Trifluoromethanesulfenyl Acetate, $CF_3S-OC(O)CH_3$, and Trifluoromethanesulfenyl Trifluoroacetate, $CF_3S-OC(O)CF_3$: Unexpected Conformational Properties

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Structural and conformational properties of two sulfenyl derivatives, trifluoromethanesulfenyl acetate, $CF_3S-OC(O)CH_3$ (**1**), and trifluoromethanesulfenyl trifluoroacetate, $CF_3S-OC(O)CF_3$ (**2**), were determined by gas electron diffraction, vibrational spectroscopy, in particular with IR (matrix) spectroscopy, which includes photochemical studies, and by quantum chemical calculations. Both compounds exist in the gas phase as a mixture of two conformers, with the prevailing component possessing a gauche structure around the S−O bond. The minor form, 15(5)% in **1** and 11(5)% in **2** according to IR(matrix) spectra, possesses an unexpected trans structure around the S−O bond. The C═O bond of the acetyl group is oriented syn with respect to the S−O bond in both conformers. UV−visible broad band irradiation of **1** and **2** isolated in inert gas matrixes causes various changes to occur. Conformational randomization clearly takes place in **2** with simultaneous formation of CF_3SCF_3. For **1** the only reaction channel detected leads to the formation of CH_3SCF_3 with the consequent extrusion of CO_2. Quantum chemical calculations (B3LYP/6-31G* and MP2 with 6-31G* and 6-311G(2df,pd) basis sets) confirm the existence of a stable trans conformer. The calculations reproduce the conformational properties for both compounds qualitatively correct with the exception of the B3LYP method for compound **2** which predicts the trans form to be prevailing, in contrast to the experiment.

Introduction

All peroxides of the type ROOR′, whose molecular structures have been determined in the gas phase, possess gauche structures with dihedral angles ϕ(ROOR′) between about 80° and 120°. Exceptions are peroxides with bulky substituents R and R′, such as bis(*tert*-butyl) peroxide and bis(trimethylsilyl) peroxide, for which vibrationally averaged dihedral angles of 166(3)° and 144-(6)° have been derived by gas electron diffraction (GED).[1] For the parent compound HOOH an equilibrium value $\phi_e = 111.8°$ was obtained from spectroscopic data.[2] The preference of gauche structures has been rationalized with orbital interactions between the p-shaped oxygen lone pair and the σ*-orbital of the opposite O−R bond. This interaction favors a dihedral angle of 90°, and repulsion between the substituents tends to increase the dihedral angle. Some peroxides, however, possess dihedral angles < 90°, such as FOOF (88.1(4)°)[3] and ClOOCl (81.0(1)°).[4] Furthermore, peroxides with sp^2-hybridized atoms bonded to both oxygen atoms, such as C(O)X or NO_2 groups, possess dihedral angles less than 90° (ϕ(COOC) = 83.5(14)° in FC(O)OOC(O)F [5] and ϕ(COON) = 84.7(13)° in $CH_3C(O)OONO_2$[6]).

Similarly, disulfanes RSSR′ possess gauche structures. Since steric repulsion between the substituents is reduced in these compounds, the dihedral angles are closer to the "ideal" value of 90°, 90.76(6)° and 90.34 in HSSH,[7,8] 85.3(37) in CH3SSCH3,[9] or 128.2(27) in ButSSBut.[10] Dihedral angles < 90° have been observed in FSSF (87.7(4)°)[11] or in FC(O)SSC(O)F (82.2(19)°.[12] A study on the structural and conformational properties of disulfanes has been reported recently.[13]

Thioperoxides of the type RSOR′, which are derivatives of the sulfenic acid HSOH, are much less stable than peroxides or disulfanes, and very little is known about their structural properties. Only very recently the microwave spectra of the parent compound were recorded.[14] The experimental rotational constants do not allow a full structure determination, but are reproduced very closely with the geometric structure derived by high-level ab initio calculations (CCSD(T)/cc-pCVQZ). This method predicts a gauche structure with a dihedral angle of 91.3°, close to that of disulfane. The calculated barriers to internal rotation around the S−O bond at the cis and trans structures are also much closer to those for disulfane than to those for hydrogen peroxide. To our knowledge, the only experimental gas-phase structures reported for sulfenic acid derivatives are those of dimethoxysulfane, $CH_3O-S-OCH_3$,[15] and dimethoxy disulfane, $CH_3O-SS-OCH_3$.[16] In both compounds the dihedral angles around the S−O bonds (ϕ(COSO) = 84(3)° and ϕ(COSS) = 74(3)°) are smaller than 90°.

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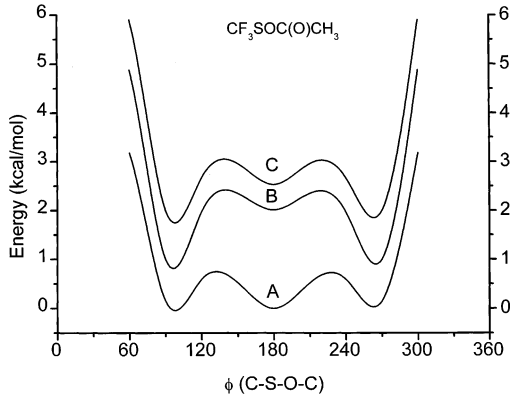

Figure 1. Calculated potential curves for internal rotation around the S−O bond in $CF_3S-OC(O)CH_3$. A: B3LYP/6-31G*, B: MP2/6-31G*, C: MP2/6-311G(2df,pd). Curves B and C are shifted by 1 and 2 kcal/mol, respectively.

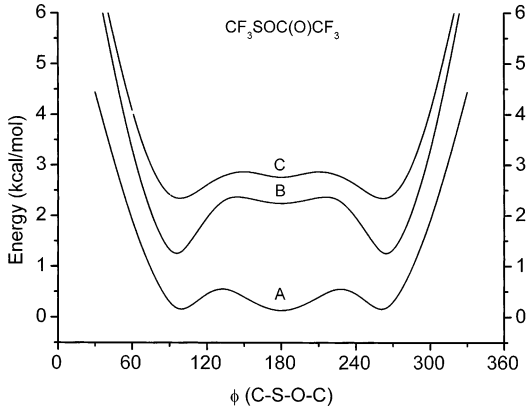

Figure 2. Calculated potential curves for internal rotation around the S−O bond in $CF_3S-OC(O)CF_3$. A: B3LYP/6-31G*, B: MP2/6-31G*, C: MP2/6-311G(2df). Curves B and C are shifted by 1 and 2 kcal/mol, respectively.

More recently, the new compound trifluoroacetylsulfenyl trifluoroacetate, $CF_3C(O)S-OC(O)CF_3$, was synthesized and characterized by IR, UV, and ^{13}C NMR spectroscopy and quantum chemical calculations.[17] According to these calculations the predominant conformer possesses a gauche structure with the C═O bonds of both $CF_3C(O)$ groups synperiplanar to the S−O bond and a trans structure around the S−O bond corresponds to a transition state. The IR(gas) spectra confirm the presence of a single conformer. In the present study we report the characterization of two sulfenic acid derivatives, trifluoromethanesulfenyl acetate, $CF_3S-OC(O)CH_3$ (**1**), and trifluoromethanesulfenyl trifluoroacetate, $CF_3S-OC(O)CF_3$ (**2**). The molecular structures and conformational properties of these two compounds were investigated by vibrational spectra, in particular IR(matrix) spectroscopy, with the complement of photochemical studies, gas electron diffraction (GED) and quantum chemical calculations.

Quantum Chemical Calculations. For both compounds two stable conformers with syn- and antiperiplanar orientation of the C═O bond with respect to the S−O bond are expected. Preliminary structure optimizations with the B3LYP/6-31G* method resulted in gauche structures around the S−O bond and the anti conformers about 4 to 6 kcal/mol higher in energy. The potential functions for internal rotation around the S−O bond were derived by structure optimizations at fixed dihedral angles between 60° and 180° using the B3LYP and MP2 method with different basis sets (Figures 1 and 2). Surprisingly, these potential functions possess a minimum for trans structures with

TABLE 1: Relative Energies, Free Energies (in kcal/mol), and C═O Vibrational Frequencies in cm^{-1}) of Stable Conformers in $CF_3S-OC(O)CH_3$ (1)

	gauche−syn	trans−syn	gauche−anti	trans−anti
		B3LYP/6-31G*		
ΔE	0.00	−0.14	4.23	8.27
$\Delta G^{0\,a}$	0.00	0.41	5.27	10.09
ν (C═O)^b	1889 (1816)	1828 (1757)	1889 (1816)	1872 (1800)
		MP2/6-31G*		
ΔE	0.00	1.01	5.48	10.50
$\Delta G^{0\,a}$	0.00	1.23	6.02	11.85
ν (C═O)^b	1876 (1770)	1831 (1727)	1870 (1764)	1857 (1752)
		MP2/6-311G(2df,pd)		
ΔE	0.00	0.73		
ΔG^0	0.00	0.95^c		

^{a} Includes different multiplicities ($m = 1$ for trans and $m = 2$ for gauche). $T = 298$ K. ^{b} The scaled frequencies using the factor reported in reference 18 is included between parenthesis. ^{c} Derived from ΔE with vibrational frequencies from MP2/6-31G* method.

TABLE 2: Relative Energies, Free Energies (in kcal/mol), and C═O Vibrational Frequencies in cm^{-1}) of Stable Conformers in $CF_3S-OC(O)CF_3$ (2)

	gauche−syn	trans−syn	gauche−anti	trans−anti
		B3LYP/6-31G*		
ΔE	0.00	−0.07	5.30	7.92
$\Delta G^{0\,a}$	0.00	−0.16	6.07	8.96
ν (C═O)^b	1902 (1829)	1857 (1785)	1883 (1810)	1879 (1806)
		MP2/6-31G*		
ΔE	0.00	1.16	6.84	10.30
$\Delta G^{0\,a}$	0.00	1.02	7.34	11.62
ν (C═O)^b	1875 (1769)	1841 (1737)	1854 (1749)	1846 (1741)
		MP2/6-311G(2df)		
ΔE	0.00	0.75		
$\Delta G^{0\,a}$	0.00	0.61^c		

^{a} Includes different multiplicities ($m = 1$ for trans and $m = 2$ for gauche). $T = 298$ K. ^{b} The scaled frequencies using the factor reported in reference 18 is included between parenthesis. ^{c} Derived from ΔE with vibrational frequencies from MP2/6-31G*method.

ϕ(C−S−O−C) = 180° in addition to the expected minima for gauche structures with ϕ(C−S−O−C) around 90°. Thus, four stable conformers with gauche and trans structures around the S−O bond, each of which can possess syn and anti orientation of the C═O bond, exist for these two sulfenyl derivatives. Relative energies, free energies calculated at 298 K and C═O vibrational frequencies for the four stable conformers are summarized in Tables 1 and 2. According to these relative energies only gauche−syn and trans−syn conformers are expected to be observed in our experiments. Due to different multiplicities of gauche ($m = 2$) and trans conformers ($m = 1$) $\Delta G° = G°$ (trans−syn) − $G°$ (gauche−syn) is expected to be more positive than ΔE. This is the case for compound **1** (Table 1).[18] For compound **2**, however, the B3LYP and MP2 methods result in calculated $\Delta G°$ values, which are slightly smaller than the corresponding ΔE values (Table 2). This trend is due to a very low torsional vibration calculated for the trans−syn conformer. All quantum chemical calculations were performed with the GAUSSIAN 98 program package.[19] Vibrational amplitudes were derived from calculated force fields (B3LYP/6-31G*) with the method of Sipachev.[20]

Experimental Section

$CF_3S-OC(O)CH_3$ (**1**), and trifluoromethanesulfenyl trifluoroacetate, $CF_3S-OC(O)CF_3$ (**2**), were prepared using reported methods in the literature,[21,22] and their purities were checked

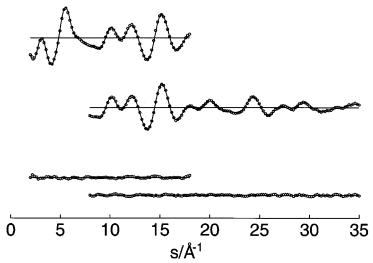

Figure 3. Averaged experimental (dots) and calculated (full line) molecular intensities for $CF_3S-OC(O)CH_3$ and residuals. Data for long (above) and short (below) nozzle-to-plate distance.

by IR and ^1H, ^{13}C, and ^{19}F NMR spectroscopy. Infrared spectra between 4000 and 400 cm^{-1} were recorded on a Bruker IFS66v Fourier transform instrument with a resolution of 1 cm^{-1}, using a 10 cm gas cell with Si windows. Raman spectra of the liquid substances were measured with a Bruker RFS100/S FT-Raman spectrometer. The sample in a 4 mm glass capillary was excited with 500 mW of a 1064 nm Nd:YAG laser (ADLAS, DYP 301, Lübeck, Germany).

Low-temperature IR spectra of Ar-matrixes (sample-to-Ar ratio 1:1000) were taken in a cryogenic system. The mixture was deposited on a metal mirror at ca. 15 K by the continuous deposition technique. For the photochemical study a 150 W high-pressure Xe lamp in combination with a water-cooled quartz lens optic was used.

Electron diffraction intensities were recorded with a Balzers Gasdiffraktograph[23] at nozzle-to-plate distances of 25 and 50 cm and with an accelerating voltage of about 60 kV. The samples were cooled to −10 °C (**1**) and −40 °C (**2**) during the experiments, and the inlet system and gas nozzle were at room temperature. The electron wavelength was calibrated for each experiment with ZnO powder. The Kodak Electron Image plates (18 × 13 cm) were analyzed with an Agfa Duoscan HiD scanner and total scattering intensity curves were obtained from the TIFF-files using the program SCAN3.[24] Experimental molecular intensities were derived in the *s*-ranges 2−18 and 8−35 $Å^{-1}$ for the long and short camera distances, respectively, in steps of $\Delta s = 0.2 Å^{-1}$ ($s = (4\pi/\lambda)\sin\theta/2$, λ is the electron wavelength, and θ is the scattering angle). The intensities for compound **1** are shown in Figure 3and those for compound **2** are similar and are given as Supporting Information.

Infrared-Matrix Spectra. The C═O stretching vibration in carbonyl groups is known to be very sensitive toward the conformational properties of the compound and, furthermore, in most compounds it is well separated from other vibrations. The IR(matrix) spectrum for $CF_3S-OC(O)CH_3$ (**1**) possesses two bands in the C═O stretching region at 1818 and 1761 cm^{-1}, demonstrating the presence of two conformers (Figure 4). Due to the experimental condition, the obtained conformational ratio corresponds to the ambient temperature. These bands appear at 1820 and 1772, and at 1804 and 1763 cm^{-1}, in the gas IR and liquid Raman, respectively. The experimentally observed shift in the matrix between the two bands of 57 cm^{-1} is in good agreement with the calculated difference between the C═O vibrations in the gauche−syn and trans−syn conformers, listed in Table 1. The B3LYP method predicts a difference of 61 cm^{-1}, the MP2 approximation of 45 cm^{-1}. The calculated wavenumber differences between gauche−syn and gauche−anti conformers (0 or 6 cm^{-1}) and between gauche−syn and trans−anti conformers (17 or 19 cm^{-1}) are much smaller than the experimental value. Thus, comparison of experimental and calculated C═O vibrations strongly suggests the assignment of the stronger band at 1818 cm^{-1} to the gauche−syn form and

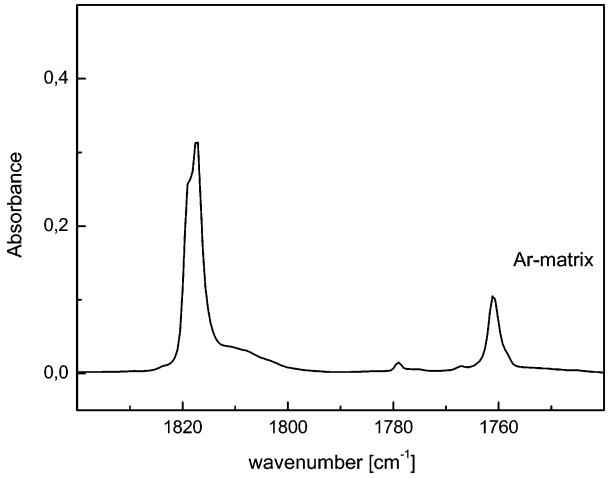

Figure 4. Ar−IR(matrix) spectrum of the C═O stretching region in $CF_3S-OC(O)CH_3$.

that of the weaker band at 1761 cm^{-1} to the trans−syn conformer. This assignment is in qualitative agreement with the relative free energies, and any other assignment would strongly contradict the predicted relative energies. The calculated line strengths (transition dipole moments) for the C═O stretches in these two conformers are very similar, with a ratio of 1.07 or 1.01 according to the B3LYP and MP2 method, respectively. Thus, from the relative areas of the two bands a good estimate of the conformational mixture is obtained, 85(5) % gauche−syn and 15(5) % trans−syn. The error limit is estimated from uncertainties in the experimental areas and in the calculated line strengths. This composition corresponds to a free energy difference of $\Delta G° = 1.0(3)$ kcal/mol.

Exposure of the matrix to broad-band UV−visible radiation results in appreciable changes. The IR bands originating in $CF_3S-OC(O)CH_3$ decrease in intensity with irradiation time, with the simultaneous appearance and growth of new bands corresponding to CH_3SCF_3 and the extrusion product CO_2.[25] No evidence for a randomization process is observed in the sequence analysis of several irradiation times.

The IR(matrix) spectrum of $CF_3S-OC(O)CF_3$ contains four bands in the C═O region. The strongest band occurs at 1839 cm^{-1}, a weaker band at 1799 cm^{-1} and two additional weak bands at 1883 and 1818 cm^{-1}. The two latter bands are assigned to the impurity $CF_3C(O)OC(O)CF_3$, which is formed on metal surfaces in the matrix apparatus. Both gas IR and liquid Raman spectra show only two bands at 1838 and 1806, and at 1830 and 1802 cm^{-1}, respectively, demonstrating the purity of the compound. The two experimental bands at 1839 and 1799 cm^{-1} are again readily assigned to the gauche−syn and trans−syn conformers. The predicted frequency shifts (45 cm^{-1} from B3LYP and 34 cm^{-1} from MP2) are in good agreement with the experimental value of 40 cm^{-1}. Any other assignment would not be compatible with the predicted relative free energies. From the relative areas and calculated line strengths, a mixture of 89-(5)% gauche−syn and 11(5)% trans−syn conformers is derived, corresponding to $\Delta G° = 1.3(4)$ kcal/mol. The two rotamers of $CF_3S-OC(O)CF_3$ are unequivocally detected when the substance isolated in an Ar matrix at low temperature is irradiated with broad-band UV−visible light. For this molecule two channels are really present. If the matrix is irradiated for 5 min, a drastic change occurs in the spectra due to photolytic interconversion of two conformers. Longer irradiation times lead to formation of CF_3SCF_3 and CO_2.

Gas Electron Diffraction. *$CF_3S-OC(O)CH_3$ (1):* The radial distribution functions (RDF) were derived by Fourier transfor-

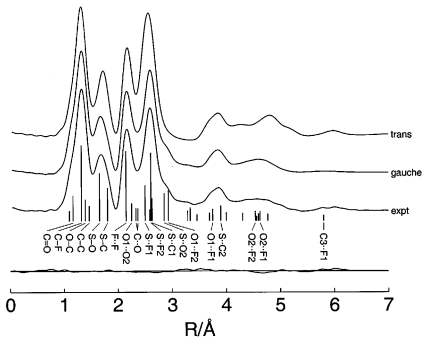

Figure 5. Experimental and calculated radial distribution functions and difference curve for $CF_3S-OC(O)CH_3$. Positions of important distances are indicated by vertical bars.

mation of the molecular intensities using an artificial damping function $\exp(-\gamma s^2)$ with $\gamma = 0.0019$ Å^2. Figure 5 compares the experimental RDF for (**1**) with curves which were calculated for the gauche−syn and trans−syn conformer. The two calculated curves differ slightly in the range $r > 4$ Å and the experimental RDF is reproduced more closely with the gauche−syn model. The structure of this conformer was refined by least-squares fitting of the molecular intensities. The following assumptions were applied in the least squares analyses: (1) C_{3v} symmetry for CH_3 and CF_3 groups with a tilt angle between the C_3 axis of the CF_3 group and the S−C bond direction and staggered orientation with respect to the S−O bond (CF_3 group) and O−C bond (CH_3 group). (2) Planarity of the acetyl group and exactly eclipsed orientation of the C═O bond with respect to the S−O bond. Quantum chemical calculations (B3LYP) predict deviations of <1° from these assumptions. (3) The C−H bond length, H−C−H bond angle and the tilt angle for the CF_3 group were not refined. (4) The geometric parameters of the trans−syn conformer were tied to those of the gauche−syn form using the calculated (B3LYP) differences. (5) Vibrational amplitudes collected in groups according to their calculated values and amplitudes, which caused large correlations with geometric parameters or which are badly determined by the GED experiment, were not refined. With these assumptions, 12 geometric parameters, $p1$ to $p12$, and seven vibrational amplitudes, were refined simultaneously. Least squares analyses were performed for different conformational mixtures and the best fit was obtained for 8(18)% contribution of the trans−syn conformer. The error limit is derived from the tables of Hamilton for a 99.5% confidence limit.[26] The following correlation coefficients had values larger than |0.7|: $p5/p6 = 0.73$, $p5/p9 = 0.76$ and $p6/p11 = 0.85$. The final results for geometric parameters are listed in Table 3 together with calculated values. Experimental and calculated vibrational amplitudes are given in Table S1 as Supporting Information.

$CF_3S-OC(O)CF_3$ (2): Figure 6 compares the experimental RDF for this compound with curves which were calculated for the gauche−syn and trans−syn conformers. The two calculated curves differ slightly in the range $r > 3.5$ Å, and again the experimental curve is reproduced closer with the gauche model. Least squares analyses analogous to those described above were performed also for this compound. The following assumptions were made: (1) C_{3v} symmetry for both CF_3 groups with tilt angles between the C_3 axes and the S−C and C−C bond directions, respectively, and staggered orientation with respect to the S−O bond ($C1F_3$) and O−C bond ($C3F_3$). The tilt angles were set to calculated values. Furthermore, the C−F bond lengths in both CF_3 groups were set equal. The calculated values differ by only 0.001 Å (B3LYP and MP2). For assumptions 2, 4, and 5, see above. With these assumptions, 13 geometric

TABLE 3: Experimental and Calculated Geometric Parameters for Gauche Conformer of $CF_3SOC(O)CH_3$ (1)[a]

	GED (r_a)		B3LYP/ 6-31G*	MP2/ 6-31G*
S−O1	1.659(4)	$p1$	1.703	1.700
S−C1	1.807(5)	$p2$	1.826	1.800
O1−C2	1.395(8)	$p3$	1.397	1.407
C2═O3	1.179(6)	$p4$	1.197	1.205
C2−C3	1.474(15)	$p5$	1.508	1.501
C1−F	1.322(3)	$p6$	1.340	1.344
C3−H	1.100[c]		1.092	1.091
S−O1−C2	118.3(9)	$p7$	117.5	116.0
O1−S−C1	96.9(17)	$p8$	98.0	96.0
O1−C2═O2	122.5(12)	$p9$	124.3	124.2
O1−C2−C3	109.5(20)	$p10$	108.2	107.7
F−C1−F	109.0(3)	$p11$	108.4	108.2
H−C3−H	109.2[c]		109.2	109.5
tilt(CF3)[b]	4.9[c]		4.9	4.3
ϕ(C1−S−O1−C2)	100.3(40)	$p12$	92.0	91.4
%(trans−syn)	8(18)		20	6

[a] Distances in Å, angles in deg, Error limits are 3σ values. For atom numbering, see Figure 7. [b] Tilt angle for CF_3 group, away from S−O bond. [c] Not refined.

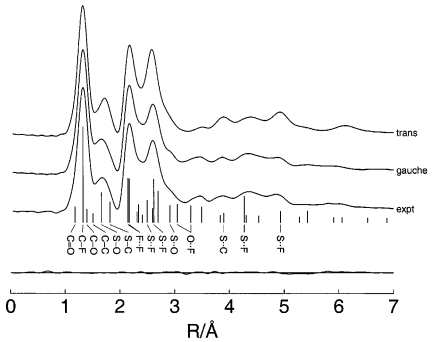

Figure 6. Experimental and calculated radial distribution functions and difference curve for $CF_3S-OC(O)CF_3$. Positions of important distances are indicated by vertical bars.

TABLE 4: Experimental and Calculated Geometric Parameters for Gauche Conformer of $CF_3SOC(O)CF_3$ (2)[a]

	GED (r_a)		B3LYP/ 6-31G*	MP2/ 6-31G*
S−O1	1.663(5)	$p1$	1.716	1.710
S−C1	1.818(7)	$p2$	1.831	1.805
O1−C2	1.396(14)	$p3$	1.367	1.377
C2═O3	1.183(6)	$p4$	1.193	1.203
C2−C3	1.513(10)	$p5$	1.550	1.536
$(C-F)_{mean}$	1.329(2)	$p6$	1.338	1.343
S−O1−C2	116.9(15)	$p7$	117.4	115.8
O1−S−C1	99.2(15)	$p8$	97.1	95.8
O1−C2═O2	127.5(14)	$p9$	127.9	128.1
O1−C2−C3	107.3(14)	$p10$	107.7	107.0
F−C1−F	109.4(5)	$p11$	108.8	108.9
F−C3−F	108.4(6)	$p12$	108.9	108.5
tilt($C1F_3$)[b]	4.9[d]		4.9	4.5
tilt($C3F_3$)[c]	0.3[d]		0.3	0.2
ϕ(C1−S−O1−C2)	101.1(27)	$p13$	93.5	91.1
%(trans−syn)	18(12)			8

[a] Distances in Å, angles in deg. For atom numbering, see Figure 7. [b] Tilt angle for CF_3 group of atom C1, away from S−O bond. [c] Tilt angle of CF_3 group of atom C3, away from C═O bond. [d] Not refined.

parameters and nine vibrational amplitudes were refined simultaneously. The best fit was obtained for a contribution of 18-(12) % trans−syn conformer. Only one correlation coefficient had a value larger than |0.7|: $p3/p6 = -0.77$. The final results for the geometric parameters are listed in Table 4, together with calculated values. Molecular models of both conformers are

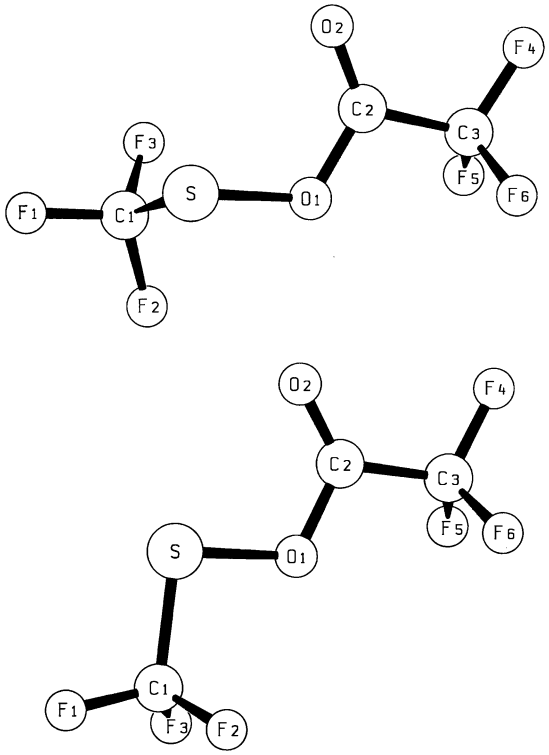

Figure 7. Molecular models for the gauche (upper) and trans (bottom) conformers of $CF_3S-OC(O)CF_3$.

shown in Figure 7. Experimental and calculated vibrational amplitudes are given in Table S2 as Supporting Information.

Discussion

Both experimental methods, vibrational spectroscopy and GED, demonstrate the presence of a mixture of two conformers in gaseous $CF_3S-OC(O)CH_3$ (**1**) and $CF_3S-OC(O)CF_3$ (**2**), with the gauche−syn conformer prevailing. The minor conformer possesses trans configuration around the S−O bond and syn orientation of the C═O bond relative to the S−O bond. Its contributions is 15(5)% in **1** and 11(5)% in **2** according to IR(matrix) spectra, corresponding to $\Delta G° = 1.0(3)$ and 1.3(4) kcal/mol, respectively. The GED method is less sensitive toward this contribution and results in 8(18)% and 18(12)% for **1** and **2**, which corresponds to $\Delta G° = 1.5(14)$ and 0.9(5) kcal/mol, respectively. Considering the large error limits of the GED method, both experimental data are in agreement with each other. Quantum chemical calculations predict the existence of four stable conformers (see Tables 1 and 2), but two conformers with anti orientation of the C═O bond are predicted to be higher in free energy by more than 5 kcal/mol than the two syn conformers and are not expected to be observable in the present experiments. The quantum chemical calculations reproduce the conformational properties for both compounds qualitatively correct with the exception of the B3LYP method for compound **2** which predicts the trans form to be prevailing, in contrast to the experiment.

UV−visible broad band irradiation of the samples **1** and **2** isolated in inert gas matrixes at cryogenic temperature leads to one and two photoevolution channels, respectively. In both experiments CO_2 extrusion and formation of CH_3SCF_3 and CF_3SCF_3, respectively, are observed. A randomization process between the two stable conformers of $CF_3S-OC(O)CF_3$ occurs as well.

TABLE 5: S-O Bond Lengths (Å) and Dihedral Angles in Sulfenyl Derivatives RS−OR′ and in Some Sufonates RO_2S-OR'

RS−OR′	S−O	ϕ (R−S−O−R′)
HS−OH[a]	1.662	91.3
$CH_3OS-OCH_3$[b]	1.625(2)	84(3)
$CH_3OSS-OCH_3$[c]	1.650(3)	74(3)
$CF_3S-OC(O)CH_3$ (**1**)[d]	1.659(4)	100(4) 180
$CF_3S-OC(O)CF_3$ (**2**)[d]	1.663(5)	101(3) 180
RO_2S-OR'		
FO_2S-OF[e]	1.606(8)	73(3)
$CF_3O_2S-OCH_3$[f]	1.555(4)	89(7)
$CF_3O_2S-OC(O)F$[g]	1.632(5)	180 72(6)

[a] Calculated with CCSD(T)/cc-pCVQZ method.[14] This calculated geometry reproduces the experimental rotational constants very closely. [b] Reference 15. [c] Reference 16. [d] This work. [e] Reference 30. [f] Reference 31. [g] Reference 32.

The existence of a stable trans structure around the S−O bond in addition to the gauche structure is unexpected. No such trans structure has been observed so far for any peroxide RO−OR′ or disulfane RS−SR′. Also, the few sulfenyl compounds RS−OR′ whose gas phase structures have been determined so far (see Introduction) possess only gauche structures. This could suggest that the type of substituents, R = CF_3 and R′ = $CH_3C(O)$ or $CF_3C(O)$, are responsible for the unusual conformational properties of **1** and **2**. The syntheses of the peroxide and disulfane analogous to **2**, $CF_3O-OC(O)CF_3$ [27] and $CF_3S-SC(O)CF_3$,[28] have been reported in the literature, but no experimental structural data of these compounds are known. Quantum chemical calculations (B3LYP/6-31G*), however, predict for both compounds potential functions for internal rotation around the O−O or S−S bonds, which possess minima only for gauche structures and maxima for trans structures, 1.0 and 4.7 kcal/mol high in the peroxide and disulfane, respectively. A GED study of $CF_3S-SC(O)F$ resulted in a mixture of two conformers, both possessing gauche structure around the S−S bond with syn (85(13)%) and anti orientation of the C═O bond relative to the S−S bond.[29] Thus, so far the trans conformation is observed only in sulfenyl derivatives with R = CF_3 and R′ = $CH_3C(O)$ or $CF_3C(O)$. Thus, conformational properties of S−O-containing compounds are rather different from those of the corresponding S−S and O−O derivatives.

A similar observation has been made for the conformational properties of sulfonates of the type RO_2S-OR'. All sulfonates, whose gas-phase structures have been reported in the literature, possess gauche structures (R′ gauche with respect to R), except for the derivative with R = CF_3 and R′ = FC(O).[30] This compound exists in the gas phase as a mixture of trans and gauche forms, with the trans conformer prevailing. In the solid state only the trans form is present.

The quantum chemical calculations reproduce the geometric parameters of **1** and **2** reasonably well, except for the S−O bond lengths and the dihedral angles ϕ(C−S−O−C), which are the two most interesting parameters in these compounds (see Tables 3 and 4). Both methods predict the S−O bond lengths too long, and the calculated dihedral angles (equilibrium values) are smaller than the experimental angles (vibrationally averaged values). Table 5 summarizes S−O bond lengths and dihedral angles in sulfenyl derivatives and in some sulfonates. The S−O bonds in the sulfenyl derivatives (S(II) compounds) are generally longer than those in the sulfonates (S(VI) compounds). The trends within each group can be rationalized qualitatively with a simple electrostatic model. The S−O bond in the sulfenyl derivatives is expected to be highly polar, S^+-O^-, and even more polar in the sulfonates. If the electronegativity of the

substituent R at the sulfur atom increases, the polarity of the bond is increased and the bond shortens. This explains the shorter bond in $CH_3OS-OCH_3$ (1.625(2) Å) compared to that in HS−OH (1.662 Å). If the electronegativity of the substituent R′ at oxygen increases, the polarity of the bond is decreased and the bond lengthens. This explains the trend between $CF_3O_2S-OCH_3$ (1.555(4) Å)[31] and $CF_3O_2S-OC(O)F$ (1.632(5) Å).[32] If the electronegativity of both substituents R and R′ increases, both effects nearly cancel. This explains the nearly equal bond lengths in HS−OH and in **1** and **2**.

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Supporting Information Available: A figure with the averaged experimental and calculated molecular intensities for $CF_3S-OC(O)CF_3$ and residuals, and two tables containing interatomic distances and experimental and calculated vibrational amplitudes for gauche conformers of $CF_3S-OC(O)CH_3$ and $CF_3S-OC(O)CF_3$, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Käss, D.; Oberhammer, H.; Brandes, D.; Blaschette, A. *J. Mol. Struct.* **1977**, *40*, 65.
(2) Koput, J. *J. Mol. Spectrosc.* **1986**, *115*, 438.
(3) Hedberg, L.; Hedberg, K.; Eller, P. G.; Ryan, R. R. *Inorg. Chem.* **1988**, *27*, 232.
(4) Birk, M.; Friedl, R. R.; Cohen, E. A.; Pickett, H. M. Sander, S. P. *J. Chem. Phys.* **1989**, *91*, 6588.
(5) Mack, H.-G. Della Védova, C. O. Oberhammer, H. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1145.
(6) Hermann, A.; Niemeyer, J.; Mack, H.-G.; Kopitzky, R.; Beuleke, M.; Willner, H.; Christen, D.; Schäfer, M.; Bauder, A.; Oberhammer, H. *Inorg. Chem.* **2001**, *40*, 1672.
(7) Marsden, C. J.; Smith, B. J. *J. Phys. Chem.* **1988**, *92*, 347.
(8) Winnewisser, G.; Yamada K. M. T. *Vib. Spectrosc.* **1991**, *1*, 263.
(9) Yokozeki, A.; Bauer, S. H. *J. Phys. Chem.* **1976**, *80*, 618.
(10) Oberhammer, H. Unpublished results.
(11) Marsden, C. J.; Oberhammer, H.; Lösking, O.; Willner, H. *J. Mol. Struct.* **1989**, *193*, 233.
(12) Mack, H.-G.; Della Védova, C. O.; Oberhammer, H. *J. Phys. Chem.* **1992**, *96*, 9215.
(13) Breitzer, J. G.; Smirnov, A. I.; Szczepura, L. F.; Wilson, S. R.; Rauchfuss, T. B. *Inorg. Chem.* **2001**, *40*, 1421−1429.
(14) Winnewisser, G.; Lewen, F.; Thoswirth, S.; Behnke, M.; Hahn, J.; Gauss, J.; Herbst. E. *Chem Eur. J.* **2003**, *9*, 5501.
(15) Baumeister, E.; Oberhammer, H.; Schmidt, H.; Steudel, R. *Heteroatom Chem.* **1991**, *2*, 633.
(16) Steudel, R.; Schmidt, H.; Baumeister, E. Oberhammer, H.; Koritsanszky, T. *J. Phys. Chem.* **1995**, *99*, 8987.
(17) Ulic, S. E.; Della Védova, C. O.; Hermann, A.; Mack, H.-G.; Oberhammer, H. *Inorg. Chem.* **2002**, *41*, 5699.
(18) Scott, A. P.; Radom, L. *J. Phys. Chem.* **1996**, *100*, 16502−16513.
(19) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratman, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Menucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslovski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzales, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzales, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98 (Revision A.6);* Gaussian, Inc.: Pittsburgh, PA, 1998.
(20) Sipachev, V. A. *J. Mol. Struct.* **2001**, 567−568, 67. Sipachev, V. A. In *Advances in Molecular Structure Research*; Hargittai, I.; Hargittai M., Eds.; JAI Press Inc.: Greenwich, CT, 1999; Vol. 5, p 263.
(21) Haas, A.; Lieb, M.; Zhang Y. *J. Fluorine Chem.* **1985**, *29*, 297.
(22) Sauer D. T.; Shreeve J. M. *Inorg. Syntheses* **1973**, *14*, 42.
(23) Oberhammer, H. *Molecular Structure by Diffraction Methods;* The Chemical Society: London, 1976; Vol. 4, p 24.
(24) Atavin, E. G.; Vilkov, L. V. *Instrum. Exp. Techn.* (in Russian) **2002**, *45*, 27.
(25) Borrajo, J.; Varetti, E. L.; Aymonino, P. J. *Anales Asoc. Quím. Argentina* **1980**, *68*, 49.
(26) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.
(27) DesMarteau, D. D:; Bernstein, P. A.; Hohorst, F. A. *J. Am. Chem. Soc.* **1971**, *93*, 3882.
(28) Burton, C. A.; Shreeve, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 6545.
(29) Hermann, A.; Ulic, S. E.; Della Védova, C. O.; Mack, H.-G.; Oberhammer, H. *J. Fluorine Chem.* **2001**, *112*, 297.
(30) Aubke, F.; Casper, B.; Müller, H. P. S.; Oberhammer, H.; Willner, H. *J. Mol. Struct.* **1995**, *346*, 11.
(31) Trautner, F.; Ben Altabef, A.; Fernandez, L. E.; Varetti, E. L.; Oberhammer, H. *Inorg. Chem.* **1999**, *38*, 3051.
(32) Della Védova, C. O.; Downs, A. J.; Novikov, V. P.; Oberhammer, H.; Parsons, S.; Romano, R. M.; Zawadski A. *Inorg. Chem.* **2004**, *43*, 4064.