

Synthesis, Structure and Conformational Properties of Fluoroformylchlorodifluoroacetyl Disulfide, $\text{FC}(\text{O})\text{SSC}(\text{O})\text{CF}_2\text{Cl}$: Conformational Transferability in $-\text{C}(\text{O})\text{SSC}(\text{O})-$ Compounds

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Pure fluoroformylchlorodifluoroacetyl disulfide, $\text{FC}(\text{O})\text{SSC}(\text{O})\text{CF}_2\text{Cl}$, has been prepared by the reaction of $\text{FC}(\text{O})\text{SCl}$ and $\text{CF}_2\text{ClC}(\text{O})\text{SH}$ in quantitative yield. The conformational properties of the novel molecule have been studied by vibrational spectroscopy (IR – gas phase, Raman – liquid phase) and quantum chemical calculations (B3LYP and MP2 methods). The gaseous compound exhibits a conformational equilibrium at room temperature where the most stable form adopts a C_1 symmetry and a *syn*-periplanar (*sp*) orientation of both carbonyl groups with respect to the disulfide bond. A second form, observed in the IR spectrum of the vapor, corresponds to a conformer in which the carbonyl bond of the $\text{FC}(\text{O})$ moiety adopts an *anti*-periplanar (*ap*) position with respect to the S–S single bond, and *gauche* with respect to the $\text{ClC}-\text{C}=\text{O}$ moiety in the chlorodifluoroacetyl group. The experimental free energy difference value $\Delta G^0 = G^0_{(\text{ap}-\text{sp})} -$

$G^0_{(\text{sp}-\text{sp})} = 1.4(3)$ kcal/mol (IR) is reproduced well by the B3LYP/6-311+G(3df) (1.1 kcal/mol) and the MP2/6-31G* (1.8 kcal/mol) methods. In addition, the structure of a single-crystal, grown in situ, was determined by X-ray diffraction analysis at low temperature. The crystalline solid [monoclinic, $P2_1/n$, $a = 5.579(3)$ Å, $b = 16.615(7)$, $c = 8.455(4)$ Å, $\beta = 106.876(8)^\circ$] consists exclusively of molecules with the (*sp-sp*) conformation and the usual *gauche* orientation around the disulfide bond [$\phi(\text{CS}-\text{SC}) = 84.2^\circ$]. Conformational transferability is thus demonstrated once again for species that contain the $-\text{C}(\text{O})\text{SSC}(\text{O})-$ group as part of a systematic program designed to analyze the behavior of this class of molecules.

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Introduction

One of the most fundamental concepts in chemistry is that of a functional group; the idea that a linked group of atoms can exhibit a set of characteristic geometric and chemical properties. This concept is especially useful to understand the chemistry of biological macromolecules which consist of polymeric combinations of a small number of building blocks. From this empirical cornerstone of chemistry – atoms and functional groups possess characteristic and additive properties that in many cases exhibit a remarkable transferability between different molecules – a series of methodologies have been developed, especially in

relation to the study of protein folding.^[1–5] The transferability principle can be used to deduce the properties of large molecules from smaller, readily accessible molecules whose geometric parameters are experimentally known. Knowledge of the structural properties and conformational preference of simple molecules containing distinct functional groups is therefore of prime interest.

Geometric structures of symmetrically substituted non-cyclic disulfides, XSSX , in the gas phase are characterized by a *gauche* conformation around the S–S bond, with dihedral angles $\phi(\text{XS}-\text{SX})$ close to 90° (e.g. $90.76(6)^\circ$ in HSSH ,^[6] $87.7(4)^\circ$ in FSSF ,^[7] $85.2(2)^\circ$ in ClSSCl ,^[8] $85.3(37)^\circ$ in CH_3SSCH_3 ,^[9] and $104.4(40)^\circ$ in CF_3SSCF_3).^[10] 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 opposing S–X bonds.^[11,12] Disulfides with very bulky substituents, such as $t\text{BuSS}t\text{Bu}$, have dihedral angles which are considerably larger than 90° [$\phi(\text{CS}-\text{SC}) = 128.2(27)^\circ$].^[13] On the other hand, the dihedral angle for $\text{FC}(\text{O})\text{SSC}(\text{O})\text{F}$ has been reported to be $82.2(19)^\circ$.^[14] Structural data for nonsymmetrically substituted disulfides of the type XSSY are more sparse in both experimental and theoretical terms. $\text{FC}(\text{O})-$

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SSCF₃^[15] and FC(O)SSCH₃^[16] have been studied in the gas phase and display $\phi(\text{CS}-\text{SC})$ dihedral angles of 95.0(27)° and 83.5(15)°, respectively.

Additionally, the presence of a carbonyl group attached to the S–S bond, as in FC(O)SSC(O)F,^[17] FC(O)SSCH₃,^[15] and FC(O)SSCF₃,^[16] may promote a conformational equilibrium, but this depends on the relative orientation of the C=O and S–S bonds. The *syn*-periplanar (*sp*) orientation, with $\phi(\text{SS}-\text{C}=\text{O}) = 0^\circ$, is the prevailing form for these species.

In order to gain additional experimental and theoretical information about the structural and conformational behavior of acyl-substituted disulfides, we became interested in molecules containing the –C(O)SSC(O)– fragment with two carbonyl groups bonded to the disulfide bond. Thus, fluoroformyltrifluoroacetyl disulfide, FC(O)SSC(O)CF₃, has been recently synthesized and its structural properties studied in both the gas and condensed phases.^[18] In the present study, we have extended the analysis to the related FC(O)SSC(O)CF₂Cl molecule, a novel compound for which the geometric structure and conformational properties have been determined by experimental and theoretical methods.

Results

Synthesis, Characterization, and Physical Properties

The synthesis of FC(O)SSC(O)CF₂Cl was adapted from that recently reported for FC(O)SSC(O)CF₃,^[18] by the reaction of chlorodifluorothioacetic acid, CF₂ClC(O)SH, with fluorocarbonylsulfonyl chloride, FC(O)SCI, according to Equation (1).



The new compound is a colorless liquid with the characteristic overpowering sulfonylcarbonyl odor. In the liquid or gaseous state, the compound is stable for days at room temperature. The vapor pressure, measured in a small section of the vacuum line (total volume ca. 15 mL) with a capacitance manometer over the temperature range 247–291 K, follows the equation $\log p = 5.857 - 2383/T$ (*p*/bar, *T*/K), and gives an extrapolated normal boiling point of 407 K (134 °C).

In the ¹⁹F NMR spectrum of the liquid, two singlets with an intensity ratio of 1:2 were observed. The more intense signal is located at $\delta = -62.6$ ppm, whereas the second signal appears at $\delta = 42.3$ ppm. The related trifluoromethyl species shows corresponding signals at $\delta = -74.9$ ppm [CF₃C(O)– group] and 41.4 ppm [FC(O)– group].^[18]

Additional evidence for the identity of FC(O)SSC(O)CF₂Cl comes from the IR spectrum of the vapor and the Raman spectrum of the liquid (Figure 1 and Table S11 in the Supporting Information). Two intense bands in the carbonyl stretching region at 1847 and 1771 cm^{−1} are characteristic of the FC=O and CF₂ClC=O groups, respectively. The strongest band in the IR spectrum of the vapor cen-

tered at 1060 cm^{−1}, is assigned to the F–C_{sp²} stretching mode. In addition, the characteristic disulfide stretching mode is observed in the Raman spectrum of the liquid as a signal of medium intensity at 535 cm^{−1}.

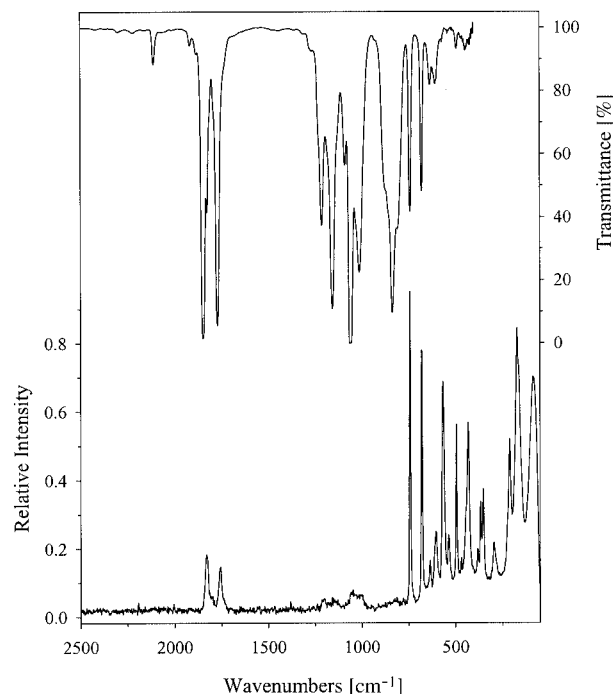


Figure 1. Gas IR at 5.0 mbar (glass cell, 200 mm optical path length, Si windows, 0.5 mm thick) and liquid Raman spectra for FC(O)SSC(O)CF₂Cl.

Quantum Chemical Calculations

In a first step, the potential function for the internal rotation around the S–S bond was derived by structure optimizations at fixed $\phi(\text{CS}-\text{SC})$ dihedral angles, whereas near-*sp* mutual orientations were supposed for both C=O double bonds and the S–S bond. The potential function obtained with the B3LYP/6-31G* method is shown in Figure 2. Minima occur at dihedral angles around $\pm 75^\circ$, whereas a rather flat maximum in the region of a *trans* C–S–S–C skeleton is observed, with imaginary frequencies, at $\phi(\text{CS}-\text{SC}) = 180^\circ$.

Besides the two enantiomeric forms that are related by rotation around the disulfide bond, several conformations are feasible, in principle, for FC(O)SSC(O)CF₂Cl, but they depend on the orientation of the C=O bonds of the FC(O) and the CF₂ClC(O) groups. Each of them can be *syn*-periplanar (*sp*) or *anti*-periplanar (*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 CF₂ClC(O) group, see Scheme 1].

The potential functions for the internal rotation around both S–C bonds were calculated (B3LYP/6-31G*) by full geometry optimization at fixed $\phi(\text{SS}-\text{C}=\text{O})$ torsional angles (Figure 3). As expected, both curves possess minima for *sp* [$\phi(\text{SS}-\text{C}=\text{O}) = 0^\circ$] and *ap* [$\phi(\text{SS}-\text{C}=\text{O}) = 180^\circ$] orientations.

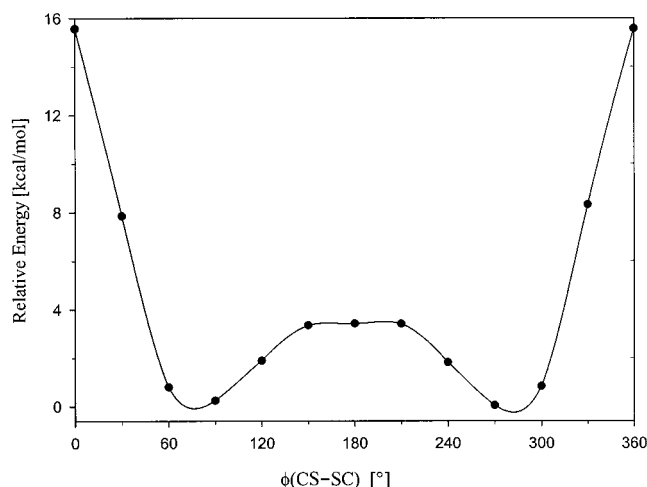
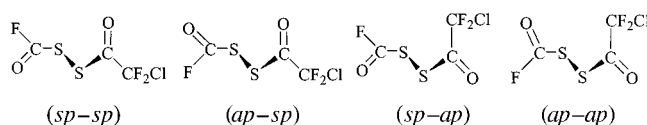


Figure 2. Calculated potential function (B3LYP/6-31G*) for the internal rotation around the S-S bond in FC(O)SSC(O)CF₂Cl.



Scheme 1. Representation of the conformers of FC(O)SSC(O)-CF₂Cl.

The calculated maxima for near-perpendicular orientations [$\phi(\text{SS}-\text{C}=\text{O}) \approx 90^\circ$] have similar energy values in both cases, which are characterized as torsional transition states (TS, $N_{\text{imag}} = 1$). The geometries of the four minima were fully optimized, including frequency calculations, with the B3LYP method and with the use of the 6-31G* and 6-311+G(3df) basis sets and the MP2/6-31G* approximation. Calculated relative energies (corrected for zero-point energy) and vibrational frequencies of the C=O stretches with their IR intensities are collected in Table 1. All three computational methods predict that the four different conform-

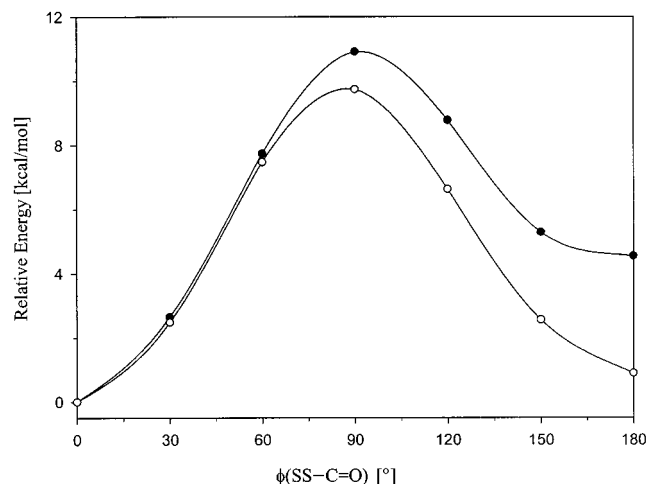


Figure 3. Potential energy curves for FC(O)SSC(O)CF₂Cl as a function of the $\phi(\text{SS}-\text{C}=\text{O})$ dihedral angles calculated with the B3LYP/6-31G* approximation. [○: $\phi(\text{SS}-\text{C1}=\text{O1})$, ●: $\phi(\text{SS}-\text{C2}=\text{O2})$, for atom numbering see Figure 5].

ers correspond to stable structures and agree with respect to the conformational preference. In the lowest-energy conformer, both carbonyl bonds adopt an *sp* orientation with respect to the S-S bond, whereas the second most stable conformer possesses an *ap* orientation of the FC(O) group with respect to the S-S single bond. Moreover, structures with *ap* orientation of the CF₂ClC(O) group with respect to the S-S bond are considerably higher in energy ($\Delta G^0 \approx 4.0$ kcal/mol or even more) and are not expected to be detectable in our experiments.

Table 1. Calculated relative energies (corrected by zero-point energy) and vibrational frequencies of the C=O stretching modes [cm^{-1}] with IR intensities [km/mol] in parentheses for FC(O)-SSC(O)CF₂Cl.

Conformer ^[a]	Method of calculation	ΔE^0	$\nu(\text{FC}=\text{O})$	$\nu(\text{O}=\text{CCF}_2\text{Cl})$
(sp-sp)	B3LYP/6-31G*	0.00 ^[b]	1922 (231)	1851 (192)
	B3LYP/6-311+G(3df)	0.00 ^[c]	1892 (249)	1827 (214)
	MP2/6-31G*	0.00 ^[d]	1894 (177)	1784 (127)
(ap-sp)	B3LYP/6-31G*	0.89	1903 (379)	1847 (190)
	B3LYP/6-311+G(3df)	1.14	1866 (453)	1826 (204)
	MP2/6-31G*	1.76	1881 (301)	1780 (127)
(sp-ap)	B3LYP/6-31G*	4.48	1923 (245)	1827 (250)
	B3LYP/6-311+G(3df)	3.74	1893 (267)	1804 (288)
	MP2/6-31G*	6.05	1897 (183)	1759 (163)
(ap-ap) ^[e]	B3LYP/6-31G*	5.29	1901 (327)	1826 (295)
	MP2/6-31G*	7.93	1872 (250)	1759 (195)

[a] First orientation (*sp* or *ap*) refers to FC(O) group, second orientation (*sp* or *ap*) to CF₂ClC(O) group. [b] $E^0 = -1820.807875$ hartree. [c] $E^0 = -1817.714699$ hartree. [d] $E^0 = -1821.140101$ hartree. [e] The (*ap-ap*) was not calculated at the B3LYP/6-311+G(3df) approximation.

In regard to the chlorodifluoromethyl group, the predominant conformer possesses a *gauche* structure with ClC-C=O values close to 80° ; the C-F bond deviates from the eclipsed orientation [$\phi(\text{FC}-\text{C}=\text{O}) = 42^\circ$]. From the potential energy curve obtained by the rotation of the CF₂Cl group around the C-C single bond (Figure 4) both *cis*

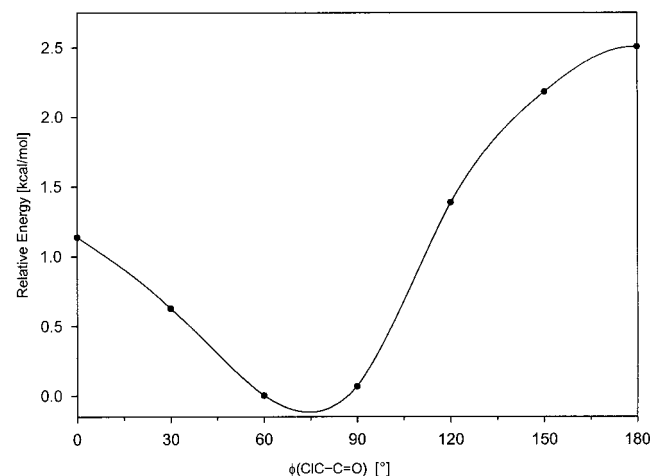


Figure 4. Potential energy curves for FC(O)SSC(O)CF₂Cl as a function of the $\phi(\text{ClC}-\text{C}=\text{O})$ dihedral angle calculated with the B3LYP/6-31G* approximation.

[$\phi(\text{ClC}-\text{C}=\text{O}) = 0^\circ$] and *trans* [$\phi(\text{ClC}-\text{C}=\text{O}) = 180^\circ$] forms correspond to torsional transition states ($N_{\text{imag}} = 1$). The calculated barrier heights (corrected for zero-point energies) are 1.1 and 2.5 kcal/mol, respectively.

Vibrational Spectra

The IR spectrum of the vapor and the Raman spectrum of liquid FC(O)SSC(O)CF₂Cl are shown in Figure 1. Both spectra are similar to those of FC(O)SSC(O)CF₃.^[18] A tentative assignment of the observed bands was performed by comparison with the calculated spectrum and the approximate description of modes is based on the calculated displacement vectors for the fundamental modes of vibration, as well as on comparisons with the spectra of related molecules, especially FC(O)SSC(O)F^[17] and CF₂ClC(O)Cl.^[19] Experimental and calculated [B3LYP/6-311+G(3df)] frequencies for the (*sp-sp*) and (*ap-sp*) conformers, together with the tentative assignments, are given in the Supporting Information (Table SII).

The ab initio calculations indicate that the (*sp-sp*) conformer is more stable than the (*ap-sp*) conformer. The vibrational spectra are consistent with this prediction, but the presence of a second conformer in the vapor phase becomes apparent. It is known that the $\nu(\text{C}=\text{O})$ normal mode of carbonyl compounds is very sensitive to conformational properties.^[20,21] As observed in Figure 5, two intense bands occur in the IR spectrum of FC(O)SSC(O)CF₂Cl vapor at 1847 and 1771 cm⁻¹, whereas a third band of low intensity appears at 1827 cm⁻¹. The first two bands are assigned to the C=O stretching modes of the FC=O and CF₂ClC=O groups in the most abundant (*sp-sp*) conformer. Comparison with the calculated frequencies then allows the assignment of the third band to the FC=O group in the (*ap-sp*) form. Thus, the calculated wavenumber difference [B3LYP/6-311+G(3df)] for the C=O stretching mode of the FC(O) group [$\nu(\text{FC}=\text{O})$, Table I] between the (*sp-sp*) and the (*ap-sp*) forms is +26 cm⁻¹, a value that is in good agreement with the experimentally observed value of +20 cm⁻¹. No significant difference is expected in the wavenumbers of the CF₂ClC=O stretching mode between the (*sp-sp*) and (*ap-sp*) forms; the calculated difference is about 2 cm⁻¹. Accordingly, the stretching mode of the (*ap-sp*) conformer is assigned to the band at 1771 cm⁻¹, which is masked by the band of the corresponding stretching mode of the (*sp-sp*) form. The conformational composition was derived from the integrated intensities of the C=O vibrations for the (*sp-sp*) and (*ap-sp*) forms, with the intensities calculated by the B3LYP/6-311+G(3df) method taken into account (Table 1). This analysis leads to a composition of 92(5)% of the more stable (*sp-sp*) form at ambient temperature (the estimated error limit includes uncertainties in the measured areas and in the calculated intensities).

A conformational equilibrium was also evident in the F–C(O) stretching region [$\nu(\text{C}_{\text{sp}^2}-\text{F})$, Table SII given in the Supporting Information] through the presence of two bands in the IR spectrum of the vapor. The more intense band is

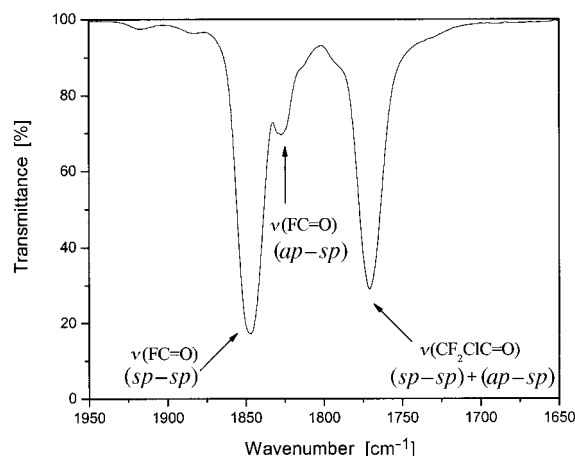


Figure 5. C=O vibrational stretching region in the IR spectrum of gaseous FC(O)SSC(O)CF₂Cl at 5.0 mbar (glass cell, 200 mm optical path length, Si windows, 0.5 mm thick).

located at 1060 cm⁻¹, which can be assigned to this mode in the main (*sp-sp*) conformer; the second band, at 1089 cm⁻¹, can be assigned to the same mode of the less stable (*ap-sp*) form. Quantum chemical calculations correctly reproduce this frequency shift of 19 cm⁻¹. According to the calculations, the other fundamental modes of the (*sp-sp*) and (*ap-sp*) conformers either differ by less than 2 cm⁻¹ or have too low an intensity to be observed in our experiments.

Crystal Structure

Because simple covalent disulfides are liquids or gases at ambient temperatures and because they are frequently labile species, very little is known about their structures in the solid state. Only with the development of special crystallization techniques has it become possible to extend detailed structural studies to the crystalline state. By using the in situ crystallization technique developed at Essen,^[22] an appropriate single-crystal of FC(O)SSC(O)CF₂Cl was grown at 193 K. The compound crystallizes in the monoclinic system (*P*₂₁/*n* spatial group) with the following unit cell dimensions: *a* = 5.579(3) Å, *b* = 16.615(7) Å, *c* = 8.455(4) Å, and *a* = *γ* = 90° and *β* = 106.876(8)°, *Z* = 4 (for the full crystallographic data and treatment information, see Table SII in the Supporting Information). Only the (*sp-sp*) conformer is observed in the crystal, with a *gauche* orientation around the S–S bond. The structure of the molecule is shown in Figure 6, and Table 2 includes the main geometric parameters derived from the structure refinement, as well as those obtained from quantum chemical calculations. The overall crystal packing, as viewed along the *ab* plane, is shown in Figure 7.

Intermolecular interactions that are dominated by F...F contacts are common for fluorinated molecules where there is no other choice for the stabilization of the packing. According to quantum chemical calculations, F...F contacts in aromatic systems can contribute up to 14 kcal/mol of local stabilization energy.^[23] In the present case, the chlorodifluo-

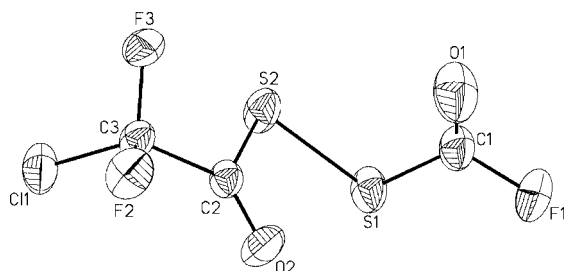


Figure 6. Molecular model with atom numbering scheme for the single-crystal structure of $\text{FC}(\text{O})\text{SSC}(\text{O})\text{CF}_2\text{Cl}$.

Table 2. Experimental and calculated geometric parameters for the *gauche* (*sp-sp*) conformer of $\text{FC}(\text{O})\text{SSC}(\text{O})\text{CF}_2\text{Cl}$.^[a]

Parameter	X-ray ^[b]	B3LYP		MP2/6-31G*
		6-31G*	6-311+G(3df)	
S1–S2	2.029 (1)	2.074	2.050	2.049
S1–C1	1.759 (4)	1.790	1.785	1.774
S2–C3	1.796 (3)	1.824	1.813	1.794
C1–C2	1.556 (4)	1.553	1.557	1.539
C1=O1	1.179 (4)	1.196	1.187	1.211
C3=O2	1.165 (4)	1.182	1.176	1.194
(C2–F) _{mean}	1.335 (4)	1.340	1.339	1.354
C3–F4	1.342 (4)	1.342	1.347	1.358
C–Cl	1.739 (3)	1.785	1.773	1.753
S2–S1–C1	99.7 (1)	99.8	101.4	98.2
S1–S2–C3	99.1 (1)	101.4	100.4	99.4
S1–C1=O1	126.7 (2)	125.7	126.2	126.0
S2–C3=O2	131.1 (3)	129.7	130.5	129.7
S1–C1–C2	111.8 (2)	112.1	112.2	112.9
F–C2–F	107.1 (2)	108.5	108.0	108.5
S2–C3–F4	106.7 (2)	106.6	106.3	106.6
(F–C–C) _{mean}	109.5 (3)	109.6	110.0	108.7
Cl–C–C	110.7 (2)	110.0	109.6	110.3
(Cl–C–F) _{mean}	110.0 (3)	109.6	109.6	109.9
$\phi(\text{SS–C=O1})$	0.8 (4)	2.9	0.9	2.0
$\phi(\text{SS–C=O2})$	4.8 (3)	2.0	2.7	2.9
$\phi(\text{CS–SC})$	84.2 (2)	77.4	83.5	71.1
$\phi(\text{ClC–C=O})$	102.3 (4)	68.8	78.9	77.2

[a] See Figure 6 for atom numbering. [b] Uncertainties are σ values.

romethyl groups interact through $\text{C–F}\cdots\text{F–C}$ contact which measure 2.817 Å. This value is within the range found in comparable structural studies, in which $\text{C–F}\cdots\text{F–C}$ contacts of 2.777 and 2.868 Å are identified as packing motifs.^[24,25] The sum of the van der Waals radii would suggest 2.7 Å as a contact distance, but this does not obviously hold for carbon-bonded fluorine.

The investigation of short nonbonded intramolecular 1,4 $\text{S}\cdots\text{O}$ contacts have attracted much attention because $\text{S}\cdots\text{O}$ distances in the range 2.77–3.16 Å have been observed in crystals.^[26] These values are much shorter than the sum of the sulfur and oxygen van der Waals radii (3.3 Å).^[27] The presence of such short $\text{S}\cdots\text{O}$ contacts in these compounds, each of which crystallizes in a different packing environment, indicates that the conformational feature results from a nonbonded intramolecular interaction. Computational results suggest that electronic conjugation gives rise to the observed $\text{S}\cdots\text{O}$ close contact.^[28] In molecules which contain the $-\text{C}(\text{O})\text{SSC}(\text{O})-$ moiety, there are two 1,4 $\text{S}\cdots\text{O}$ distances, defined by one sulfur atom of the disulfide bond and the

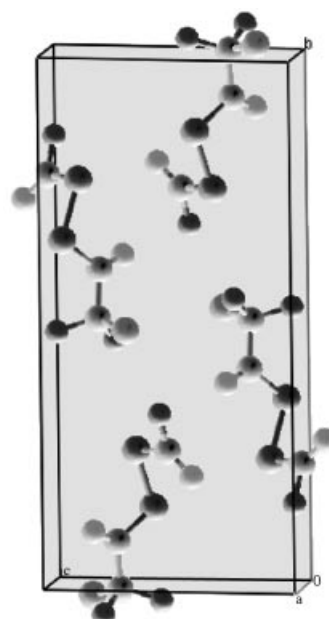


Figure 7. Stereoscopic illustration of the crystal packing of $\text{FC}(\text{O})\text{SSC}(\text{O})\text{CF}_2\text{Cl}$ at 193 K.

oxygen atom in the carbonyl group bonded to the other sulfur atom. Following Figure 6, these 1,4 $\text{S}\cdots\text{O}$ distances for $\text{FC}(\text{O})\text{SSC}(\text{O})\text{CF}_2\text{Cl}$ are labeled as $\text{S1}\cdots\text{O2}$ and $\text{S2}\cdots\text{O1}$, with values of 3.016 Å and 3.078 Å, respectively. The $\phi(\text{SS–C=O})$ dihedral angles around the corresponding C–S bonds are 4.8 and 0.8°, respectively. Following Burling et al.,^[28] these nearly planar conformations favor electronic delocalization of the nonbonded π electrons of the sulfur atom, which results in an increased attractive interaction between the sulfur and oxygen atoms.

Discussion

According to the vibrational spectra, the title molecule exists in the gas phase as a mixture of two conformers that differ in the relative orientation of the $\text{FC}(\text{O})$ group and the S–S single bond, with the *sp* conformer prevailing over the *ap* form. At room temperature, the more stable conformer accounts for 92(5)% of the vapor species. The standard Gibbs free-energy difference [$\Delta G^0 = G^0_{(\text{ap-sp})} - G^0_{(\text{sp-sp})}$] derived from the IR spectrum of the vapor (1.4 kcal/mol) is reproduced satisfactorily at the B3LYP/6-311+G(3df), B3LYP/6-31G*, and MP2/6-31G* levels of calculation. On the other hand, only the *sp* conformation is observed for the mutual orientation of the $\text{CF}_2\text{ClC=O}$ double bond and the S–S single bond, with a calculated mean value of $\Delta G^0 = G^0_{(\text{sp-ap})} - G^0_{(\text{sp-sp})}$ of 4.7 kcal/mol. This behavior parallels that recently reported for $\text{FC}(\text{O})\text{SSC}(\text{O})\text{CF}_3$, with $\Delta G^0 = G^0_{(\text{ap-sp})} - G^0_{(\text{sp-sp})} = 1.14(15)$ kcal/mol from the IR spectrum of the matrix isolated vapor and *sp* orientation of the S–S single bond with respect to the C=O double bond in the $-\text{C}(\text{O})\text{CF}_3$ moiety.^[18]

The chlorodifluoroacetyl group adopts a *gauche* orientation in the crystal, with a corresponding dihedral angle

$\phi(\text{ClC}-\text{C}=\text{O})$ of $102.3(4)^\circ$ [$\phi(\text{F}_3\text{C}_3-\text{C}=\text{O}) = 136.4(3)^\circ$]. As already commented in this paper, quantum chemical calculations predict a different behavior for a molecule with the (*sp-sp*) conformation, with $\phi(\text{ClC}-\text{C}=\text{O})$ and $\phi(\text{F}_3\text{C}_3-\text{C}=\text{O})$ dihedral angles of 78.9 and 160.7° , respectively. The predominant conformer found experimentally for chlorodifluoroacetyl chloride [$\text{CF}_2\text{ClC}(\text{O})\text{Cl}$] in the gas phase possesses a *gauche* orientation of the chlorine atoms [$\phi(\text{ClC}-\text{C}=\text{O}) = 104.6(10)^\circ$],^[29] whereas a second stable conformer where the $\text{C}-\text{Cl}$ bond eclipses the $\text{C}=\text{O}$ bond is higher in energy by $\Delta G^0 = 1.1(3)$ kcal/mol.^[29] From a study of the Raman spectrum of the liquid at different temperatures, a ΔH^0 value of $1.03(11)$ kcal/mol was determined, whereas for the sample dissolved in liquid xenon, this value decreases to $0.71(17)$ kcal/mol.^[19] For the free molecule of the title compound, this last conformation corresponds to a rotational transition state; the calculated barrier is only 1.1 kcal/mol. Thus, the barrier to rotation appears to be quite low for the chlorodifluoroacetyl moiety, and the discrepancy between the X-ray structure and the calculated geometrical properties probably reflects the distortions induced by the crystal packing.

Transferability is then evident in the conformational properties of $\text{FC}(\text{O})\text{SSC}(\text{O})\text{CF}_2\text{Cl}$. Extensive studies of carbonylsulfonyl compounds with the general formula $\text{XC}(\text{O})-\text{SY}$ have established the preference for a *syn*-periplanar conformation around the $\text{C}-\text{S}$ bond.^[20,30–33] In the case of disulfides (so that Y corresponds to an $-\text{SR}$ group), the preferred mutual orientation of the $\text{C}=\text{O}$ and $\text{S}-\text{S}$ bonds is also *sp*.^[12,14–16] It has also been established experimentally that the *ap* conformation appears as a second stable form that makes appreciable contributions to the vapor at room temperature when X is a fluorine atom,^[14,17,34,35] whereas only the *sp* conformation is adopted by species containing the $\text{CF}_3\text{C}(\text{O})\text{S}$ moiety.^[36–38]

Breitzer et al.^[39] have reported the analysis of the crystal structures of several disulfides. A plot of the $\text{S}-\text{S}$ bond length versus the disulfide torsion angles reveals the greatest density of data points in the bond length region 2.00 – 2.06 Å and torsion angles between 75 and 90° . A similar pattern has also been observed for the structures of gaseous disulfides. In accordance with this trend, the disulfide bond length and torsion angle in crystalline $\text{FC}(\text{O})\text{SSC}(\text{O})\text{CF}_2\text{Cl}$ are $2.029(1)$ Å and $84.2(2)^\circ$, respectively.

The two computational methods we have used predict dihedral angles for the molecular skeleton with values similar to those obtained from the X-ray analysis. The methods are less successful in the reproduction of the lengths of some of the bonds around sulfur. Thus, even with large basis sets [$6-311+\text{G}(3\text{df})$], the B3LYP method predicts the $\text{S}-\text{X}$ bonds to be too long (by up to 0.026 Å for the $\text{S1}-\text{C1}$ bond). While these bonds are better described by the MP2 method with the modest $6-31\text{G}^*$ basis set, this method fails to reproduce the $\text{C}=\text{O}$ double bond lengths well, which are also made out to be too long (0.032 Å for the $\text{C1}=\text{O1}$ bond). In practice, however, the contraction of polar bonds is to be expected upon crystallization and compensation for this phenomenon allows both methodologies to satisfacto-

rily reproduce the molecular dimensions of the crystalline solid.

Experimental Section and Instrumentation

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), three U-traps and valves with PTFE stems (Young, London, UK). 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 monitor 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 appropriate amount of the compound was taken out for the experiments, and then the ampules were flame-sealed again.^[40]

$\text{CF}_2\text{ClC}(\text{O})\text{SH}$ was synthesized by the reaction of either $\text{CF}_2\text{ClC}(\text{O})\text{Cl}$ or $[\text{CF}_2\text{ClC}(\text{O})]_2\text{O}$ (98% Aldrich) with H_2S (98% Linde, Germany) in a metal reactor.^[41] This method was adapted from the literature procedure for the synthesis of $\text{CF}_3\text{C}(\text{O})\text{SH}$.^[42] $\text{CF}_2\text{ClC}(\text{O})\text{Cl}$ was synthesized by the reaction of chlorodifluoroacetic acid (98% Merck) with PCl_5 according to the usual method. $\text{FC}(\text{O})\text{SCl}$ was obtained by the reaction of commercial $\text{ClC}(\text{O})\text{SCl}$ (Aldrich 95%) with SbF_5 following the reported method.^[43,44]

Conventional vacuum techniques were used to condense equimolar quantities (typically 2.5 mmol) of $\text{CF}_2\text{ClC}(\text{O})\text{SH}$ and $\text{FC}(\text{O})\text{SCl}$ into a 6 mm o.d. glass ampule. The vessel was flame-sealed and placed in a -40°C ethanol bath. At this temperature, the reaction proceeded rapidly, as judged by the disappearance of the yellow color [due to $\text{FC}(\text{O})\text{SCl}$] of the reaction mixture. The mixture was then warmed to -10°C and preserved at that temperature for about 1 h. Subsequently the products were separated by “trap-to-trap” condensation through traps held at -30°C , -60°C and -196°C . Pure $\text{FC}(\text{O})\text{SSC}(\text{O})\text{CF}_2\text{Cl}$ was retained as a colorless liquid in the -60°C trap. The yield was nearly quantitative and, apart from the HCl generated in the reaction, only minor quantities of OCS and SiF_4 were observed as byproducts in the U-trap at -196°C .

X-ray Diffraction at Low Temperature: An appropriate crystal of $\text{FC}(\text{O})\text{SSC}(\text{O})\text{CF}_2\text{Cl}$ ca. 0.3 mm in diameter was obtained on the diffractometer at a temperature of $193(2)$ K with a miniature zone melting procedure with the use of focused infrared laser radiation.^[22] The diffraction intensities were measured at low temperatures with a Nicolet R3m/V four-circle diffractometer. Intensities were collected with graphite-monochromatized $\text{Mo}-K_\alpha$ radiation with the ω -scan technique. The crystallographic data, conditions and some features of the structure are listed in Table SI2 (Supporting Information). The structure was solved by Patterson syntheses and refined by full-matrix least-squares methods on F with the SHELXTL-Plus program.^[45] Absorption correction details are given in Table SI2 (Supporting Information). All atoms were assigned anisotropic thermal parameters. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666, E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-416694.

Vibrational Spectroscopy: Gas-phase infrared spectra were recorded with a resolution of 1 cm^{-1} in the range 4000 – 400 cm^{-1} with a Bruker IFS 66v FTIR instrument and Raman spectra of liquid

FC(O)SSC(O)CF₂Cl with a Bruker RFS 100/S FT-Raman spectrometer. The liquid sample was contained in a 4 mm glass capillary and the spectrum excited with 500 mW of 1064 nm radiation from a Nd:YAG laser (ADLAS, DPY 301, Lübeck, Germany).

NMR Spectroscopy: For the ¹⁹F NMR measurements, neat samples were held in flame-sealed, thin-walled 3 mm o.d. tubes placed inside 5 mm NMR tubes. The spectra were recorded with a Bruker Avance DRX-300 spectrometer operating at 282.41 MHz. The spectrum was measured with the sample at room temperature with a mixture of CD₃CN and CCl₄ as an external lock and reference, respectively.

Theoretical Calculations: All quantum chemical calculations were performed with the GAUSSIAN03 program package^[46] under the Linda parallel execution environment with two coupled PC's. MP2 and B3LYP methods with standard basis sets up to 6-311+G(3df) and gradient techniques were used for the geometry optimizations and calculation of the vibrational properties. Transition states were optimized by the Synchronous Transit-guided Quasi-Newton (STQN) method, and torsional barrier heights were calculated from the relative energies of the TS and the stable structure with the zero-point energies of the species taken into account. All the computed TS structures show only one imaginary frequency, which corresponds to the torsion involved in the conformational transition.

Supporting Information (see footnote on the first page of this article): Observed and calculated vibrational data for (*sp-sp*) and (*ap-sp*) conformers; X-ray crystallographic data and structural refinement details.

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