Structures and Conformations of ((Trifluoroacetyl)imido)(trifluoromethyl)sulfur Fluoride, $CF_3C(O)N{=}S(F)CF_3$

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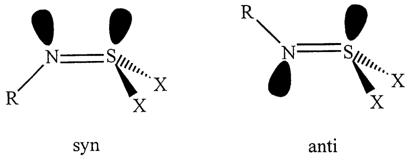
The molecular structure and conformational properties of ((trifluoroacetyl)imido)(trifluoromethyl)sulfur fluoride, $CF_3C(O)N{=}S(F)CF_3$, were determined by gas electron diffraction (GED) and vibrational spectroscopy (IR (gas) and Raman (liquid)). Furthermore, quantum chemical calculations (HF, MP2, and B3LYP with 6-31G* basis sets) were performed. The vibrational spectra were assigned by comparison with related molecules and calculated (HF and B3LYP) frequencies and intensities. According to the GED analysis the main conformer (90(6)%) possesses an anti−syn structure with anti orientation of the N−C bond relative to the F−S−CF_3 bisector and syn orientation of the C=O bond relative to the N=S bond. The second conformer (10(6)%) possesses a syn−syn structure. The experimental Gibbs free energy difference ($\Delta G^\circ = 1.3(4)$ kcal/mol) is reproduced correctly by the two quantum chemical methods (1.35 kcal/mol from MP2 and 1.04 kcal/mol from B3LYP). The conformational properties of this compound are in contrast to those of imidosulfurous difluorides, $RNSF_2$, and dichlorides, $RN{=}SCl_2$, for which only syn structures around the N=S double bond were observed.

Introduction

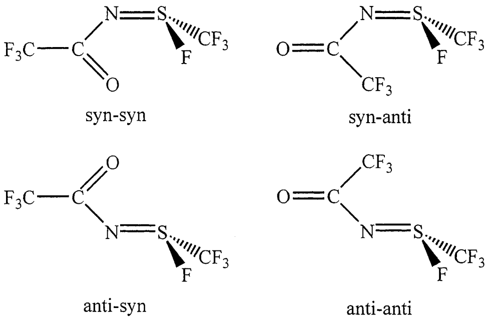
All imidosulfurous difluorides of the type $RN{=}SF_2$ with R = Cl,[1] CF_3,[2,3] NC,[4] FC(O),[5] $CF_3C(O)$,[6] and FSO_2 [7] as well as imidosulfurous dichlorides with R = CF_3 [8] and FC(O)[9] possess syn conformation around the N=S double bond (see Chart 1). Although the anti form appears to be sterically more favorable, quantum chemical calculations predict its energy to be higher by about 5−10 kcal/mol than that of the syn conformer. These predicted relative energies depend on the substituent R and on the computational method. Natural bond orbital (NBO) analyses reveal that the syn form is stabilized by orbital interactions (anomeric effects) between the lone pairs of nitrogen and sulfur with the antiperiplanar or anticlinal orbitals: lp(S) → σ*(N−R) and lp(N) → σ*(S−X). The only exception observed so far is $FC(O)N{=}S(F)CF_3$ (**1**).[10] For this compound the gas electron diffraction (GED) analysis resulted in a mixture of anti (79(12)%) and syn (21(12)%) conformers (ΔG°(syn − anti) = 0.79(36) kcal/mol), with relative syn orientation of the C=O and N=S bonds in both conformers. This result was reproduced qualitatively by quantum chemical calculations including electron correlation, which predict energy differences of 0.28 (B3LYP/6-31G*) and 0.64 (MP2/6-31G*) kcal/mol. The energy difference is overestimated by the HF/6-31G* method (2.41 kcal/mol). In the present study we report the determination of the geometric structure and conformational properties of $CF_3C(O)N{=}S(F)CF_3$ (**2**), using vibrational spectroscopy, GED, and quantum chemical calculations.

CHART 1



syn anti

CHART 2



syn-syn syn-anti anti-syn anti-anti

Quantum Chemical Calculations

Structure optimizations for **2** were performed for the four possible conformations shown in Chart 2, using HF and MP2 approximations and the B3LYP hybrid method with 6-31G* basis sets. The relative energies of the four conformers derived with the two latter methods are listed in Table 1. The relative

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TABLE 1: Calculated Relative Energies and Gibbs Free Energies (kcal/mol) for the Various Conformers of $CF_3C(O)N{=}S(F)CF_3$

	B3LYP/6-31G*		MP2/6-31G*	
	ΔE	$\Delta G°$	ΔE	$\Delta G°$
syn−syn	0.66	1.04	0.97	1.35
syn−anti	4.63	4.87	4.33	4.57
anti−syn	0.00	0.00	0.00	0.00
anti−anti	4.89	4.99	5.71	5.81

Gibbs free energies were calculated only with the B3LYP method. The correction between ΔE and $\Delta G°$ obtained with this method was applied also for the MP2 results. To ensure that the four conformations correspond to minima on the energy hypersurface, vibrational frequencies were calculated with the B3LYP/6-31G* method. No imaginary frequencies were observed. Both computational methods predict the same sequence in relative stability of the four conformers, anti−syn > syn−syn > syn−anti > anti−anti, with the two latter forms much higher in energy than the two former conformers. Vibrational amplitudes of the two low-energy forms anti−syn and syn−syn were calculated from unscaled theoretical force fields (B3LYP). All vibrational frequencies obtained with the HF method, except those for torsional vibrations, were scaled with a factor of 0.9. Quantum chemical calculations were performed with the GAUSSIAN 98 program suite,[11] and vibrational amplitudes were calculated with the program ASYM40.[12]

Vibrational Spectra

The observed wavenumbers, approximate descriptions of fundamental modes, and calculated wavenumbers are collected in Table 2. For this molecule $3N - 6 = 33$ normal modes of vibration are expected, but only 29 are observed in the spectra. The main conformer belongs to the C_1 class of symmetry. Observed bands in IR and Raman spectra were assigned to the normal modes by comparison with vibrational spectra of related molecules $FC(O)N{=}S(F)CF_3$,[13] $CF_3C(O)N{=}SF_2$,[6] $CF_3C(O)NCO$,[14] $FC(O)N{=}SF_2$,[15] $ClSO_2N{=}SF_2$,[16] $CF_3SO_2N_3$,[17] and CF_3SO_2NCO,[18] as well as with the evaluation of characteristic wavenumbers, and taking into account the normal coordinate analysis and quantum chemical calculations.

A characteristic and strong band centered at 1737 cm^{-1} in the IR spectrum of the vapor phase and at 1721 cm^{-1} in the Raman spectrum of the liquid can be assigned to the C=O fundamental mode. This band in the IR (gas) spectrum possesses a slight shoulder to higher wavenumbers. The B3LYP method predicts a splitting of the C=O vibration in the two low-energy forms of 17 cm^{-1} (1789 cm^{-1} in anti−syn and 1806 cm^{-1} in syn−syn) and similar intensities for both vibrations. The splitting is small since the orientations of the C=O bond relative to the N=S bond are equal in both conformers. The predicted C=O vibrations for the two high-energy conformers, syn−anti (1834 cm^{-1}) and anti−anti (1829 cm^{-1}), are shifted by 40 cm^{-1} or more. Thus, the observation of a shoulder to higher wavenumbers indicates the presence of a small amount of the syn−syn form, with the anti−syn conformer being the prevailing contribution. The IR (gas) spectra, however, do not provide a qualitative value for the conformational composition.

The band appearing at 1347 cm^{-1} in the IR spectra and at 1353 cm^{-1} in the Raman spectra can be assigned to the C−C stretching fundamental mode by comparison with the value found in $CF_3C(O)N{=}SF_2$.[6] Four deformations are expected for the CCO group: the rocking mode can be observed in the Raman spectrum at 202 cm^{-1}, while the other symmetric deformation was assigned to the band appearing in the Raman spectrum at 416 cm^{-1}. The feature corresponding to the out-of-plane deformation band was observed at 787 cm^{-1} in the Raman spectrum. On the basis of theoretical calculations, the torsion mode of this group is expected below 120 cm^{-1}, and it was not observed in our spectra.

TABLE 2: Assignments of Fundamental Modes and Experimental and Calculated Wave Numbers for $CF_3C(O)N{=}SFCF_3$

mode	approximate description[a]	IR	Raman	HF/6-31G* [b] (cm^{-1})	B3LYP/6-31G* (cm^{-1})
ν_1	C=O stretch	1737	1721	1803	1789
ν_2	C−C stretch	1347	1353	1395	1358
ν_3	CF_3 asym stretch		1306	1317	1300
ν_4	CF_3 asym stretch		1286	1289	1272
ν_5	CF_3 asym stretch	1258	1254	1287	1264
ν_6	CF_3 asym stretch	1237	1220	1241	1215
ν_7	CF_3 sym stretch	1186	1186	1198	1175
ν_8	CF_3 sym stretch	1123	1108	1150	1133
ν_9	N=S stretch		988	975	984
ν_{10}	C−N stretch	847	849	870	866
ν_{11}	CC(O) oop def		787	799	781
ν_{12}	CF_3 sym def	770	768	781	765
ν_{13}	CF_3 sym def	737	734	773	735
ν_{14}	SF stretch	715	714	725	714
ν_{15}	CF_3 asym def	592	590	581	584
ν_{16}	CF_3 asym def	563	563	556	552
ν_{17}	CF_3 asym def			542	544
ν_{18}	CF_3 asym def	524	525	514	516
ν_{19}	S−C stretch	472	472	482	464
ν_{20}	CSF wagging		444	443	436
ν_{21}	CC(O) def		416	409	405
ν_{22}	CSF twisting		349	354	341
ν_{23}	CF_3 asym def		311	320	310
ν_{24}	CF_3 asym def			311	303
ν_{25}	CF_3 asym def		249	243	235
ν_{26}	CF_3 asym def		228	222	211
ν_{27}	CC(O) rocking		202	195	189
ν_{28}	CSF def		176	170	163
ν_{29}	CNS def		115	105	101
ν_{30}	N=S torsion		82	63	65
ν_{31}	N−C torsion			62	59
ν_{32}	SCF_3 torsion			39	34
ν_{33}	CCF_3 torsion			17	22

[a] stretch = stretching; def = deformation; asym = asymmetric; sym = symmetric; oop = out-of-plane. [b] Scaled with 0.90.

The feature observed at 847 cm^{-1} in IR spectra and 849 cm^{-1} in Raman spectra was assigned to the C−N stretching fundamental mode, a position that can be compared with the same mode in $FC(O)N{=}S(F)CF_3$ [13] (854 cm^{-1}), $CF_3C(O)N{=}SF_2$ [6] (855 cm^{-1}), and $FC(O)N{=}SF_2$ [15] (859 cm^{-1}). The N=S stretching mode can be assigned to the band centered at 988 cm^{-1} in the Raman spectrum. The feature corresponding to CNS deformation can be observed in the Raman spectrum at 115 cm^{-1}.

By comparison with the observed behavior in $FC(O)N{=}SFCF_3$,[13] the CSF entity in $CF_3C(O)N{=}S(F)CF_3$ presents two stretching modes and three deformation modes: the S−F stretching at 715 and 714 cm^{-1} in IR and Raman spectra, respectively, and the S−C stretching fundamental mode at 472 cm^{-1} in both spectra. The CSF deformation can be related to the Raman band appearing at 176 cm^{-1}, while the wagging and the twisting can be assigned to the features appearing in the Raman spectra at 444 and 349 cm^{-1}, respectively.

A total of six C−F stretching vibrations, two asymmetric and one symmetric for each CF_3 group, are expected, all of them possessing high IR and weak Raman intensities. The asymmetric modes are assigned to the features centered at 1306, 1286, 1254, and 1220 cm^{-1} in the Raman spectrum, and the symmetric

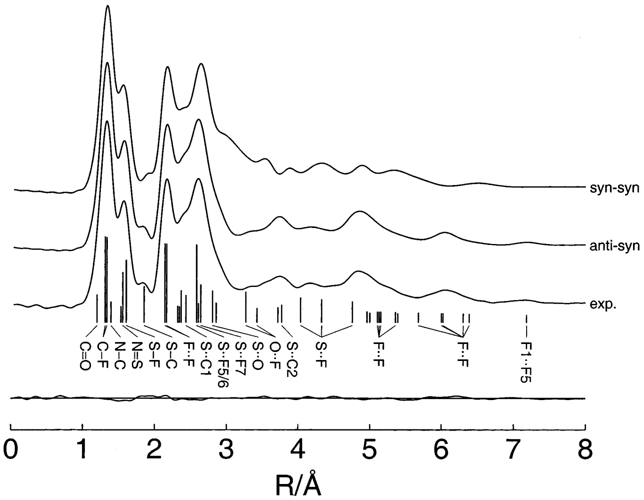


Figure 1. Calculated RDFs for syn−syn and anti−syn conformers along with the experimental RDF curve. The difference curve refers to a mixture of 90% anti−syn and 10% syn−syn. Important interatomic distances of the anti−syn conformer are indicated by vertical bars. A full list of all distances is given in Table 4.

modes were assigned to the bands that appear at 1186 and 1123 cm^{-1} in the IR spectrum and to the peaks observed at 1186 and 1108 cm^{-1} in the Raman spectrum. The two CF_3 groups possess 10 deformations (two symmetric and eight asymmetric) and two torsions. The symmetric deformation modes are assigned to the bands appearing at 770 and 737 cm^{-1} in the IR spectrum (768 and 734 cm^{-1} in the Raman spectrum), and the asymmetric deformation fundamental modes to the IR bands at 592, 563, and 524 cm^{-1} and the Raman peaks at 311, 249, and 228 cm^{-1}. The remaining two could not be observed in our spectrum, but according to the calculations are expected to appear at 542 and 311 cm^{-1}. The two torsion fundamental modes could not be observed in the spectra, but they are expected to appear below 40 cm^{-1}. This assignment was made by comparison with the reported values for $FC(O)N{=}SFCF_3$,[13] $CF_3C(O)N{=}SF_2$,[6] and $CF_3C(O)NCO$.[14] A signal appearing at 82 cm^{-1} in the Raman spectrum was assigned to the S=N skeletal torsion.

Structure Analysis

The experimental radial distribution function (RDF) was calculated by Fourier transformation of the molecular intensities. This curve (see Figure 1) can be fitted satisfactorily only with an anti−syn structure. The fit is improved slightly if a small amount of the syn−syn conformer is added. The calculated RDFs for these two conformers are shown in Figure 1. A preliminary molecular model, which was derived from the experimental RDF, was refined by least-squares fitting of the molecular intensities. The following assumptions, which are based on MP2 results for geometric parameters and on B3LYP results for vibrational amplitudes, were made in the least-squares analysis: (1) Both CF_3 groups were constrained to C_{3v} symmetry, and the differences between the C−F bond lengths and F−C−F angles in both groups were fixed to the calculated values. One C−F bond of the C-bonded CF_3 group was assumed to eclipse the C=O bond, and the calculated torsional angle of the S-bonded CF_3 group ($\phi(N{=}S{-}C{-}F_5)$) was used. Furthermore, the tilt angle between the C_3 axis of the CF_3 group and the S−C bond direction was set to the calculated result. This tilt occurs away from the S−F bond. No tilt angle was introduced for the C-bonded CF_3 group in accordance with the quantum chemical calculations (tilt 0.4° (MP2) and 0.1° (B3LYP)). (2) The N−C bond length, which could not be refined due to high correlations with other bond distances, was set to 1.392 Å. This value was chosen on the basis of the experimental bond length in FC(O)N=S(F)CF3 (1.391(8) Å) and the calculated values in both compounds (1.402 and 1.401 Å, respectively). (3) The bond angles N−C−C and N=S−F were fixed to the MP2 values. (4) The calculated torsional angle of the trifluoroacetyl group around the N−C bond ($\phi(S{=}N{-}C{-}C)$) was used in the refinement. (5) Vibrational amplitudes, which either caused large correlations with geometric parameters or were badly determined in the GED experiment, were set to the calculated amplitudes (B3LYP). (6) Bond lengths and bond angles of the minor syn−syn conformer were tied to those of the prevailing anti−syn form, using the calculated differences. Dihedral angles were set to calculated values. Calculated amplitudes were used for this conformer. With these assumptions 12 geometric parameters (p1 to p12) and 11 vibrational amplitudes (l1 to l11) were refined simultaneously. The following correlation coefficients had values larger than |0.6|: p2/p9 = 0.68, p3/p4 = −0.60, p4/p5 = −0.61, p10/p11 = −0.65, p10/p12 = 0.69, p11/p12 = −0.92, p12/l6 = 0.70. Possible systematic errors for refined parameters due to constraints for geometric parameters were estimated by additional least-squares refinements, in which the fixed N−C bond was varied by ±0.005 Å, fixed bond angles were varied by ±2°, and dihedral angles were varied by ±4°. Changes in refined paramters were smaller than their error limits (3σ values).

TABLE 3: Experimental and Calculated Geometric Parameters for the Anti−Syn Conformer of $CF_3C(O)N{=}S(F)CF_3$ [a]

	GED[b]		MP2/ 6-31G*[c]	B3LYP/ 6-31G*[c]
C=O	1.200(8)	p1	1.223	1.214
(C−F)$_{mean}$	1.323(3)	p2	1.339	1.335
ΔCF = (C2−F) − (C3−F)	0.011[d]		0.011	0.014
C2−F	1.329(3)		1.344	1.342
C3−F	1.318(3)		1.333	1.328
C−C	1.533(10)	p3	1.534	1.548
N−C	1.392[e,d]		1.402	1.393
N=S	1.554(8)	p4	1.569	1.577
S−F	1.604(6)	p5	1.662	1.659
S−C	1.853(7)	p6	1.842	1.874
C−N=S	111.2(11)	p7	111.0	112.4
N−C=O	129.6(13)	p8	127.5	127.5
N−C−C	110.6[d]		110.6	111.1
F−C2−F	108.4(2)	p9	108.7	108.7
F−C3−F	109.7(2)[f]		109.7	109.0
tilt (C3F$_3$)[g]	2.5[d]		2.5	2.9
N=S−F	112.6[b]		112.6	111.7
N=S−C	98.2(19)	p10	97.1	97.5
F−S−C	94.8(20)		90.8	92.0
ϕ(C−N=S−C)	−163.5(44)	p11	−168.6	−168.6
ϕ(C−N=S−F)	97.8(38)	p12	97.5	96.2
ϕ(S=N−C−C)	−19.8[d]		−19.8	−16.6
ϕ(N=S−C−F5)	186.5[d]		186.5	189.2
$\Delta G°$ (kcal/mol)	1.32(37)		1.35	1.04
% anti−syn	90(6)		90	85

[a] Distances in angstroms; angles in degrees. For atom numbering, see Figure 2. [b] r_a values. Parameters p1−p12 were refined in the least-squares analysis; error limits are 3σ values. [c] Mean values are given for the parameters, which are not unique. [d] Not refined. [e] The value was chosen by comparison with the corresponding value in FC(O)N=S(F)CF$_3$ (see the text). [f] The difference between the C−C−F and the S−C−F angles was fixed to the calculated value (MP2). [g] Tilt angle between the C_3 axis and the S−C bond, away from the S−F bond.

Least-squares analyses with different but fixed contributions of the minor conformer were performed. The quality of the fit was measured by the agreement factor for the intensities of the long nozzle-to-plate distance (R_{50}). The minimum (R_{50} = 5.1%

TABLE 4: Experimental and Calculated Vibrational Amplitudes of the Anti−Syn Conformer of $CF_3C(O)N{=}S(F)CF_3$ [a]

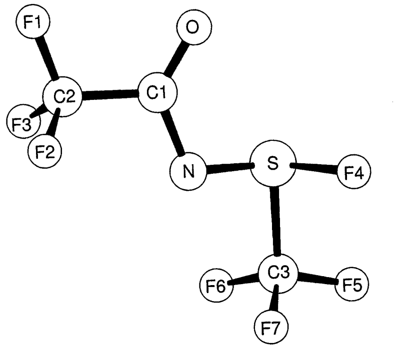
		amplitude		
	dist, Å	GED[b]		B3LYP[c]
C=O	1.20	0.037		0.037
C−F	1.32−1.33	0.045(2)	l1	0.045
N−C	1.39	0.049		0.049
C−C	1.53	0.053(9)	l2	0.052
N=S	1.55	0.045(2)	l1	0.044
S−F	1.60	0.048		0.048
S−C	1.85	0.053(9)	l2	0.056
F···F	2.16	0.059		0.059
N···O	2.35	0.055		0.055
C1···F1	2.35	0.066		0.066
C1···F2/3	2.35	0.075(5)	l3	0.076
C2···O	2.37	0.063		0.063
N···C2	2.41	0.069		0.069
S···C1	2.43	0.070		0.070
C3···F4	2.55	0.096		0.096
N···C3	2.58	0.084		0.084
S···F	2.58−2.64	0.075(5)	l3	0.076
O···F1	2.60	0.097(33)	l4	0.105
N···F4	2.63	0.087		0.087
N···F3	2.79	0.142(23)	l5	0.197
N···F2	2.79	0.224		0.224
S···O	2.80	0.097(33)	l4	0.121
F4···F5	2.81	0.142(23)	l5	0.186
N···F6/7	2.86−2.93	0.142(23)	l5	0.179
F4···F7	2.87	0.241		0.241
O···F	3.27−3.51	0.137(51)	l6	0.206
C1···F4	3.40	0.128		0.128
N···F1/5	3.56−3.73	0.096(14)	l7	0.072
F4···F6	3.72	0.096(14)	l7	0.082
S···C2	3.78	0.096(14)	l7	0.075
C1···C3	3.87	0.096(14)	l7	0.085
S···F2/3	4.07−4.32	0.156(31)	l8	0.167
C1···F6/7	4.10−4.25	0.156(31)	l8	0.174
F···F	4.38−5.22	0.457		0.457
O···C3	4.54	0.096(29)	l9	0.114
S···F1	4.76	0.096(29)	l9	0.101
C3···F3	4.80	0.273		0.273
C2···F6	4.80	0.278		0.278
C2···F4	4.81	0.137		0.137
C2···C3	4.87	0.124		0.124
O···F	4.89−5.37	0.158		0.158
C1···F5	4.92	0.085		0.085
C2···F7	5.06	0.158(49)	l10	0.249
F···F	5.08−6.01	0.158(49)	l10	0.249
C3···F2	5.17	0.349		0.349
F···F	5.38−5.71	0.171		0.171
F···F	6.00−6.42	0.293		0.293
C2···F5	6.06	0.096(29)	l9	0.106
C3···F1	6.06	0.150(79)	l11	0.127
F1···F7	6.33	0.226		0.226
F1···F5	7.18	0.150(79)	l11	0.119

[a] Values in angstroms; error limits in parentheses are 3σ values. For atom numbering, see Figure 2. [b] Amplitudes l1−l11 were refined in the least-squares analysis. Amplitudes with the same number were refined in a group. [c] Mean values are used for amplitudes, which are not unique.

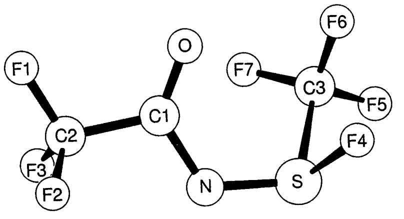
and R_{25} = 8.0%) occurred for a contribution of 10(6)%. The error limit was obtained by the Hamilton test on a 1% significance level.[19] The final results are summarized in Tables 3 (geometric parameters) and 4 (vibrational amplitudes), and molecular models are shown in Figure 2.

Discussion

In contrast to imidosulfurous difluorides and dichlorides, for which only the syn conformation around the N=S bond is observed, compounds with mixed substitution at sulfur, **1** and **2**, favor the anti conformation. Both compounds exist in the gas phase as a mixture of anti−syn and syn−syn forms. The contribution of the higher energy syn−syn conformer is larger in **1** (21(12)%) than in **2** (10(6)%), although this difference is smaller than the experimental uncertainties. This trend in the experimental conformational compositions is confirmed by the quantum chemical calculations, which predict a slightly larger energy difference for **2**, 0.66 kcal/mol (B3LYP) and 0.97 kcal/mol (MP2) vs 0.28 kcal/mol (B3LYP) and 0.64 kcal/mol (MP2) for **1**. The Gibbs free energy difference $\Delta G°$ derived from the GED experiment (1.3(4) kcal/mol) is reproduced correctly by both computational methods, which predict 1.35 kcal/mol (MP2) and 1.04 kcal/mol (B3LYP). Since substitution of one fluorine atom at sulfur by one CF_3 group leads to a slight preference of the anti conformation around the N=S bond, it is expected that this anti form is even more stabilized in imidosulfurous compounds with two CF_3 groups bonded to sulfur. No experimental structures for such $RN{=}S(CF_3)_2$ compounds have been reported so far. Therefore, quantum chemical calculations (B3LYP/6-31G*) were performed for $FC(O)N{=}S(CF_3)_2$ and $CF_3C(O)N{=}S(CF_3)_2$. Surprisingly, the calculations predict for these compounds a preference of the syn form with the anti conformer higher in energy by 1.0 and 0.4 kcal/mol, respectively.



anti-syn



syn-syn

Figure 2. Molecular models with atom numbering for anti−syn and syn−syn conformers.

Figure 2 shows the structures of the two conformers. In the prevailing anti−syn form the S−C bond is orientated antiperiplanar and the S−F bond nearly perpendicular with respect to the N−C bond (ϕ(C−N=S−C) = −164(5)° and ϕ(C−N=S−F) = 98(4)°). The N=S bond in **1** and **2** (1.549(5) and 1.554(8) Å, respectively) is much longer than that in imidosulfurous difluorides (1.48 ± 0.01 Å)[1−7] and in dichlorides (1.515 ± 0.005 Å).[8,9] The lengthening of this bond can be attributed partially to the lower electronegativity of the substituents and partially to the absence of anomeric interactions in the anti−syn conformer. The calculations (Table 5) predict this bond to be only about 0.02 Å longer in the anti form than that in the syn form. However, strong steric repulsions in the syn form oppose the shortening due to anomeric interactions. This steric repulsion is evident from the C−N=S and N=S−C angles, which are about 10° larger in the syn form (120.6° and

TABLE 5: Calculated (MP2/6-31G*) Skeletal Geometric Parameters of Anti−Syn and Syn−Syn Conformers of $CF_3C(O)N{=}S(F)CF_3$ [a]

	anti−syn	syn−syn		anti−syn	syn−syn
N═S	1.569	1.551	C−N═S	111.0	120.6
N−C	1.402	1.404	N═S−F	112.6	113.9
S−F	1.662	1.658	N═S−C	97.1	108.8
S−C	1.842	1.892	F−S−C	90.8	90.9
			C−N═S−F	97.5	58.6
			C−N═S−C	−168.6	−41.1

[a] Distances in angstroms, angles in degrees.

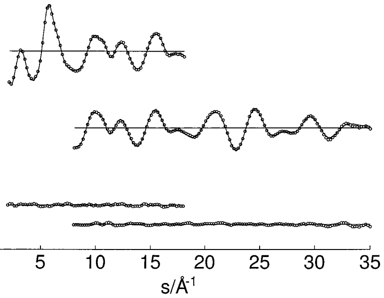


Figure 3. Averaged molecular intensities for long (top) and short (bottom) nozzle-to-plate distances and residuals.

108.8°) than in the anti form (111.0° and 97.1°). A large structural difference between syn and anti conformers is also predicted for the S−C bond length, which is about 0.05 Å longer in the syn form than in the anti form.

If we neglect systematic differences between experimental r_a values and calculated equilibrium r_e values for geometric parameters, both computational methods reproduce experimental bond distances to within ±0.02 Å, except for the S−F bond. The calculated values are too long by about 0.06 Å. A similar failure of these quantum chemical methods has been observed also for $CF_3N{=}SF_2$ [3] and $FC(O)N{=}SF_2$.[5] Bond angles are reproduced to within ±2° or better.

Experimental Section

$CF_3C(O)N{=}SFCF_3$ was obtained by reaction between $CF_3C(O)NH_2$ and CF_3SF_3, in the presence of NaF.[20] The product was purified at reduced pressure by several trap-to-trap distillations. $CF_3C(O)N{=}SFCF_3$ reacted with the humidity of the air and had to be handled in a vacuum line and dry bag.

The gas IR spectrum at 5 Torr was recorded between 4000 and 400 cm^{-1} (resolution 2 cm^{-1}) with an FT IR Perkin-Elmer Paragon 500 spectrometer, using a gas cell equipped with KBr windows. Raman spectra of the liquid between 3500 and 50 cm^{-1} were obtained using a Jobin Yvon V1000 spectrometer equipped with both argon and krypton ion lasers (Spectra-Physics model 165), and radiation of 514.5 nm (Ar^+) was used for excitation. The sample was kept at −5 °C to avoid decomposition and handled in Pyrex capillaries.

The GED intensities were recorded with a KD-G2 Gas Diffraktograph[21] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. The sample and gas nozzle were at room temperature. The photographic plates were analyzed with the usual methods,[22] and averaged molecular intensities in the s-ranges 2−18 and 8−35 $Å^{-1}$ ($s = (4\pi/\lambda)(\sin \theta/2)$, λ = electron wavelength, θ = scattering angle) are shown in Figure 3.

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