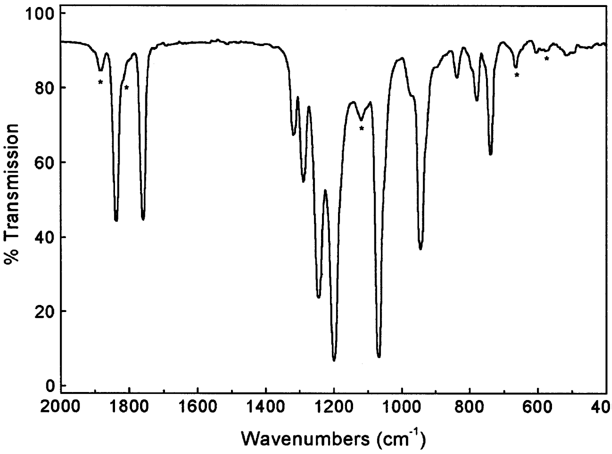

Figure 2. IR spectrum of gaseous CF$_3$C(O)SOC(O)CF$_3$, 2 mbar at 10 cm optical path length and room temperature ($* \equiv$ CF$_3$C(O)OC(O)CF$_3$, impurity).

values are about 18−27° larger than those of the corresponding syn counterparts (syn−syn and syn−anti).

In all conformations, the CF$_3$ group of the CF$_3$C(O)O moiety adopts an eclipsed orientation with respect to the C=O double bond. However, the position of the CF$_3$ group in the CF$_3$C(O)S moiety depends on the orientation of the carbonyl bond relative to the S−O single bond: In the anti conformers (anti−syn and anti−anti), the CF$_3$ group is in eclipsed orientation, whereas, in the syn structures (syn−syn and syn-anti), the position of the CF$_3$ group is staggered. The barriers to internal rotation of the two CF$_3$ groups around the C−C bonds differ appreciably. The B3LYP method predicts this barrier to be 0.54 kcal/mol in the CF$_3$C(O)O moiety and 1.58 kcal/mol in the CF$_3$C(O)S moiety. The optimized parameters for the four forms are available from the authors upon request.

(b) Vibrational Spectroscopy. Figure 2 presents the gas-phase infrared spectrum of CF$_3$C(O)SOC(O)CF$_3$. In Table 3, all vibrational data observed in the gas phase are collected together with the theoretically predicted wavenumbers (B3LYP/6-31G*) for the syn−syn conformer and the corresponding assignment. The vibrational modes were assigned by comparison with the theoretical wavenumbers and intensities and by comparison with relevant reported data. The assignments in Table 3 are based on the potential energy distribution, which was derived from the calculated Cartesian force field (B3LYP/6-31G*) with the program ASYM40.[33]

In carbonyl compounds, the C=O vibrational frequency is known to be very sensitive to conformational properties. In the spectral region of the C=O stretching mode, we observed only two bands at 1838 (ν(O−C2=O2)) and 1761 cm^{-1} (ν(S−C1=O1)), respectively (for atom numbering, see Figure 3). The weak, but characteristic, band at 783 cm^{-1} was assigned to the S−O stretching mode, which allows the identification of this new compound. This assignment, which agrees with the result of the quantum chemical calculations, is confirmed by the experimental values for the parent compound HSOH (IR(gas): 769 cm^{-1})[34] and for *tert*-butylsulfenic acid, which possesses infrared absorptions between 880 and 765 cm^{-1}, depending on the solvent.[35]

Table 3. Experimental and Calculated Vibrational Wavenumbers of CF$_3$C(O)SOC(O)CF$_3$[a,b]

	IR (gas)		B3LYP/6-31G*		
	$\tilde{\nu}$ [cm^{-1}]	I^c	$\tilde{\nu}$ [cm^{-1}]	I^d	assignment
$*$	1882	w			
ν_1	1838	m	1900	205.3	ν(C2=O2)
$*$	1817	sh			
ν_2	1761	m	1843	201.7	ν(C1=O1)
ν_3	1319	w	1322	50.5	ν(C2−C4)/ν_s(C4F$_3$)/δ_s(C4F$_3$)
ν_4	1290	w	1297	105.3	ν(C1−C3)/ν_s(C3F$_3$)/δ_s(C3F$_3$)
ν_5	1248	s	1271	302.9	ν_{as}(C4F$_3$)
ν_6			1250	222.2	ν_{as}(C3F$_3$)
ν_7	1201	vs	1227	266.7	ν_{as}(C4F$_3$)
ν_8			1213	178.9	ν_{as}(C3F$_3$)
ν_9	1070	vs	1097	503.3	ν(O−C2)/ν_s(C4F$_3$)
$*$	1051	sh			
	1007	sh			
	974	w			
ν_{10}	947	m	947	252.6	ν_s(C3F$_3$)/δ(CF$_3$C1(O))/ν(S−C1)
	900	sh			
$*$	876	vw			
ν_{11}	839	w	852	12.3	ν(O−C2)/ν_s(C4F$_3$)/ρ(CF$_3$C2(O))
	795	sh			
ν_{12}	783	w	769	47.5	ν(S−O)
$*$	760	sh			
ν_{13}			760	11.2	oop(CC2(O)O)
ν_{14}	742	w	735	79.7	δ_s(C3F$_3$)/ν_s(C3F$_3$)
ν_{15}	723	sh	717	4.3	δ_s(C4F$_3$)/ν(S−O)/ν_s(C4F$_3$)
ν_{16}	702	vvw	688	1.8	oop(CC1(O)S)
$*$	667	w			
ν_{17}	634	vvw	607	3.3	ρ(CF$_3$C1(O))/δ_s(C3F$_3$)/δ(O−S−C1)
$*$	600	w			
	575	vw			
ν_{18}	557	vw	564	2.3	δ_{as}(C4F$_3$)
$*$	523	w			
ν_{19}			523	2.9	δ_{as}(C3F$_3$)/ν(S−C1)
ν_{20}			512	8.0	δ_{as}(C4F$_3$)
ν_{21}	459	vw	495	5.2	δ_{as}(C3F$_3$)
$*$	420	vw			
ν_{22}			411	1.3	δ_{as}(C4F$_3$)/δ(CF$_3$C2(O))
ν_{23}			397	1.7	δ(CF$_3$C2(O))/δ_{as}(C3F$_3$)
ν_{24}			355	3.9	ν(C2−C4)/ρ_s(C4F$_3$)/δ_s(C4F$_3$)
ν_{25}			313	9.9	ρ_s(C4F$_3$)/δ_s(S−O−C2)
ν_{26}			301	1.9	ρ_s(C3F$_3$)/δ(O−S−C1)/ρ_{as}(C4F$_3$)
ν_{27}			272	11.9	δ(S−O−C2)/ρ_s(C3F$_3$)/ ρ_{as}(C4F$_3$)/ρ_{as}(C3F$_3$)
ν_{28}			241	8.4	ρ_{as}(C3F$_3$)
ν_{29}			191	1.2	ρ_{as}(C4F$_3$)/δ(O−S−C1)/oop(CC2(O)O)
ν_{30}			170	0.8	ρ(CF$_3$C2(O))/ρ(CF$_3$C1(O))/ ρ_s(C4F$_3$)/δ(S−O−C2)/ρ_s(C3F$_3$)
ν_{31}			142	0.8	ρ(CF$_3$C1(O))/ρ_s(C3F$_3$)/ ρ(CF$_3$C2(O))/δ(CF$_3$C1(O))
ν_{32}			77	0.3	τ(S−O)
ν_{33}			51	0.0	τ(C1−S)
ν_{34}			37	0.2	τ(O−C2)
ν_{35}			29	0.4	τ(C3F$_3$)/τ(C4F$_3$)
ν_{36}			19	0.0	τ(C4F$_3$)/τ(C3F$_3$)

[a] $* \equiv$ CF$_3$C(O)OC(O)CF$_3$ (impurity). [b] For atom numbering, see Figure 3. [c] Key: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; vvw, very very weak; sh, shoulder. [d] Calculated IR intensities in km mol^{-1}.

(c) UV Spectroscopy. In Figure 4, the UV spectrum of CF$_3$C(O)SOC(O)CF$_3$ (a) is shown together with the spectra of CF$_3$C(O)OH (b), CF$_3$C(O)OC(O)CF$_3$ (c), and CF$_3$C(O)SH (d). The UV spectrum of the sulfenic ester exhibits two absorptions at 212 and 236 nm, as well as a weak, broad band at 284 nm. It is reasonable, in comparison with CF$_3$C(O)OH (210 nm), to assign the band at 212 nm to the $\pi \rightarrow \pi^*$ transition as originated by the C(O)O chromophore. The band at 236 nm is attributed to the $\pi \rightarrow \pi^*$ transition in the

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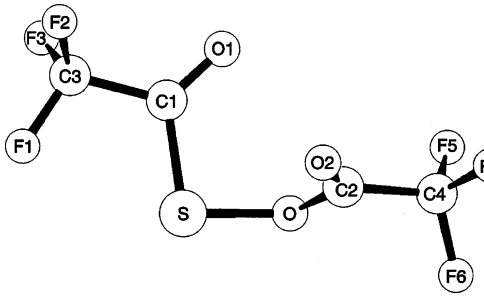

Figure 3. Molecular model of the syn−syn conformer of $CF_3C(O)SOC(O)CF_3$ with atom numbering.

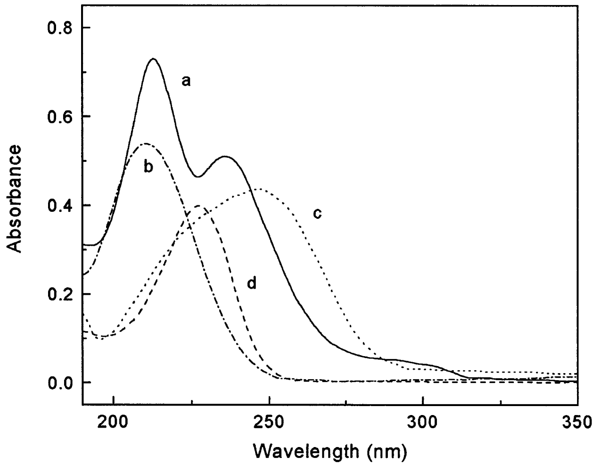

Figure 4. Gas-phase UV spectra of $CF_3C(O)SOC(O)CF_3$, <1 mbar (a), $CF_3C(O)OH$ (b), $CF_3C(O)OC(O)CF_3$ (c), and $CF_3C(O)SH$ (d).

C(O)S chromophore, taking into account the observed bands for $CF_3C(O)SH$ (226 nm) and $CF_3C(O)SCl$ (236 nm).[36] The feature at 284 nm can be assigned to the S−O group. This is in agreement with other compounds, which possess only UV absorptions due to the S−O group (*t*-$BuSOC_2H_5$, 266 nm;[37] CCl_3SO-*t*-Bu, 277 nm;[38] $CCl_3SOC_2H_5$, 275 nm;[37] $CF_3SOC_2H_5$, 262 nm[39]).

(d) NMR Spectroscopy. In the ^{13}C NMR spectrum of the sample at room temperature, four quartets at 115.1 ($C3F_3$), 113.9 ($C4F_3$), 180.8 (C(O)S), and 154.3 (C(O)O) ppm relative to TMS are observed. The coupling constants $^1J_{CF}$ and $^2J_{CF}$ are determined to be 290.7 and 286.1 or 42.9 and 46.3 Hz, respectively. In Table 4, all NMR data are compared to those of some similar compounds containing the $CF_3C(O)$ group. The quartet at 180.8 ppm was assigned in comparison with $CH_3C(O)SOCH_3$ (192.3 ppm [C(O)]).[40]

Besides the signals of the S−O compound, in the ^{13}C NMR spectra, signals due to impurities that arise at room temperature and in the course of days were obtained. One of them, as expected, was $CF_3C(O)OC(O)CF_3$.

Table 4. NMR Data for $CF_3C(O)SOC(O)CF_3$ and Related Compounds

δ/ppm or J/Hz	$CF_3C(O)SOC(O)CF_3$[a,b]	$CF_3C(O)OOC(O)CF_3$[c,d]	$CF_3C(O)OC(O)CF_3$[c,d]
$\delta C(CF3)(S)$	115.1		
$\delta_C(CF_3)(O)$	113.9	114.4	113.8
$\delta_C(CO)(S)$	180.8		
$\delta_C(CO)(O)$	154.3	153.8	150.4
$^1J_{CF}(S)$	290.7		
$^1J_{CF}(O)$	286.1	286.2	284.0
$^2J_{CF}(S)$	42.9		
$^2J_{CF}(O)$	46.3	46.5	48.4

[a] Measured in solution of $CDCl_3$. [b] At room temperature. [c] At −30 °C. [d] Reference 25.

Discussion

The gas-phase infrared spectrum shows two strong bands in the carbonyl region at 1838 and 1761 cm^{-1} (see Figure 2 and Table 3). The quantum chemical calculations predict the syn−syn conformer to be 1.7 (HF) to 2.4 (MP2, B3LYP) kcal mol^{-1} more stable than the anti−syn form (this corresponds to the presence of about 2−5% of the anti−syn conformer at room temperature). These calculated energy differences indicate that the two IR bands at 1838 and 1761 cm^{-1} arise from the two carbonyl stretching vibrations of the syn−syn rotamer. The difference between the two experimental wavenumbers ($\Delta = 77$ cm^{-1}) is somewhat larger than the calculated difference in the syn−syn form (1900 and 1843 cm^{-1}, $\Delta = 57$ cm^{-1}). It agrees exactly with the calculated difference in the anti−syn conformer (1902 and 1824 cm^{-1}, $\Delta = 78$ cm^{-1}), but this agreement seems to be accidental.

In the carbonyl region, there is no sign for the presence of a second conformer, but this may be due to the fact that the bands are not resolved, as indicated by the calculations, which predict quite similar C=O stretching wavenumbers for the syn−syn and anti−syn structures (see previous discussion). However, a small shoulder (974 cm^{-1}) at the high-wavenumber side of the band at 947 cm^{-1} may reveal the presence of a small amount of the anti−syn structure (calculated wavenumbers: syn−syn, 947 cm^{-1}; anti−syn, 967 cm^{-1}).

Finally, we conclude that, on the basis of experimental and theoretical wavenumbers, it is not possible to decide unambiguously whether the syn−syn or the anti−syn conformer is the prevailing structure at room temperature. Only a few normal modes of the two forms differ significantly in their theoretical values. These differences fall into a 20 cm^{-1} range, that is, in the same range as many differences between calculated and theoretical values (Table 3). Because of the large calculated energy differences between the syn−syn and anti−syn conformer and because of the experimental and theoretical results of other molecules of the type $CF_3C(O)SX$ (X = Cl, H, CH_3)[41] or $CF_3C(O)OY$ (Y = H,[42] $OC(O)CF_3$,[25] ONO_2[43]), which all possess planar syn structures, the conclusion is justified: the syn−syn form represents the main conformer. According to the IR spectrum and the quantum chemical calculations, the presence of a

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small amount of a second conformation (anti−syn) could not be excluded. The two other possible conformations (syn−anti and anti−anti) were not considered, because of the very large theoretical energy differences (see Table 1).

No experimental values for the torsional angle around the S−O bond and other geometric parameters are available for comparison with theoretical values, because the molecule was not stable enough to perform a structure determination with gas-phase electron diffraction. Nevertheless, we can draw some conclusions about the torsional angle δ(C−S−O−C) by comparison with theoretical and experimental data for the corresponding peroxides and disulfides. The experimental torsional angle δ(C−O−O−C) in $CF_3C(O)OOC(O)CF_3$ (87(3)°)[25] is reproduced very well by the B3LYP/6-31G* method (86°). The corresponding value for δ(C−S−O−C) in the syn−syn conformer of $CF_3C(O)SOC(O)CF_3$ (77°) is about 10° smaller. The MP2/6-31G* values show the same difference (δ(C−O−O−C) = 81.0 and δ(C−S−O−C) = 72°). For further comparison, we also performed calculations for the corresponding disulfide, $CF_3C(O)SSC(O)CF_3$, which exhibits smaller values for δ(C−S−S−C) in the case of the syn−syn rotamer (B3LYP/6-31G*, 74°; MP2/6-31G*, 70°). Similarly, the calculated (B3LYP) torsional angle in the disulfide FC(O)SSC(O)F is slightly smaller (82°) than that in the corresponding peroxide (86)°. These predicted values are in good agreement with the experimental values of 82(2)°[17] and 84(2)°,[24] considering the experimental uncertainties. From these results, we conclude that quantum chemical methods (B3LYP and MP2 with 6-31G* basis sets) reproduce experimental torsional angles in peroxides and disulfides very well. Comparison of calculated values for the sulfenyl compound with those for peroxides and disulfides reveals that the conformational properties around the S−O bond are more similar to those around the S−S bond than to those around the O−O bond.

According to B3LYP calculations, the trans structure of the syn−syn $CF_3C(O)S{-}OC(O)CF_3$ is higher in energy by 1.86 kcal/mol relative to the ground-state structure. This trans barrier to internal roation around the S−O bond is intermediate between the barriers around the O−O bond in the analogous peroxide, $CF_3C(O)O{-}OC(O)CF_3$, (1.54 cal/mol) and around the S−S bond in the disulfide $CF_3C(O)S{-}SC(O)CF_3$ (3.04 kcal/mol).

$CF_3C(O)SOC(O)CF_3$ is specially suited to analyze differences between esters and thioesters. A more extended double bond character of the C−O single bond in esters than that of the C−S single bond in thioesters was claimed to explain the high transference potential of acetyl groups by acetyl-CoA.[6] Two factors can be taken into account to evaluate this extended biochemical concept, the rotational barriers around these bonds and the deviation of the O=C−S−O and O=C−O−S torsional angles from 0° in the most stable syn−syn conformer. The deviation of these torsional angles from 0° is slightly higher for the thioester moiety (HF/6-31G*, −2.9°; MP2/6-31G*, −3.4°; B3LYP/6-31G*, −3.6°) than for the ester moiety (HF/6-31G*, −1.70°; MP2/6-31G*, 1.1°; B3LYP/6-31G*, −0.9°), which would indicate a more extended double bond character of the C−O than of the C−S single bond. The opposite trend, however, is obtained by analyzing the rotational energy barriers around the C−S and C−O single bonds, respectively. Values of 13.19 and 10.56 kcal mol^{-1} were calculated for the height of the barrier around the C−S and C−O single bonds, respectively, with the B3LYP/6-31G* approximation. These apparently contradictory results and the small differences found in these calculations do not allow a definite conclusion to be drawn about the extension of double bond character in esters and thioesters.

Conclusion

Trifluoroacetylsulfenyl trifluoroacetate, $CF_3C(O)SOC(O)CF_3$, was successfully obtained by the reaction of $CF_3C(O)SCl$ with $AgOC(O)CF_3$ and characterized by IR, UV, and ^{13}C NMR spectroscopy and chemical analyses. This new compound represents the first sulfenic ester with two identical acylic substituents attached to the S−O bond. As reported for other sulfenyl carboxylates, it is quite unstable and decomposes fast to trifluoroacetic anhydride, $CF_3C(O)OC(O)CF_3$, and sulfur. From the gas-phase IR spectrum, it can be concluded that $CF_3C(O)SOC(O)CF_3$ exists as one predominant conformeric form at room temperature. Small amounts (≤5%) of a second conformer (anti−syn), however, could not be excluded. This is in accordance with the quantum chemical calculations (HF/6-31G*, MP2/6-31G*, and B3LYP/6-31G*), which predict the syn−syn conformer to be 1.7−2.4 kcal mol^{-1} more stable than the anti−syn structure. Because of the instability of $CF_3C(O)SOC(O)CF_3$, it was not possible to obtain experimental structural data. The most striking feature which could be observed from the theoretical structural parameters is the torsional angle around the S−O bond, δ(C−S−O−C). In the syn−syn conformer, this angle adopts values between 72° and 78°. These values lie in the same range as those for δ(C−S−S−C) in the syn−syn conformer of the corresponding disulfide $CF_3C(O)SSC(O)CF_3$ and are about 10° smaller than experimental and calculated angles δ(C−O−O−C) of the peroxide $CF_3C(O)OOC(O)CF_3$. Concerning the extension of the double bond character in esters and thioesters, no significant differences were found in the $CF_3C(O)SOC(O)CF_3$ molecule.

Acknowledgment. The authors thank Prof. Dr. P. J. Aymonino (Lanais EFO) for his generous and valuable contributions to this work. They acknowledge the Fundación Antorchas (República Argentina), Alexander von Humboldt Stiftung, the British Council, and DAAD (Deutscher Akademischer Austauschdienst, Germany) for financial support and for the DAAD-Agencia Nacional de Promoción Científica y Tecnológica (Programa PROALAR) and Alexander von Humboldt Stiftung-Fundación Antorchas Awards to the German-Argentinean cooperation and the British Council-Fundación Antorchas Award to the British-Argentinean cooperation. They also thank Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) (PIP 4695/96), Facultad de Ciencias Exactas (UNLP), and Comisión de Investigaciones Científicas de la Provincia de Buenos Aires

(CIC), República Argentina, for financial support. H.-G.M. and H.O. thank the HLRS (Stuttgart, Germany) for access to substantial computer time. H.-G.M. also acknowledges financial support by the Fonds der Chemischen Industrie.

Supporting Information Available: Additional table of calculated data. This material is available free of charge via the Internet at http://pubs.acs.org.

IC025659F