

S-(Fluoroformyl)O-(Trifluoroacetyl) Thioperoxide, FC(O)S–OC(O)CF₃: Gas-Phase Structure and Conformational Properties

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The geometric structure and conformational properties of S-(fluoroformyl)O-(trifluoroacetyl) thioperoxide, FC(O)S–OC(O)CF₃, were investigated by gas electron diffraction, matrix isolation infrared spectroscopy, and quantum chemical calculations (B3LYP with the 6-31G* and aug-cc-pVTZ basis sets and MP2 with the 6-31G* basis set). The experimental methods result in a mixture of two conformers with gauche conformation around the S–O bond. In the main conformer (82(7)% according to GED at 298 K), the C=O bond of the FC(O) group is oriented syn with respect to the S–O bond and $\phi(\text{C}=\text{O} \cdots \text{S}-\text{O}) = 75(3)^\circ$. In the minor conformer (18(7)%), this C=O is oriented anti. Both conformers possess syn orientation of the C=O bond of the CF₃C(O) group. The conformational properties and geometric parameters are reproduced reasonably well by the quantum chemical calculations, except for the S–O bond length, which is predicted too long by 0.04 Å (B3LYP/aug-cc-pVTZ).

Introduction

It is well known that unstrained peroxides of the type ROOR' possess gauche structures with dihedral angles $\phi(\text{ROOR}')$ between about 80° and 130°. For the parent compound HOOH, an equilibrium angle of 111.8° has been derived from spectroscopic data.¹ Exceptions are peroxides with very bulky substituents such as bis(*tert*-butyl)peroxide ($\phi = 166(3)^\circ$) and bis-(trimethylsilyl)peroxide ($\phi = 144(6)^\circ$).² A generally accepted explanation for the preference of gauche orientation of the substituents is the interaction between the *n*_o lone pairs of the two oxygen atoms and anomeric effects between the p-shaped lone pairs with the opposite $\sigma^*(\text{O}-\text{R})$ bonds. These interactions favor a dihedral angle of about 90°, and steric interactions between the substituents tend to increase this angle. If both substituents R and R' possess sp²-hybridized atoms, such as C(O)X or NO₂, it might be expected that long-range conjugation between the p-shaped oxygen lone pairs and the π -bonds of the substituents favor planar COOC or COON skeletons, or lead at least to a pronounced opening of the dihedral angle. Experimental structure determinations, however, contradict this expectation, and dihedral angles of less than 90° have been derived for FC(O)OOC(O)F ($\phi(\text{COOC}) = 83.5(14)^\circ$)³ or CH₃C(O)OONO₂ ($\phi(\text{COON}) = 84.7(13)^\circ$).⁴

Similar structural properties are observed for disulfides of the type RSSR'. Because of the longer S–S bond as compared to the O–O bond, steric repulsions between substituents are

reduced and dihedral angles have values closer to 90° (90.76(6)° in HSSH,⁵ 85.3(37)° in CH₃SSCH₃,⁶ or 128.2(27)° in ^tBuSS^tBu⁷). Again, sp²-hybridized substituents lead to a dihedral angle <90° in FC(O)SSC(O)F ($\phi(\text{CSSC}) = 82.2(19)^\circ$).⁸

Thioperoxides of the type RSOR', which are formal derivatives of the sulfenic acid HSOH, are much less stable than peroxides or disulfides, and very little is known about their structural properties. The parent compound possesses a gauche structure with a dihedral angle ($\phi(\text{HSOH}) = 91.3^\circ$) very close to that in disulfide.⁹ This value has been derived with high level ab initio calculations (CCSD(T)/cc-pCVQZ), which reproduce experimental rotational constants very closely. Gas electron diffraction (GED) studies for dimethoxysulfide, CH₃O–S–OCH₃,¹⁰ and dimethoxy disulfide, CH₃O–SS–OCH₃,¹¹ result in dihedral angles around the S–O bonds of $\phi(\text{COSO}) = 84(3)^\circ$ and $\phi(\text{COSS}) = 74(3)^\circ$, which are smaller than 90°. Recently, very unexpected conformational properties were determined for two molecules containing O–S bonds, both with one sp²-hybridized substituent bonded to oxygen, CF₃S–OC(O)CH₃ and CF₃S–OC(O)CF₃. IR(matrix) spectra and GED result in mixtures of two conformers. In addition to the expected gauche form with dihedral angles of 100(4)° and 101(3)°, respectively, a minor conformer with trans structure around the S–O bond is present.¹² Both conformers possess synperiplanar orientation of the C=O bond relative to the S–O bond. These experimental results are reproduced by quantum chemical calculations. The calculated potential functions for internal rotation around the S–O bond possess a minimum for the trans structure at $\phi(\text{CSOC}) = 180^\circ$, in addition to minima for gauche structures with $\phi(\text{CSOC})$ around 90°. This unexpected result suggests the study of the conformational properties of thio peroxides with two sp²-hybridized substituents. Conjugation

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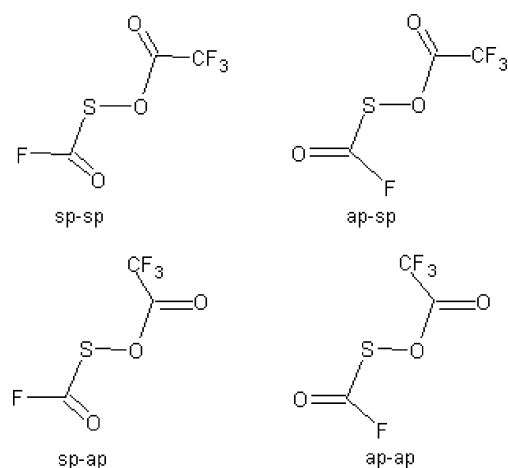
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CHART 1



between the p-shaped lone pairs of sulfur and oxygen with the π -systems of the two substituents may be expected to stabilize a planar trans conformer. IR(gas), UV, and ^{13}C NMR spectroscopy of the symmetrically substituted trifluoroacetylsulfonyl trifluoroacetate, $\text{CF}_3\text{C}(\text{O})\text{S}-\text{OC}(\text{O})\text{CF}_3$, did not provide a definite answer about the conformational properties of this compound.¹³ In the present study, we report an IR(matrix) and GED investigation of *S*-(fluoroformyl)O-(trifluoroacetyl) thio-peroxide, $\text{FC}(\text{O})\text{S}-\text{OC}(\text{O})\text{CF}_3$, supplemented by quantum chemical calculations.

Quantum Chemical Calculations

Several conformations are feasible for this compound, depending on the orientation of the $\text{C}=\text{O}$ bonds of the $\text{FC}(\text{O})$ and $\text{CF}_3\text{C}(\text{O})$ groups, each of which can be synperiplanar (sp) or antiperiplanar (ap) with respect to the $\text{S}-\text{O}$ bond. This leads to four possible conformers, (sp-sp), (ap-sp), (sp-ap), and (ap-ap) (the first orientation refers to the $\text{FC}(\text{O})$ group and the second to the $\text{CF}_3\text{C}(\text{O})$ group, see Chart 1), independent of the configuration (gauche or trans) around the $\text{S}-\text{O}$ bond. Geometries of possible conformers of $\text{FC}(\text{O})\text{S}-\text{OC}(\text{O})\text{CF}_3$ (**1**) (Chart 1) with gauche and trans structure around the $\text{S}-\text{O}$ bond were optimized using B3LYP/(6-31G* and MP2/6-31G* levels of approximation. According to these two methods, six of the eight feasible conformers correspond to stable structures, and imaginary frequencies were predicted for the two trans structures with the $\text{C}=\text{O}$ bond of the $\text{C}(\text{O})\text{CF}_3$ group antiperiplanar (trans (sp-ap) and trans (ap-ap)). The predicted relative energies, ΔE , free energies, ΔG° , and vibrational frequencies of the $\text{C}=\text{O}$ stretches for the six stable conformers are listed in Table 1, which also includes results at the B3LYP/aug-cc-pVTZ level of approximation for the most stable forms. The calculations

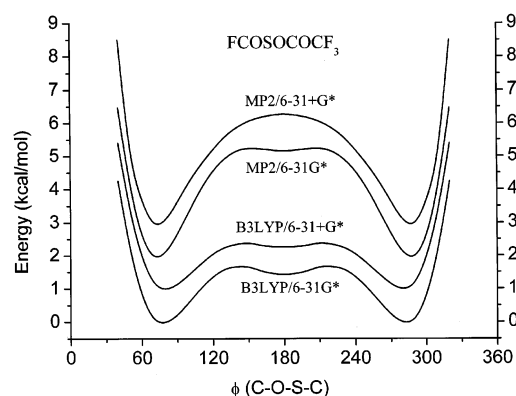


Figure 1. Calculated potential function for internal rotation around the $\text{S}-\text{O}$ bond in $\text{FC}(\text{O})\text{S}-\text{OC}(\text{O})\text{CF}_3$. The individual curves are shifted by 1 kcal/mol.

predict the lowest energy for the gauche (sp-sp) conformer and very high energies ($\Delta G^\circ > 6$ kcal/mol) for gauche structures with the $\text{C}=\text{O}$ bond of the $\text{C}(\text{O})\text{CF}_3$ group antiperiplanar (gauche (sp-ap) and gauche (ap-ap)). These conformers will not be observable in the experiment. The B3LYP/6-31G* calculation predicts the existence of four conformers with $\Delta G^\circ < 2$ kcal/mol; the MP2/6-31G* approximation predicts only two low energy forms (see Table 1). The potential function for internal rotation around the $\text{S}-\text{O}$ bond was calculated by structure optimizations at fixed dihedral angles $\phi(\text{CSOC})$ from 40° to 180° and is shown for the (sp-sp) form in Figure 1. Both B3LYP and MP2 methods with small basis set (6-31G*) predict a very shallow minimum for the trans structure in addition to the prominent minima for the gauche structure. The depth of the trans minimum in these curves for electronic energies is only 0.21 (B3LYP) and 0.07 kcal/mol (MP2), respectively, and it decreases further to 0.17 and 0.03 kcal/mol, if zero point vibrational energies are included. This shallow minimum implies a very low calculated torsional vibration of about 10 cm^{-1} , resulting in a high entropy for the trans conformer. This makes the ΔG° values (0.87 and 2.12 kcal/mol) smaller than the ΔE values (1.45 and 3.19 kcal/mol), despite the lower multiplicity of the trans form ($m = 1$) than that of the gauche form ($m = 2$). If diffuse functions are included in the basis sets (6-31+G*), the minimum becomes even more shallow (B3LYP) or it disappears completely (MP2, see Figure 1). Similarly, MP2/6-31+G* calculations for the trans (ap-sp) conformer predict an imaginary frequency. These theoretical results make the existence of a trans minimum uncertain and the experimental observation of a trans structure of $\text{FC}(\text{O})\text{SO}-\text{C}(\text{O})\text{CF}_3$ very unlikely. Thus, a mixture of two gauche conformers, gauche (sp-sp) and gauche (ap-sp), is expected to be observed in the experiments. All quantum chemical calculations were performed with the Gaussian 03 program

TABLE 1: Calculated Relative Energies, Free Energies (kcal/mol),^a and Vibrational Frequencies of $\text{C}=\text{O}$ Stretches (cm^{-1}) for $\text{FC}(\text{O})\text{SO}(\text{O})\text{CF}_3$

	B3LYP	ΔE	ΔG^{ob}	$\nu(\text{FC}=\text{O})$	$\nu(\text{CF}_3\text{C}=\text{O})$	MP2	ΔE	ΔG^{ob}	$\nu(\text{FC}=\text{O})$	$\nu(\text{CF}_3\text{C}=\text{O})$
gauche (sp-sp) ^c	6-31G*	0.00	0.00	1929	1897	6-31G*	0.00	0.00	1908	1870
	aug-cc-pVTZ	0.00	0.00	1894	1868					
gauche (ap-sp)	6-31G*	0.81	0.81	1900	1884	6-31G*	1.33	1.23	1898	1871
	aug-cc-pVTZ	1.33	1.18	1870	1857					
trans (sp-sp)	6-31G*	1.45	0.87	1937	1861	6-31G*	3.19	2.12	1918	1843
	aug-cc-pVTZ	1.16	0.86	1900	1833					
trans (ap-sp)	6-31G*	2.23	1.57	1893	1862	6-31G*	4.49	3.71	1876	1842
gauche (sp-ap)	6-31G*	5.97	6.58	1927	1899	6-31G*	7.36	7.77	1906	1858
gauche (ap-ap)	6-31G*	6.72	7.28	1903	1894	6-31G*	8.48	8.89	1884	1856

^a 1 cal = 4.18 J. ^b Accounts for different multiplicities of gauche ($m = 2$) and trans ($m = 1$) structures. ^c Gauche or trans refers to the configuration around $\text{S}-\text{O}$ bond, first orientation (sp or ap) refers to $\text{FC}(\text{O})$ group, and second orientation refers to $\text{CF}_3\text{C}(\text{O})$ group (see Chart 1).

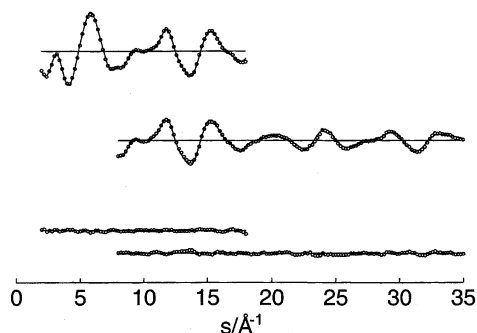


Figure 2. Experimental (dots) and calculated (full line) molecular intensities, and long (above) and short (below) nozzle-to-plate distances and residuals.

package.¹⁴ Vibrational amplitudes were derived from calculated (B3LYP/6-31G*) force fields via the method of Sipachev.¹⁵

Experimental Section

Synthesis. FC(O)SOC(O)CF₃ was prepared according to the literature procedure.¹⁶ The compound was isolated by repeated trap-to-trap condensation. The purity of FC(O)SOC(O)CF₃ was checked by IR and ¹⁹F NMR spectroscopy.

IR(matrix) spectra were recorded in the range 4000–400 cm^{−1} with a Bruker IFS66V spectrometer and with a resolution of 1 cm^{−1}. Mixtures of FC(O)SOC(O)CF₃ and Ar (1:1000) were deposited at 15 K on an aluminum-plated copper mirror in a He-cooled cryostat by the continuous deposition technique. Details of the matrix-isolation apparatus have been given elsewhere.¹⁷

Electron diffraction intensities were recorded with a Gasdiffraktograph KD-G2¹⁸ at two nozzle-to-plate distances (25 and 50 cm) and with an accelerating voltage of about 60 kV. The compound was kept at −7 °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 SCAN3.¹⁹ Experimental molecular intensities in the *s*-ranges 2–18 and 8–35 Å^{−1} in steps of $\Delta s = 0.2 \text{ Å}^{-1}$ ($s = (4\pi/\lambda) \sin \theta/2$, λ is the electron wavelength and θ is the scattering angle) are shown in Figure 2.

Matrix Isolation Infrared Spectroscopy

It is well known that the C=O stretching vibration in carbonyl groups is sensitive toward the orientation of this group relative to the rest of the molecule. The region of these stretching vibrations in the IR(matrix) spectrum of FC(O)S–OC(O)CF₃ is shown in Figure 3.

This spectrum was recorded with the compound/Ar mixture from 25 to 150 °C before deposition in the matrix. The presence of four major bands in this region demonstrates the presence of two conformers. Because the intensities of the two bands at 1818 and 1834 cm^{−1} increase, if the mixture is at higher temperature before deposition in the matrix, these two bands are assigned to the minor gauche (ap–sp) conformer and the other two bands at 1827 and 1850 cm^{−1} to the main gauche (sp–sp) form. From a van't Hoff plot, a ΔG° value of 0.3(7) kcal/mol might be calculated. However, the IR relative intensities used to estimate this value might be affected by byproducts formed in the decomposition of the title compound. Although a qualitative behavior is evident (Figure 3), this deduced value will no longer be used in the development of this work because of the lack of confidence.

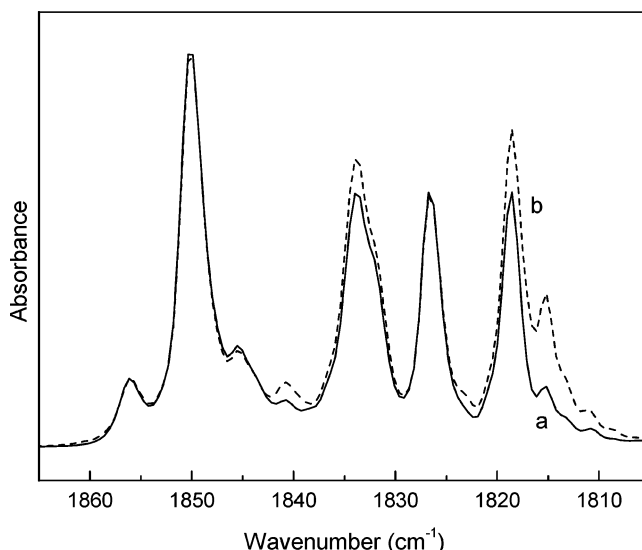


Figure 3. C=O stretching region of the IR(matrix) spectrum: (a) at 25 °C; (b) at 150 °C.

TABLE 2: Experimental and Calculated Geometric Parameters for the Gauche (sp–sp) Conformer of FC(O)S–OC(O)CF₃

	GED ^a		B3LYP/ 6-31G*	B3LYP/ aug-cc-pVTZ	MP2/ 6-31G*
S–O1	1.647(5)	p1	1.703	1.686	1.700
O1–C1	1.382(16)	p2	1.369	1.363	1.376
S–C3	1.771(6)	p3	1.779	1.772	1.763
C1–C2	1.524(10)	p4	1.548	1.556	1.535
C1=O2	1.188(3)	p5	1.193	1.185	1.203
C3=O3	1.179(3) ^b	p5	1.184	1.176	1.193
C2–F	1.326(3)	p6	1.338	1.336	1.341
C3–F4	1.335(3) ^b	p6	1.347	1.350	1.356
S–O1–C1	114.3(12)	p7	117.0	117.9	115.2
O1–S–C3	101.9(19)	p8	98.1	98.6	97.1
O1–C1=O2	130.0(22)	p9	127.2	127.3	127.4
O1–C1–C2	104.0(27)	p10	108.0	108.1	107.4
S–C3=O3	131.5(19)	p11	129.0	129.7	128.9
S–C3–F4	103.3(13)	p12	106.3	106.3	106.4
F–C2–F	108.0(6)	p13	109.0	109.1	108.9
ϕ (S–O1–C1=O2)	−2.2 ^c		−2.2	−2.6	−1.8
ϕ (O1–S–C3=O2)	−2.6 ^c		−2.6	−3.1	−2.3
ϕ (C3–S–O1–C2)	75.2(28)	p14	77.3	80.5	73.0

^a r_a values in angstroms and degrees. Error limits in parentheses are 3σ values and refer to the last digit. See Figure 5 for atom numbering.

^b Difference from the previous parameter fixed to calculated (B3LYP) value. ^c Not refined. Negative value implies shortening of the O2...O3 distance upon torsion around the O–C and S–C bonds.

This is the only assignment that is consistent with calculated differences between vibrational frequencies and with calculated relative free energies (see Table 1). For both conformers, the lower frequency vibration belongs to the CF₃C=O group and the higher frequency vibration to the FC=O group. As discussed above, the existence of a trans (sp–sp) form is very unlikely based on quantum chemical calculations. Such a conformer can now be excluded on the basis of the vibrational data. The experimental difference between the lowest (1818 cm^{−1}) and highest (1850 cm^{−1}) C=O stretching frequency is 32 cm^{−1}, much lower than the predicted splitting of 76 cm^{−1} (B3LYP/6-31G*), 67 cm^{−1} (B3LYP/aug-cc-pVTZ), or 75 cm^{−1} (MP2-6-31G*) for the trans (sp–sp) form. For the two gauche conformers, the calculated difference between lowest and highest C=O frequency is 45 cm^{−1} (B3LYP/6-31G*), 37 cm^{−1} (B3LYP/

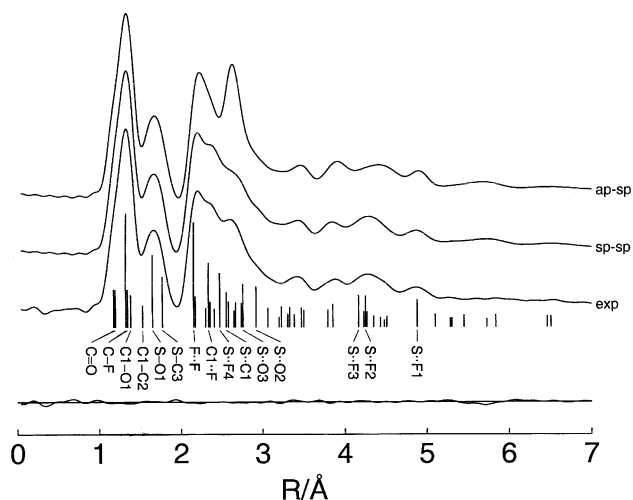


Figure 4. Experimental and calculated radial distribution functions for FC(O)S–OC(O)CF₃ with difference curve for mixture. Important interatomic distances are indicated by vertical bars.

aug-cc-pVTZ), and the same difference for the MP2/6-31G* level of approximation, in reasonable agreement with the observed value of 32 cm⁻¹. All other conformers listed in Table 1 are excluded on the basis of their calculated relative free energies.

Gas Electron Diffraction

The experimental radial distribution function (RDF) was derived by Fourier transformation of the molecular intensities applying an artificial damping function $\exp(-\gamma s^2)$ with $\gamma = 0.0019 \text{ Å}^2$. Figure 4 compares the experimental RDF with those calculated for gauche (sp–sp) and gauche (ap–sp) conformers. Both calculated curves differ strongly in the range $2.3 < r < 3.0 \text{ Å}$. This difference is due to changes in the S–C3=O3 and S–C3–F4 angles when the FC(O) group is rotated from sp to ap orientation (for atom numbering, see Figure 5). The S–C=O

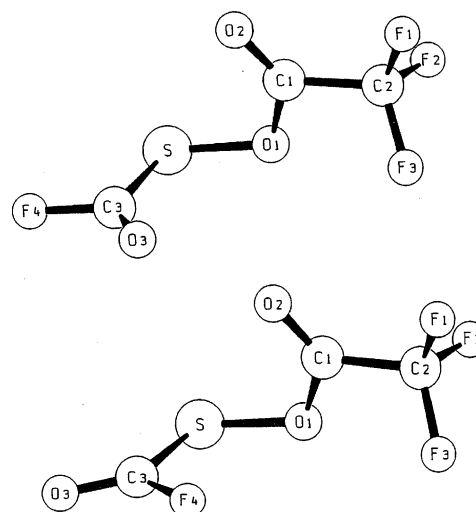


Figure 5. Molecular models for gauche (sp–sp) (above) and gauche (ap–sp) (below) conformers and atom numbering.

angle decreases by about 6°, and the S–C–F angle increases by about the same amount upon this rotation. This makes the S...O3 and S...F4 distances, which differ appreciably in the sp orientation (2.70 and 2.45 Å), almost equal (2.59 and 2.60 Å) in the ap orientation. The two very closely spaced distances produce the sharp peak at 2.60 Å in the RDF for the ap–sp conformer (see Figure 4). Comparison of the experimental RDF with calculated curves demonstrates that the (sp–sp) form is the prevailing conformer. The calculated RDF for the trans (sp–sp) form (not shown in Figure 4) differs appreciably from the experimental curve in the region $r > 3.5 \text{ Å}$, and any contribution >10% can be excluded on the basis of the GED data, in agreement with the assignment of the IR(matrix) spectrum (see above).

Geometric parameters of the gauche (sp–sp) conformer were refined by least-squares fitting of the molecular intensities. The

TABLE 3: Interatomic Distances, Experimental, and Calculated Vibrational Amplitudes for the Gauche (sp–sp) Conformer of FC(O)S–OC(O)CF₃^a

	dist.	amplitude GED		amplitude B3LYP		dist.	amplitude GED		amplitude B3LYP
C3=O2	1.18	0.036		0.036	O2...C3	3.30	0.246		0.246
C1=O1	1.19	0.036		0.036	O2...F3	3.33	0.216		0.216
C2–F	1.33	0.044(3)	11	0.044	C1...O3	3.38	0.218		0.218
C3–F4	1.34	0.044(3)		0.044	O1...F1	3.47	0.075		0.075
O1–C1	1.38	0.047		0.047	O2...O3	3.50	0.329		0.329
C1–C2	1.52	0.045(7)	12	0.050	O1...F4	3.79	0.077(14)	14	0.074
S–O1	1.65	0.047		0.047	S...C2	3.85	0.077(14)	14	0.067
S–C3	1.77	0.045(7)	12	0.050	S...F3	4.17	0.190(37)	17	0.188
F...F	2.16	0.061(6)	13	0.056	O3...F3	4.24	0.466		0.466
O3...F4	2.16	0.051		0.051	S...F2	4.26	0.190(37)	17	0.173
O1...C2	2.30	0.077(14)	14	0.066	O2...F4	4.26	0.267		0.267
C1...F	2.34	0.077(14)	14	0.070	C1...F4	4.35	0.148		0.148
O1...O2	2.34	0.051		0.051	C2...O3	4.43	0.285		0.285
C2...O2	2.40	0.068(26)	15	0.060	C2...C3	4.48	0.176		0.176
S...F4	2.47	0.077(14)	14	0.070	C3...F4	4.51	0.306		0.306
S...C1	2.55	0.068(26)	15	0.062	S...F1	4.88	0.106(25)	18	0.106
O1...F3	2.58	0.239		0.239	O3...F1	5.10	0.390		0.390
O1...C3	2.65	0.068(26)	15	0.063	C3...F2	5.29	0.234		0.234
O2...F1	2.67	0.081(22)	16	0.103	C3...F1	5.29	0.250		0.250
O1...F2	2.75	0.214		0.214	O3...F2	5.45	0.335		0.335
S...O3	2.75	0.068(26)	15	0.058	C2...F4	5.73	0.161		0.161
S...O2	2.92	0.081(22)	16	0.100	F3...F4	5.84	0.303		0.303
O1...O3	3.06	0.130		0.130	F2...F4	6.46	0.207		0.207
C1...C3	3.20	0.149		0.149	F1...F4	6.51	0.248		0.248
O2...F2	3.23	0.192		0.192					

^a Values in angstroms; error limits are 3σ values and refer to the last digit. For atom numbering, see Figure 5. Amplitudes without error limits have not been refined.

following assumptions were made on the basis of the quantum chemical calculations (B3LYP/6-31G*): (1) planarity of the fluoroformyl and trifluoroacetyl group; (2) C_{3v} symmetry for the CF₃ group with the C2–F1 bond eclipsing the C1=O2 bond; (3) the differences between the two C=O bonds and between the C–F bonds in the CF₃ and C(O)F groups were constrained to calculated values; (4) geometric parameters of the minor gauche (ap–sp) conformer were tied to those of the (sp–sp) form with the calculated differences; and (5) vibrational amplitudes were collected in groups, and amplitudes that caused large correlations or that were badly determined in the GED analysis were not refined. With these assumptions, 14 geometric parameters p1–p14 and eight vibrational amplitudes l1–l8 for the (sp–sp) conformer were refined simultaneously. The following correlation coefficients had absolute values larger than 0.7: $p_2/p_6 = -0.73$, $p_2/p_{13} = -0.73$, $p_6/p_{13} = 0.80$, and $p_2/l_1 = -0.85$. Least-squares analyses were performed for various contributions of the (ap–sp) form, and the lowest agreement factor R was obtained for 18(7)% (ap–sp) conformer ($\Delta G^\circ = 0.91(24)$ kcal/mol). The error limit was obtained from the tables of Hamilton for a 99.5% confidence limit.²⁰ The final geometric parameters are listed together with calculated values in Table 2, and vibrational amplitudes are given in Table 3.

Conclusions

The main interest in the present investigation was the conformational properties of FC(O)S–OC(O)CF₃. Although quantum chemical calculations do not provide unambiguous results concerning the number of stable conformers, they make the existence of conformers with trans orientation around the S–O bond very unlikely. This has been confirmed by the assignment of the IR(matrix) spectrum, which excludes the presence of such a trans conformer. According to the GED analysis, any possible contribution of this form is estimated to be less than 10%. In accordance with the assignment of the vibrational spectra, the GED intensities were fit with a mixture of gauche (sp–sp) and gauche (ap–sp) conformers. The ratio of 82(7)%:18(7)% measured at 298 K corresponds to $\Delta G^\circ = 0.91(24)$ kcal/mol, and this free energy difference is reproduced very well by quantum chemical calculations (0.81, 1.23, and 1.18 kcal/mol for B3LYP and MP2 using a 6-31G* basis set and B3LYP/aug-cc-pVTZ, respectively).

The existence of only two conformers with gauche orientation around the S–O bond is consistent with the conformational properties of all peroxides ROOR' and disulfides RSSR'. As pointed out in the Introduction, thioperoxides RSOR' also prefer gauche conformation with the exception of CF₃S–OC(O)CH₃ and CF₃S–OC(O)CF₃, where small contributions of trans conformers have been observed recently. In this context, it seems to be surprising that no such trans form is present in FC(O)S–OC(O)CF₃.

Two molecules would be worthy of further comparison with the title substance. Thus, whereas FC(O)OOC(O)CF₃ has not been prepared yet, FC(O)SSC(O)CF₃ was synthesized and analyzed by our group.²¹ In this previous work, results from both GED and X-ray have been reported. The forms of both FC(O)SOC(O)CF₃ and FC(O)SSC(O)CF₃ are very similar and are derived from the CSOC or CSSC torsion angles.

The comparison of the torsion angles between sulfenic esters, disulfides, and peroxides reveals that sulfenic esters are closer to disulfides than to peroxides from the structural point of view (CSOC = 75.2(28)°, this work; CSSC = 77.7(21)°;²¹ COOC = 83.5 (14)°²²). This property has been also discussed in our preceding work concerning the CF₃C(O)SOC(O)CF₃ molecule.¹³

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