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Article

Fluoroformyl Trifluoroacetyl Disulfide, FC(O)SSC(O)CF_3: Synthesis, Structure in Solid and Gaseous States, and Conformational Properties[#]

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Fluoroformyl trifluoroacetyl disulfide, FC(O)SSC(O)CF_3, is prepared by quantitative reaction between FC(O)SCl and $CF_3C(O)SH$. The conformational properties and geometric structure of the gaseous molecule have been studied by vibrational spectroscopy (IR(gas), Raman(liquid), IR(matrix)), gas electron diffraction (GED), and quantum chemical calculations (B3LYP and MP2 methods). The disulfide bond length derived from the GED analysis amounts 2.023(3) Å, and the dihedral angle around this bond, ϕ(CS–SC), is 77.7(21)°, being the smallest dihedral angle measured for noncyclic disulfides in the gas phase. The compound exhibits a conformational equilibrium at room temperature having the most stable form C_1 symmetry with a synperiplanar (sp-sp) orientation of both carbonyl groups with respect to the disulfide bond. A second form was observed in IR spectra of the Ar matrix isolated compound at cryogenic temperatures, corresponding to a conformer that possess the carbonyl bond of the FC(O) moiety in antiperiplanar position with respect to the S–S single bond (ap-sp). A $\Delta H° = H°_{(ap-sp)} - H°_{(sp-sp)} = 1.34(11)$ kcal/mol has been determined by IR(matrix) spectroscopy. The structure of single crystal of FC(O)SSC(O)CF_3 was determinate by X-ray diffraction analysis at low temperature using a miniature zone melting procedure. The crystalline solid (monoclinic, $P2_1/n$, $a = 5.240(4)$Å, $b = 23.319(17)$Å, $c = 6.196(4)$Å, $\beta = 113.14(3)°$) consists exclusively of the (sp-sp) conformation. The geometrical parameters agree with those obtained for the molecule in the gas phase.

Introduction

Geometric gas-phase structures of noncyclic disulfides XSSX are characterized by a gauche conformation around the S–S bond, with dihedral angles ϕ(XS–SX) close to 90°: 90.76(6)° in HSSH;[1] 87.7(4)° in FSSF;[2] 85.2(2)° in ClSSCl;[3] 85.3(37)° in CH_3SSCH_3;[4] 104.4(40)° in CF_3SSCF_3.[5] In this conformation the p-shaped lone pairs of the sulfur atoms are perpendicular to each other and their mutual repulsion is minimized. Furthermore, such a structure is favored by the anomeric effect by electron donation from the sulfur lone pairs into the empty σ* orbitals of the opposite S–X bonds.[6,7] This effect depends strongly on the relative energies of the two orbitals involved and can explain the

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short S−S and long S−F bonds in FSSF. Disulfides with very bulky substituents, such as Bu^{t}SSBu^t, have dihedral angles which are considerable larger than 90° (ϕ(CS−SC) = 128.2(27)).[8] The smallest dihedral angle for a gaseous disulfide has been reported for FC(O)SSC(O)F, with ϕ(CS−SC)= 82.2(19).[9]

Structural studies of nonsymmetrically substituted disulfides of the type XSSY are less common, both experimental and theoretical data being scarce for these systems. $FC(O)SSCF_3$[10] and $FC(O)SSCH_3$[11] have recently been studied in the gas phase and possess dihedral angles of ϕ(CS−SC) = 95.0(27) and 83.5(15)°, respectively.

The presence of an acyl group attached to the disulfide S−S bond, as in FC(O)SSC(O)F,[12] $FC(O)SSCH_3$,[10] and $FC(O)SSCF_3$,[11] may lead to conformational equilibria, depending on the relative orientation of the C═O double bond and the S−S single bond. The synperiplanar orientation, with ϕ(SS−C(O)) = 0°, is the prevailing form for these species. Thus, the conformational properties of acyl-substituted disulfides (−C(O)SS−) seems to be the same as those observed for sulfenylcarbonyl compounds of the type XC(O)SY, for which the preference for the syn conformer (ϕ(C(O)−SY) = 0°) has been well established.[13−17]

To gain additional experimental and theoretical information about the structural and conformational behavior of acyl-substituted disulfides, we became interested in the study of molecules of the type −C(O)SSC(O)−, with two carbonyl groups bonded to the disulfide bond. Thus, in this study we report the synthesis and characterization of fluoroformyl trifluoroacetyl disulfide, $FC(O)SSC(O)CF_3$. As far as we know, no previous reports for this species exist in the literature. In this study, its geometric structure and conformational properties in the gas phase have been determined by gas electron diffraction and vibrational spectroscopic methods (IR(gas), IR(matrix), and Raman(liquid)), supplemented by quantum chemical calculations. Furthermore, the crystal structure was determined by X-ray diffraction using an in situ crystallization method.

Experimental Section

Preparation. $FC(O)SSC(O)CF_3$ was synthesized by reacting trifluorothioacetic acid, $CF_3C(O)SH$, with fluorocarbonylsulfenyl chloride, FC(O)SCl, according to the following reaction:

$$CF_3C(O)SH + FC(O)SCl \rightarrow FC(O)SSC(O)CF_3 + HCl$$

Conventional vacuum techniques were used to condense equimolar quantities (typically 2.5 mmol) of $CF_3C(O)SH$ and FC(O)SCl into a 6 mm o. d. glass tube. The tube was flame sealed. The tube was placed in a −90 °C ethanol bath. At this temperature the reaction proceeded fast, observed by the vanishing yellow color (due to FC(O)SCl) of the reaction mixture. The mixture was then allowed to warm to −20 °C and remained at that temperature for about 1 h. Subsequently the products were separated by "trap-to-trap" condensation through traps held at −50, −80, and −196 °C. Pure $FC(O)SSC(O)CF_3$ was retained as a colorless liquid in the −80 °C trap. The yield was nearly quantitative, and apart from HCl generated in the reaction, only minor quantities of OCS, SiF_4, and CO_2 were observed as byproducts in the U-trap at −196 °C.

$CF_3C(O)SH$ was synthesized by reaction of either $CF_3C(O)Cl$ or $(CF_3C(O))_2O$ (98% Aldrich) with hydrogen sulfide, H_2S (98% Linde, Germany), in a metal reactor according to the literature procedure.[18] $CF_3C(O)Cl$ was synthesized by reacting trifluoroacetic acid with pentachlorophosphorane according to the usual method. FC(O)SCl was synthesized by reaction of commercial ClC(O)SCl (Aldrich 95%) with SbF_5 by following the reported method.[19,20]

Physical Properties and Spectroscopic Characterization. The new compound is a colorless liquid, with the characteristic overpowering sulfenylcarbonyl odor. The compound is stable at room temperature for days in the liquid or gaseous state. The vapor pressure of $FC(O)SSC(O)CF_3$ follows, in the temperature range between 230 and 277 K, the equation $\log p = 8.520 - 2079/T$ (p/mbar, T/K), and the extrapolated boiling point reaches 104 °C. The white solid melts at −72 °C. A similar temperature was used for crystallization in the X-ray diffraction experiment (−75(2) °C).

In the ^{19}F NMR spectrum two singlets with an intensity ratio of 1:3 were observed. The more intense signal is locate at −74.9 ppm, while the second signal appears at 41.4 ppm. The symmetric $CF_3C(O)$- and FC(O)-substituted disulfides $CF_3C(O)SSC(O)CF_3$[21] and FC(O)SSC(O)F[20] show singlets at −74.3 and 41.8 ppm, respectively, in good agreement with the values obtained for $FC(O)SSC(O)CF_3$.

The mass spectrum of $FC(O)SSC(O)CF_3$ shows the presence of decomposition or unwanted reaction products, evidenced by peaks belonging to elemental sulfur, with the characteristic m/z 32 peak progression. Nevertheless, the molecular ion peak was observed as a low intensity signal at m/z 208 and several fragments of $FC(O)SSC(O)CF_3$ were assigned. Thus, peaks at m/z values of 47 (9, COF^+), 69 (100, CF_3^+), 97 (18, CF_3CO^+), and 111 (10, $SSC(O)F^+$) were observed in the mass spectrum (in parentheses the relative abundance is given).

The UV−vis spectrum of the vapor shows a band at $\lambda_{max} = 232$ nm with medium absorption cross section ($\sigma_{max} = 6.7 \times 10^{-18}$ cm^2), which is assigned to a $\pi \rightarrow \pi^*$ transition of the trifluoroacetyl $CF_3C(O)S$ chromophore, taking into account the observed bands

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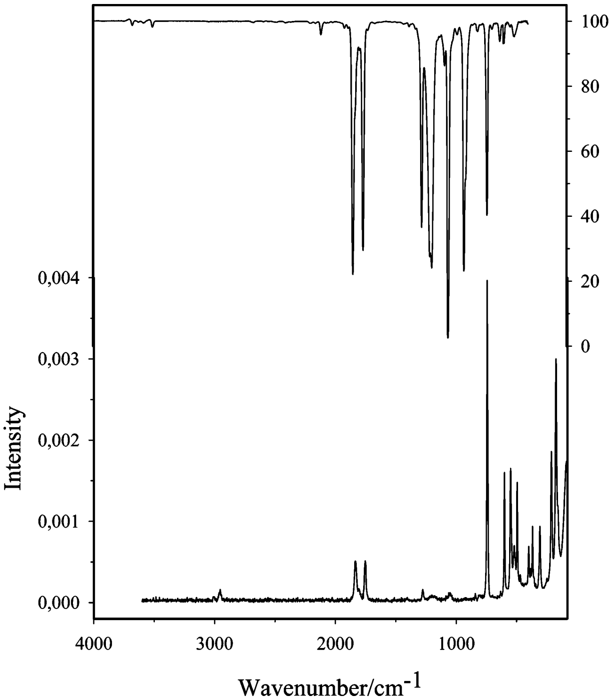

Figure 1. Gaseous IR ($P = 19$ mbar) and liquid Raman spectra for $FC(O)SSC(O)CF_3$.

for $CF_3C(O)SH$ (226 nm) and $CF_3C(O)SCl$ (236 nm)[22] and $CF_3C(O)SOC(O)CF_3$ (236 nm).[23] Continuous increasing absorption at lower wavelengths could indicate the existence of an intense absorption band below 200 nm, which could be possible due to an equivalent transition in the fluorocarbonyl FC(O)S chromophore, similar to those observed for the related FC(O)SSC(O)F molecule.[20]

Additional evidence for the identity of $FC(O)SSC(O)CF_3$ comes form the analysis of its IR(gas) and Raman(liquid) spectra (see Figure 1 and Table S1 in the Supporting Information). The two intense bands in the carbonyl stretching region at 1849 and 1765 cm^{-1} are characteristic for the FC═O and CF_3C═O groups, respectively. The strongest band in the IR(gas) spectrum centered at 1062 cm^{-1} is assigned to the F−C(sp^2) stretching mode. The characteristic disulfide stretching is observed in the Raman(liquid) spectrum as an intense signal at 549 cm^{-1}.

Instrumentation. (A) General Procedure. Volatile materials were manipulated in a glass vacuum line equipped with two capacitance pressure gauges (221 AHS-1000 and 221 AHS-10, MKS Baratron, Burlington, MA) and three U-traps and valves with PTFE stems (Young, London, U.K.). The vacuum line was connected to an IR cell (optical path length 200 mm, Si windows 0.5 mm thick) contained in the sample compartment of an FTIR instrument (Impact 400D, Nicolet, Madison, WI). This allowed us to observe the purification processes and to follow the course of the reactions. The pure compound was stored in flame-sealed glass ampules under liquid nitrogen in a long-term Dewar vessel. The ampules were opened with an ampule key on the vacuum line, an appropriated amount was taken out for the experiments, and then they were flame-sealed again.[24]

(B) Matrix Spectroscopy. In a stainless steel vacuum line (1.1 L volume), a small amount of $FC(O)SSC(O)CF_3$ (ca. 0.05 mmol) was mixed with an 1:1000 excess of Ar. For each experiment ca. 0.6 mmol of this mixture was passed via a stainless steel capillary through a heated quartz nozzle, which was placed directly in front of the matrix support. The temperature of the matrix support was held at 14 K, and the nozzle temperature was adjusted at the temperatures 20, 60, 120, 190, 260, and 330 °C. Details of the matrix apparatus have been given elsewhere.[25] Matrix IR spectra were recorded on an IFS66v/S FT spectrometer (Bruker, Karlsruhe, Germany) in the reflectance mode with a transfer optic. A DTGS detector with a KBr/Ge beam splitter in the region $\nu = 4000-400$ cm^{-1} was used. In this region 64 scans were coadded for each spectrum by means of apodized resolution of 1 cm^{-1}.

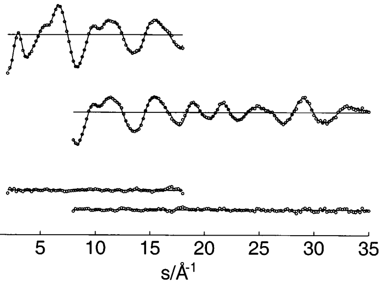

Figure 2. Experimental (dots) and calculated (full line) molecular intensities for long (above) and short (below) nozzle-to-plate distances and residuals for $FC(O)SSC(O)CF_3$.

(C) Gas Electron Diffraction. Electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2[26] at two nozzle-to-plate distances (25 and 50 cm) and with an accelerating voltage of about 60 kV. The compound was kept at 0 °C during the experiment, and the inlet system and gas nozzle were at room temperature. The photographic plates (Kodak electron image plates 13 × 18 cm) were analyzed with an Agfa Duoscan HiD scanner, and total scattering intensity curves were obtained with the program SCAN3.[27] Experimental molecular intensities for $FC(O)SSC(O)CF_3$ in the s-ranges 2−18 and 8−35 Å^{-1} 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) are shown in Figure 2.

(D) X-ray Diffraction at Low Temperature. An appropriate crystal of $FC(O)SSC(O)CF_3$ of ca. 0.3 mm diameter was obtained on the diffractometer at a temperature of 198 K with a miniature zone melting procedure using focused infrared laser radiation.[28] The diffraction intensities were measured at low temperatures on a Nicolet R3m/V four-circle diffractometer. Intensities were collected with graphite-monocromatized Mo Kα radiation using the ω-scan technique. The crystallographic data, conditions, and some features of the structure are listed in Table S3 (Supporting Information). The structure was solved by Patterson syntheses and refined by full-matrix least-squares methods on F, with the SHELXTL-Plus program.[29] Absorption correction details are given elsewhere. All atoms were assigned to anisotropic thermal parameters. Atomic coordinates and equivalent isotropic displacement coefficients are given in Table S4, and anisotropic displacement parameters (10^3Å)

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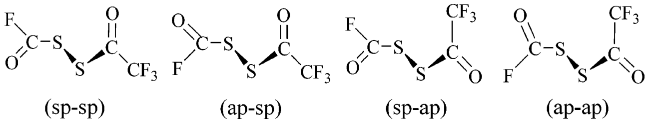
Chart 1. Schematic Representation of the Conformers of $FC(O)SSC(O)CF_3$



for $FC(O)SSC(O)CF_3$ are given in Table S5 (Supporting Information). X-ray crystallographic data in CIF format are given as Supporting Information.

(E) Vibrational Spectroscopy. Gas-phase infrared spectra were recorded with a resolution of 1 cm^{-1} in the range 4000−400 cm^{-1} on the Bruker IFS 66v FTIR instrument, and FT-Raman spectra were run of liquid $FC(O)SSC(O)CF_3$ with a Bruker RFS 100/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, DPY 301, Lübeck, Germany).

(F) NMR Spectroscopy. For the ^{19}F NMR measurements, neat samples were flame-sealed in thin-walled 3 mm o.d. tubes and placed into 5 mm NMR tubes. The spectra were recorded with a Brucker Avance DRX-300 spectrometer operating at 282.41 MHz. The sample was measured at room temperature using a mixture of CD_3CN and $CFCl_3$ as an external lock and reference.

(G) UV−Visible Spectroscopy. UV−visible spectra of gaseous samples were recorded using a glass cell (optical path length of 10 cm) equipped with quartz windows placed in the sample compartment of a Lambda 900 spectrometer (Perkin-Elmer, Norwalk, CT). The measurements were carried out in the spectral range of 200−600 nm.

(H) Theoretical Calculations. All quantum chemical calculations were performed with the GAUSSIAN03 program package.[30] Vibrational amplitudes were derived from calculated (B3LYP/6-31G*) force fields with the method of Sipachev.[31,32]

Quantum Chemical Calculations

Several conformations are in principle feasible for $FC(O)SSC(O)CF_3$, depending on the torsional angle around the S−S bond and on the orientation of the C═O bonds of the FC(O) and $CF_3C(O)$ groups. Each of them can be synperiplanar (sp) or antiperiplanar (ap) relative to the S−S bond. This leads to four possible conformers, (sp-sp), (ap-sp), (sp-ap), and (ap-ap) (the first orientation refers to the FC(O) group, and the second, to the $CF_3C(O)$ group; see Chart 1).

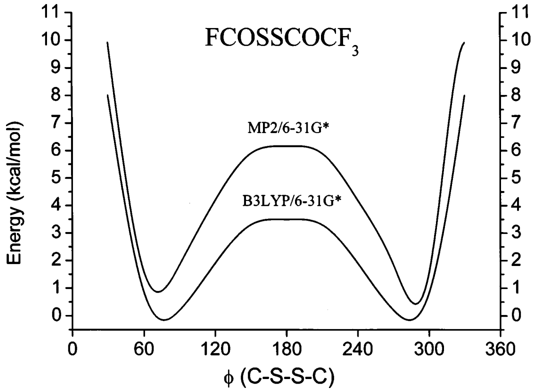


Figure 3. Calculated potential function for internal rotation around the S−S bond in $FC(O)SSC(O)CF_3$.

Table 1. Calculated Relative Energies, Free Energies (kcal/mol), and Vibrational Frequencies of C═O Stretches (cm^{-1}) with IR Intensities (km/mol) in Parentheses for $FC(O)SSC(O)CF_3$

orientation	method	ΔE	$\Delta G°$	ν(FC═O)	ν(CF_3C═O)
(sp-sp)[a]	B3LYP/6-31G*	0.00	0.00	1921 (254)	1849 (212)
	B3LYP/6-311+G*	0.00	0.00	1899 (307)	1828 (246)
	MP2/6-31G*	0.00	0.00	1896 (191)	1778 (142)
(ap-sp)	B3LYP/6-31G*	1.05	1.02	1903 (363)	1847 (221)
	B3LYP/6-311+G*	1.34	1.17	1875 (464)	1826 (254)
	MP2/6-31G*	1.88	1.64	1881 (291)	1776 (150)
(sp-ap)	B3LYP/6-31G*	3.22	3.94	1924 (254)	1835 (259)
	B3LYP/6-311+G*	3.14	3.72	1900 (312)	1813 (314)
	MP2/6-31G*	4.69	5.26	1900 (190)	1762 (170)
(ap-ap)	B3LYP/6-31G*	4.15	4.76	1902 (328)	1834 (307)
	B3LYP/6-311+G*	4.39	4.89	1874 (408)	1812 (388)
	MP2/6-31G*	6.35	6.89	1879 (277)	1760 (188)

[a] First orientation (sp or ap) refers to the FC(O) group, and the second orientation, to the $CF_3C(O)$ group.

In a first step the potential function for internal rotation around the S−S bond was derived by structure optimizations of the (sp-sp) conformer at fixed dihedral angles ϕ(CS−SC). Potential functions obtained with the B3LYP and MP2 method and 6-31G* basis sets are shown in Figure 3.

Minima occur at 77.9° (B3LYP) and 71.0° (MP2). The functions possess rather flat maxima in the region of trans C−S−S−C skeleton with imaginary frequencies at ϕ(CS−SC) = 180°. The geometries of the four conformers were fully optimized including frequency calculations with the B3LYP method (6-31G* and 6-311*+G*) method and the MP2 approximation using 6-31G* basis sets. Predicted relative energies, ΔE, free energies, $\Delta G°$, and vibrational frequencies of the C═O stretches with their strengths are collected in Table 1. For the lowest energy form both C═O bonds adopt an sp orientation with respect to the S−S bond. The second most stable conformer possesses an ap orientation of the FC(O) group. Structures with ap orientation of the $CF_3C(O)$ group are considerably higher in energy ($\Delta G°$ is ca. 4.0 kcal/mol or even more) and are not expected to be observable in our experiments. All three computational methods agree with respect to this conformational preference for $FC(O)SSC(O)CF_3$. The geometric parameters are listed together with experimental values (see Table 2).

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Vibrational Spectra

The IR(gas) and Raman(liquid) spectra of FC(O)SSC(O)CF_3 are shown in Figure 1. A tentative assignment of the observed bands was performed by comparison with the calculated spectrum, and the approximated description of modes is based on the calculated displacement vectors for the fundamentals, as well as on comparison with spectra of related molecules, especially FC(O)SX (X = Cl,[33] SC(O)F,[12] CH_3[34]) and CF_3C(O)SY (Y = H, Cl).[35] Experimental and calculated (B3LYP/6-311+G*) frequencies and their assignments are given as Supporting Information (Table S1).

In the region of the C═O stretching mode, which is characteristic for the presence of various conformers (see Table 1), only two bands occurs in the IR(gas) spectrum with a slight shoulder at the higher frequency band. Similar features are observed in the Raman(liquid) spectrum. More detailed information of the of the conformational properties can be derived from the IR(matrix) spectra of the C═O stretching range. Figure 4 shows such spectra that were recorded using different temperatures of the spray-on nozzle for the FC(O)SSC(O)CF_3/Ar mixtures.

On the basis of the calculated frequencies (Table 1), the highest frequency at 1840 cm^{-1} is assigned to the FC═O group in the (sp-sp) conformer. The low intensity intermediate band at 1819 cm^{-1} belongs to the same group in the (ap-sp) form. The calculated difference (B3LYP/6-311+G*) for this mode (ν(FC═O), Table 1) between (sp-sp) and (ap-sp) forms is 24 cm^{-1}, in good agreement with the experimentally observed value of 21 cm^{-1}. The third band in this region with very low intensity at room temperature, which increases upon increasing temperature of the spray-on nozzle, could not be attributed to FC(O)SSC(O)CF_3 conformers. In view of the very low band intensity displayed in the room-temperature spectrum, it is assumed to belong to an unidentified decomposition product. The CF_3C═O stretching modes in both conformers are assigned to the band at 1758 cm^{-1}. The predicted difference between these two C═O stretches is 2 cm^{-1} (B3LYP and MP2).

Conformational equilibrium was also noticed in the F−C(O) stretching region, evidenced by the presence of two bands. An intense band located at 1054 cm^{-1} was assigned to the main (sp-sp) conformer, while a second band at 1085 cm^{-1} (with low intensity) increases in intensity with increasing temperature of the matrix gas mixtures prior to matrix deposition. This band is assigned to the ν(C(sp^2)−F) mode of the less stable (ap-sp) form. From quantum chemical calculations, other fundamental modes in (sp-sp) and (ap-sp) conformers differ by less than 2 cm^{-1} and are not expected to be observed in either IR(gas) or IR(matrix) experiments.

Because the synperiplanar/antiperiplanar conformational change in the fluoroformyl group involves significant variations in the bond strengths of both C═O and C(sp^2)−F bonds, two pairs of bands are suitable to study the conformational distribution: (i) the C═O stretching bands; (ii) the F−C(sp^2) stretching bands. The area ratios of the carbonyl stretching bands belonging to both conformers are determinate and plotted on a logarithmic scale as a function of the reciprocal absolute temperature. These ratio values correspond closely to the concentration ratios of the two conformers. Such a van't Hoff plot for ν(FC═O) (1819/1840 cm^{-1}) is shown in Figure 5. A value of standard enthalpy difference $\Delta H° = 1.34(11)$ kcal/mol was derived for the (sp-sp) ↔ (ap-sp) conformational equilibrium in FC(O)SSC(O)CF_3. With the calculated (B3LYP/6-311+G*) entropy difference for both conformers ($\Delta S° = 0.67$ cal/K mol), the standard free energy difference ($\Delta G° = 1.14(15)$ kcal mol^{-1}) is obtained.

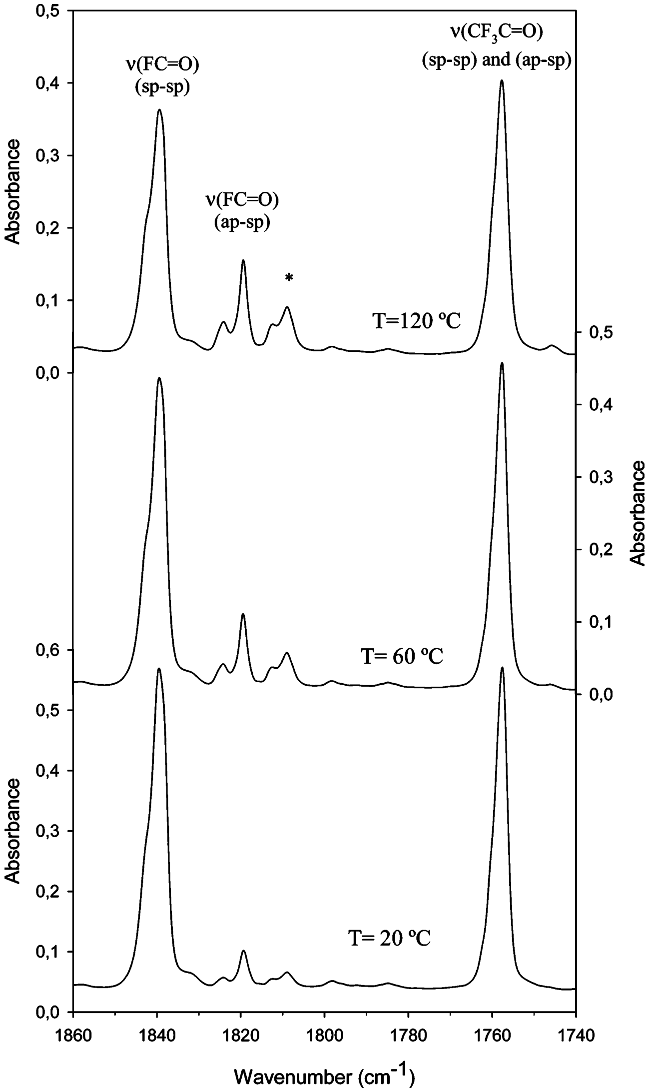

Figure 4. IR spectra in the carbonyl stretching region for FC(O)SSC(O)CF_3 isolated in Ar matrixes at 14 K using different nozzle deposition temperatures. The band marked with an asterisk corresponds to an unidentified decomposition product.

Gas Electron Diffraction

The experimental radial distribution function (RDF) was derived by Fourier transformation of the molecular intensi-

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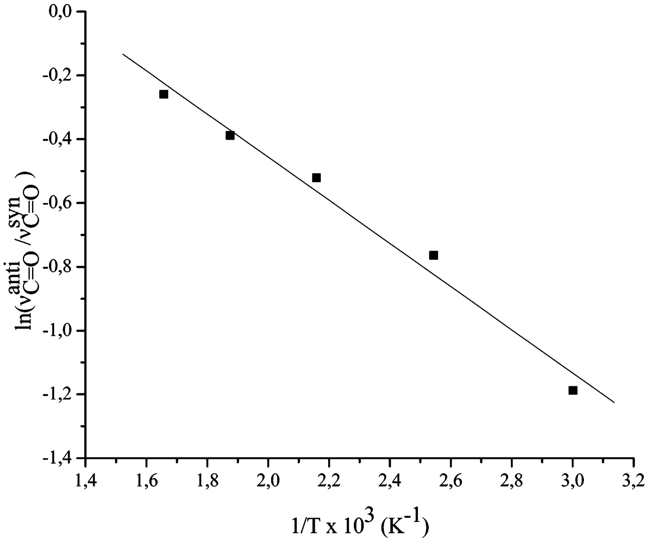

Figure 5. Van't Hoff plot using the ratios of integrated band areas (IR(matrix)) of carbonyl stretching modes (1819/1840 cm^{-1}) obtained after quenching the rotamer equilibria of (sp-sp) and (ap-sp) forms of FC(O)SSC(O)CF_3 at different deposition nozzle temperatures.

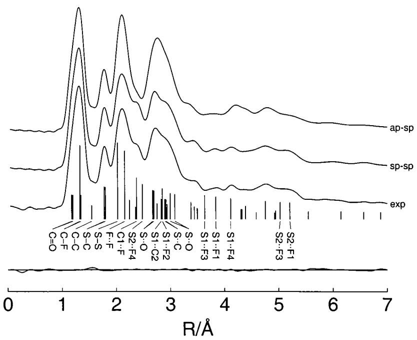

Figure 6. Experimental and calculated radial distribution functions for FC(O)SSC(O)CF_3. Important interatomic distances of the (sp-sp) conformer are indicated by vertical bars.

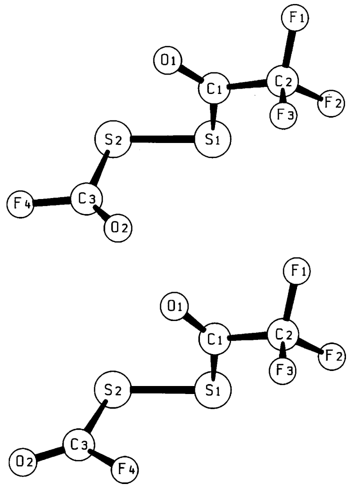

Figure 7. Molecular models and atom numbering for the two conformers of FC(O)SSC(O)CF_3.

Table 2. Experimental and Calculated Geometric Parameters for the Gauche (sp-sp) Conformer of FC(O)SSC(O)CF_3

				B3LYP		
param	GED[a]		X-ray	6-31G*	6-311+G*	MP2/6-31G*
S1−S2	2.023(3)	p_1	2.017(2)	2.073	2.084	2.049
S1−C1	1.776(3)	p_2	1.756(4)	1.798	1.794	1.778
S2−C3	1.799(3)[b]	p_2	1.773(5)	1.820	1.816	1.791
C1−C2	1.544(7)	p_3	1.526(6)	1.550	1.553	1.537
C1═O1	1.190(3)	p_4	1.190(5)	1.197	1.190	1.215
C3═O2	1.178(3)[b]	p_4	1.149(5)	1.185	1.176	1.194
$(C2-F)_{mean}$	1.329(2)	p_5	1.308(5)	1.340	1.335	1.343
C3−F4	1.338(2)[b]	p_5	1.334(5)	1.345	1.353	1.354
S2−S1−C1	99.0(8)	p_6	99.3(2)	99.9	99.9	98.2
S1−S2−C3	100.2(8)[b]	p_6	100.6(2)	101.0	100.7	99.5
S1−C1═O1	125.5(5)	p_7	127.1(3)	125.9	126.3	125.9
S2−C3═O2	129.6(5)[b]	p_7	130.7(4)	129.9	130.4	129.7
S1−C1−C2	115.8(15)	p_8	112.1(3)	112.7	112.7	113.6
$(F-C2-F)_{mean}$	108.2(3)	p_9	108.5(4)	108.8	108.7	108.7
S2−C3−F4	104.5(4)	p_{10}	107.6(3)	106.2	106.2	106.5
ϕ(SSC(O1))	−5.9c	p_{11}	−6.1(4)	−5.9	−5.2	−5.9
ϕ(SSC(O2))	−2.6[c]	p_{12}	8.0(5)	−2.6	−2.6	−2.5
ϕ(CSSC)	77.7(21)		77.7(2)	77.9	82.1	71.0
τ (CF_3)[d]	47.4(46)		32.2(4)	49.4	49.9	52.0

[a] r_a values in Å and deg. Error limits in parentheses are 3σ values and refer to the last 1 digit. See Figure 7 for atom numbering. [b] Difference to previous parameter fixed to calculated (B3LYP) value. [c] Not refined. Negative value implies shortening of the O1···O2 distance. [d] Torsional angle for CF_3 group; for τ = 0° the C2−F1 bond eclipses the C1═O2 bond.

ties. The experimental RDF is shown in Figure 6, and molecular models of the two possible conformers with atom numbering are shown in Figure 7.

Comparison between this curve and RDF's calculated for the (sp-sp) and (ap-sp) conformers (Figure 6) reveals that the experimental curve is reproduced better by the RDF for the (sp-sp) form. Both calculated curves differ appreciably in the range $2.3 < r < 3.2$ Å. These differences are due to changes in the S−C═O2 and S−C−F4 angles when the FC(O) group is rotated from sp to ap orientation (see Figure 7 for atom numbering). Upon this rotation the S−C═O2 angles decreases by about 6° and the S−C−F4 angles increases by about the same amount. In the least-squares analysis of a mixture of (sp-ap) and (ap-ap) conformers, only the geometric parameters of the prevailing (sp-sp) form were refined.

The following assumptions were made on the basis of quantum chemical calculations (B3LYP/6-31G*): (1) planarity of the fluoroformyl and trifluoroacetyl group with the torsional angles around the S−C bonds (ϕ(SS−CO1) and ϕ(SS−CO2)) constrained to calculated values; (2) C_{3v} symmetry of the CF_3 group; (3) differences between the two C═O bonds, between the C−F bonds in the FC(O) and CF_3 groups, between the S−S−C angles, and between the S−C═O angles set to calculated values; (4) differences between geometric parameters of the two conformers constrained to the B3LYP values; (5) vibrational amplitudes collected in groups according to their calculate values. Amplitudes that caused either large correlations or were poorly determined in the GED experiment were not refined. With these assumptions 12 geometric parameters (p_1-p_{12}) and 12 vibrational amplitudes (l_1-l_{12}) were refined simultaneously. The following correlation coefficients had absolute values larger than 0.7: $p_8/p_{12} = -0.74$; $p_8/l_4 = 0.82$; $p_8/l_{12} = -0.71$; $l_4/l_{12} = -0.79$. The best fit was obtained for a contribution of 16(11)% of the (ap-sp) conformer, corresponding to $\Delta G° = 1.0(5)$ kcal/mol. The error limit was obtained from the tables of Hamilton for a 99.5% confidence limit.[36] The final geometric parameters of the main conformer are listed together with the solid-state structure and with

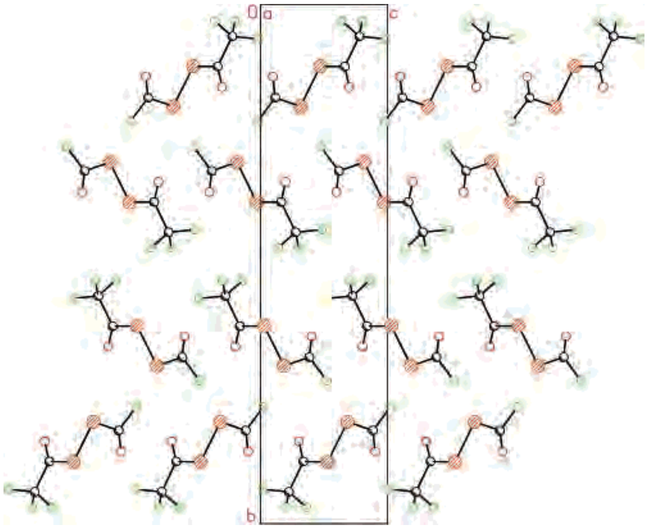

Figure 8. Stereoscopic illustration of the crystal packing of FC(O)SSC(O)CF_3 at 198 K.

calculated values in Table 2, and vibrational amplitudes are given in Table S2 (Supporting Information).

Crystal Structure

FC(O)SSC(O)CF_3 crystallize in the monoclinic crystal system ($P2_1/n$ spatial group) with unit cell dimensions of $a = 5.240(4)$ Å, $b = 23.319(17)$ Å, $c = 6.196(4)$ Å, $\alpha = \gamma = 90°$, $\beta = 113.14(3)°$, and $Z = 4$ (for all of the whole crystallographic data and treatment information, see Table S3 in the Supporting Information). The crystal packing as viewed along the *bc* plane is shown in Figure 8. It consist of alternating layers of molecules oriented along the *a* axis forming an arrangement such that CF_3 and FC(O) groups of different layers are face to face, separated by nonbonded CF_3···S and C(O)F···S distances of 3.107 and 3.148 Å, respectively. The shortest nonbonded contacts inside each layer are related to FC(O)···C(O)CF_3 and FC(O)···CF_3 interactions, with distances of 3.037 and 3.217 Å, respectively.

Only the (sp-sp) conformer is observed in a single crystal of FC(O)SSC(O)CF_3 at 198 K, with gauche orientation around the S−S bond. The ϕ(CS−SC) dihedral angle is exactly equal to that obtained in the gas phase (ϕ(CS−SC) = 77.7(2)°). Whereas the torsion angle for the CF_3 group in gaseous phase is 47(5)°, a value of 32.2(4)° was derived from X-ray data. This appears to be a distortion due to packing effects since calculations for FC(O)SSC(O)CF_3 as an isolated free molecule agree with the value obtained in the GED experiments.

The investigations of short nonbonded intramolecular 1,4 S···O contacts have attracted great attention because in the crystal structures of 1,4 S···O containing compounds the S···O distances lie in the range 2.77−3.16 Å.[37] This distance is shorter than the sum of the sulfur and oxygen van der Waals radii (3.3 Å).[38] The presence of such short S···O contacts in these compounds, each of which crystallizes in different packing environment, indicates that this conformational feature results from a nonbonded intramolecular interaction. Computational results suggest that electronic conjugation gives rise to the observed S···O close contact.[39]

In FC(O)SSC(O)CF_3, there are two 1,4 S···O distances, defined by one sulfur atom of the disulfide bond and the oxygen atom in the carbonyl group bonded to the other sulfur atom. Following Figure 7, these 1,4 S···O distances are labeled as S4···O2 and S2···O4. The values for these distances are 3.048 and 3.046 Å for S4···O2 and S2···O4, respectively. The ϕ(SS−C(O)) dihedral angles around the corresponding C−S bonds show values of −8.0 and 6.1°, respectively. This nearly planar sp conformation favors electronic delocalization of the nonbonded π electrons of the sulfur atom, resulting in an increment in the magnitude of the attractive interaction between the sulfur and oxygen atoms.

Discussion

Conformational properties of sulfenylcarbonyl compounds, with general formulas XC(O)SY, have been extensively studied, and the preference for a synperiplanar conformation around the C−S bond was established.[13−17] In the case of disulfides (Y correspond to an −SR group), the preferred mutual orientation of the C═O bond and the S−S simple bond is also synperiplanar.[7,9−11] Furthermore, it has been established experimentally that the antiperiplanar conformation appears as a second stable form with appreciable contribution at room temperature, when X is a fluorine atom.[9,12,40,41] FC(O)SSC(O)CF_3 seems to be a suitable species for studying the transferability of conformational properties between carbonylsulfenyl and disulfide compounds. According to vibrational spectroscopy and GED, FC(O)SSC(O)CF_3 exists in the gas phase at room temperature as a mixture of two conformers, depending on the relative orientation of the FC(O) group and the S−S single bond with the (sp-sp) conformer being the prevailing form. From IR(matrix) spectra of Ar/FC(O)SSC(O)CF_3 mixtures deposited at different temperatures of the spray-on nozzle, a contribution of around 16% of the second form is obtained at room temperature. The relative Gibbs free energy $\Delta G°$ derived from the IR(matrix) experiments (1.14(15) kcal/mol) is reproduced correctly by the B3LYP/6-311+G* method (1.17 kcal/mol), while the MP2/6-31G* value is slightly larger (1.64 kcal/mol). On the other hand, only a synperiplanar conformation was observed for the mutual orientation of the CF_3C═O double bond and the S−S single bond. This result is in agreement with the conformational behavior displayed by other species containing the CF_3C(O)S moiety.[23,35,42]

In all disulfides XSSX substituted with carbon-containing groups (X = FC(O), CF_3, CH_3, Bu^t), the S−S bond lengths

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are similar (between 2.018(4) Å in Bu^tSSBu^t and 2.030 (5) Å in CF_3SSCF_3). This observation was rationalized with the anomeric effect.[6,10] The anomeric interaction lp(S) → σ*(S−C) for carbon-substituted groups bonded to the disulfide bond is similar in these compounds, leading to similar disulfide bond lengths. Following this trend, the S−S bond length in $FC(O)SSC(O)CF_3$ is 2.023(3) Å.

Considering systematic differences between the geometric parameters derived with GED and X-ray diffraction, results obtained for $FC(O)SSC(O)CF_3$ in both gas and crystalline phases agree well. Quantum chemical calculations fail to reproduce the experimental disulfide bond. The S−S bond length is predicted too long by both B3LYP (2.084 Å) and MP2 (2.049 Å) methods, as compared with the experimental gas-phase value of 2.023(3) Å. As mentioned in the Introduction, the dihedral angles in disulfides adopt values around 90°, with the exceptions of CF_3SSCF_3 and Bu^tSSBu^t, which ϕ(CS−SC) are 104.4(40) and 128.3(27)°, respectively. To our knowledge, the smallest experimental angle reported for gas-phase structures of noncyclic disulfides occurs in FC(O)SSC(O)F (82.2(19)°). ϕ(CS−SC) in $FC(O)SSC(O)CF_3$ is even slightly smaller with a value of 77.7(21)°.

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Supporting Information Available: X-ray crystallographic data in CIF format, observed and calculated vibrational data, interatomic distances, experimental and calculated vibrational amplitudes for the gauche (sp-sp) conformer, crystal data and structure refinement details, atomic coordinates and equivalent isotropic displacement parameters, and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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