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((Fluoroformyl)imido)(trifluoromethyl)sulfur Fluoride, $FC(O)N{=}S(F)CF_3$: Unexpected Conformational Properties

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The geometric structure and conformational properties of ((fluoroformyl)imido)(trifluoromethyl)sulfur fluoride, $FC(O)N{=}S(F)CF_3$, are investigated by gas electron diffraction (GED) experiments, IR (gas) spectroscopy, and quantum chemical calculations (HF, MP2, and B3LYP with 6-31G* basis sets). The GED intensities are reproduced best with a mixture of 79(12)% trans-syn and 21(12)% cis-syn conformers. "Trans/cis" describes the orientation around the S═N double bond (FC(O) group relative to sulfur substituents), and "syn" refers to the orientation of the C═O bond relative to the S═N bond. From the intensities of the C═O bands in the IR (gas) spectrum, a composition of 86(8)%:14(8)% is derived. These ratios correspond to $\Delta G°(\mathrm{GED}) = 0.79(36)$ and $\Delta G°(\mathrm{IR}) = 1.09(35)$ kcal mol^{-1}. The preference of a trans structure around the S═N double bond is unexpected, since all imidosulfur compounds studied thus far possess a cis configuration. The conformational properties are reproduced qualitatively correctly by all theoretical calculations. The predicted energy differences $\Delta E(\mathrm{HF}) = 2.41$, $\Delta E(\mathrm{MP2}) = 0.64$, and $\Delta E(\mathrm{B3LYP}) = 0.28$ kcal mol^{-1} are larger or slightly smaller than the experimental values. Additional theoretical calculations (B3LYP) for several imidosulfur compounds reveal that only $FC(O)N{=}S(F)CF_3$, with mixed substitution at sulfur and the FC(O) group bonded to nitrogen, prefers the trans structure.

Introduction

All imidosulfur difluorides of the type $RN{=}SF_2$, with R = Cl,[1] CF_3,[2,3] SF_5,[4] CN,[5] FC(O),[6] and FSO_2,[7] whose gas-phase structures are known possess a cis configuration around the N═S double bond with the substituent R and the SF_2 group cis to each other. This also implies a cis orientation of the nitrogen and sulfur lone pairs (Chart 1). Similarly, $CF_3N{=}SCl_2$[8] and $ClN{=}S(CF_3)_2$[9] adopt a cis configuration. No trans stuctures have been observed for such compounds in gas electron diffraction (GED) experiments. In the case of $CF_3N{=}SF_2$, quantum chemical calculations have been performed also for the trans configuration. The B3LYP/6-31G* method results in a stable structure 5.6 kcal mol^{-1} higher in energy than the cis form, and the MP2/6-31G* method predicts an imaginary frequency for this structure, indicating that this is a transition state. In ((fluoroformyl)imido)sulfur difluoride, $FC(O)N{=}SF_2$, two conformations are possible with the C═O bond syn or anti to the S═N bond. Only the syn form was observed in the GED experiment, and from vibrational spectra, the contribution of the anti conformer was estimated to be <3%. HF/6-31G* calculations predict the anti form to be higher in energy by 1.9 kcal mol^{-1}. $FC(O)N{=}S(F)CF_3$, initially synthesized by Duncan, was characterized by IR (gas) and ^{19}F NMR spectroscopy.[10] Two bands at 1855 and 1800 cm^{-1} were observed in the C═O stretching region. The weaker one at 1855 cm^{-1} was assigned to an impurity ($FC(O)N{=}SF_2$). On the other hand, no impurity was observed in the NMR spectra. In the present paper, we report a structural and conformational study of $FC(O)N{=}S(F)CF_3$ using a GED analysis, vibrational data, and quantum chemical calculations.

Chart 1

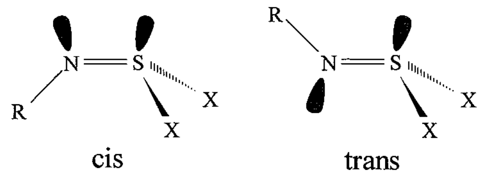

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Chart 2

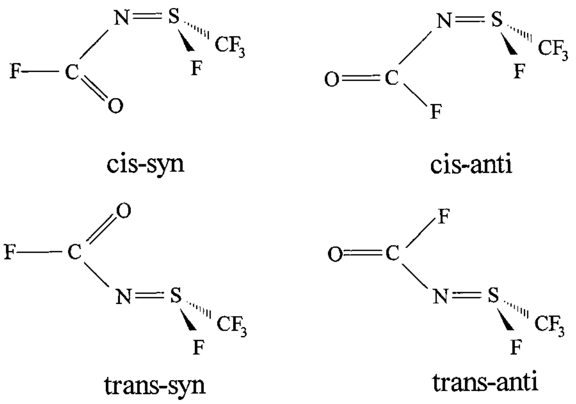

Table 1. Calculated Energies (kcal mol^{-1}) for the Various Conformers of FC(O)N=S(F)CF$_3$ Relative to the Trans-Syn Form

	HF/6-31G*	MP2/6-31G*	B3LYP/6-31G*
trans-syn	0.00	0.00	0.00
trans-anti	3.67	1.47	1.20
cis-syn	2.41	0.64	0.28
cis-anti	5.82	1.83	1.50

Table 2. Experimental and Calculated Geometrie Parameters for the Trans-Syn Conformer of FC(O)N=S(F)CF$_3$[a]

	GED[b]		MP2/ 6-31G*[c]	B3LYP/ 6-31G*[c]
N=S	1.549(5)	p_1	1.563	1.573
N−C1	1.391(8)	p_2	1.401	1.395
S−F2	1.599(4)	p_3	1.658	1.660
S−C2	1.852(6)	p_4	1.838	1.874
C=O	1.186(5)	p_5	1.206	1.202
mean C−F	1.323(1)	p_6	1.336	1.333
ΔCF = (C1−F) − (C2−F)	0.010[d]		0.010	0.010
C1−F	1.331(1)		1.341	1.338
C2−F	1.321(1)		1.331	1.328
S=N−C1	112.4(11)	p_7	111.1	111.9
N=S−F2	108.8(33)	p_8	112.0	111.4
N=S−C2	97.4(12)	p_9	97.0	97.5
F−C2−F	109.7(4)	p_{10}	109.9	110.1
tilt (CF$_3$)[e]	2.8[d]		2.5	2.8
F2−S−C2	90.3(14)	p_{11}	90.8	91.8
N−C1=O	129.9(12)	p_{12}	129.6	129.6
N−C1−F1	108.2(12)	p_{13}	108.3	108.6
Φ(C1−N=S−C2)	158(8)	p_{14}	167.8	168.3
Φ(C1−N=S−F2)	−110(9)		−98.5	−96.7
Φ(S=N−C1−F1)	166[d]		163.9	166.3
Φ(N=S−C2−F3)	169(5)	p_{15}	173.1	172.1
GED % trans-syn	79(12)		74[f]	61[f]
% trans-syn (IR)	86(8)			

[a] Distances in angstroms; angles in degrees. For atom numbering, see Figure 2. [b] r_a values. Parameters p_1−p_{15} were refined in the least-squares analysis. [c] Mean values are given for parameters which are not unique. [d] Not refined. [e] Tilt angle between the C_3 axis and the S−C bond, away from the N=S bond. [f] Estimated from calculated relative energies.

Quantum Chemical Calculations

The structures of the four possible conformations of FC(O)N=S(F)CF$_3$ (Chart 2) were optimized using ab initio (HF/6-31G* and MP2/6-31G*) and densitiy functional theory (B3LYP/6-31G*) methods. All four conformers correspond to stable structures. Calculated relative energies obtained with the three methods are given in Table 1, and geometric parameters of the most stable trans-syn form are listed in Table 2. The vibrational frequencies were calculated with the B3LYP method, and no conformer was found to possess an imaginary frequency. These calculations were performed with the Gaussian 98[11] program. Vibrational amplitudes were derived from calculated force constants with the program ASYM40.[12] Furthermore, the conformational properties of other imidosulfur compounds with R = CF$_3$ or FC(O) and with fluorines and/or CF$_3$ groups bonded to sulfur were calculated with the B3LYP/6-31G* method. The results are given in the Discussion.

GED Analysis

The experimental radial distribution function (RDF) was derived by Fourier transformation of the molecular intensities, applying the artificial damping function $\exp(-\gamma s^2)$ with $\gamma = 0.0019$ Å^2. Comparison of calculated RDF's for the four possible conformers with the experimental curve (Figure 1) demonstrated that the trans-syn conformer is the prevailing component. Only this conformer reproduces the experimental RDF reasonably well. The remaining differences can be accounted for by a small contribution of the cis-syn form. In the least-squares fitting of the experimental intensities, a diagonal weight matrix was applied to the intensities. Planarity was assumed for the FC(O) group and C_{3v} symmetry for the CF$_3$ group. The tilt angle between the C_3 axis of the CF$_3$ group and the S−C bond direction and the torsional angle of the FC(O) group around the N−C bond, Φ(S=N−C1−F1), were set to the B3LYP values. Vibrational amplitudes which caused high correlations or which were badly determined in the GED experiment were set to the calculated values (B3LYP). The fit of the molecular intensities improved considerably if about 20% cis-syn conformer was added. The calculated RDF for this form is shown in Figure 1. The differences between corresponding bond lengths and angles of the minor cis-syn conformer and the trans-syn structure were kept constant at theoretical (B3LYP) values. The dihedral angles Φ(C1−N=S−C2), Φ(S=N−C1−F1), and Φ(N=S−C1−F3) and vibrational amplitudes of the cis-syn form were constrained to calculated values. Least-squares refinements in which trans-anti or cis-anti conformers were mixed with the prevailing trans-syn form did not lead to satisfactory fits of the molecular intensities. With the above assumptions and constraints, 15 geometric parameters and 7 vibrational amplitudes for the prevailing trans-syn conformer were refined simultaneously. Only one correlation coefficient had a value larger than $|0.7|$: $p_7/p_{12} = -0.72$. Least-squares analyses were performed with several fixed contributions of the cis-syn form, and the quality of the fit was measured by the agreement factors for the long (R_{50}) and short (R_{25}) nozzle-to-plate distances. The best fit was obtained for a mixture of 79(12)% trans-syn and 21(12)% cis-syn conformers ($R_{50} = 0.031$, $R_{25} = 0.103$). The error limit for the contributions was derived with Hamilton's test[13] on a 1% significance level. This composition corresponds to $\Delta G° = \Delta G°(\text{cis-syn}) - \Delta G°(\text{trans-syn}) = 0.79(36)$ kcal mol^{-1}. The results of the GED analysis are given in Table 2 (geometric

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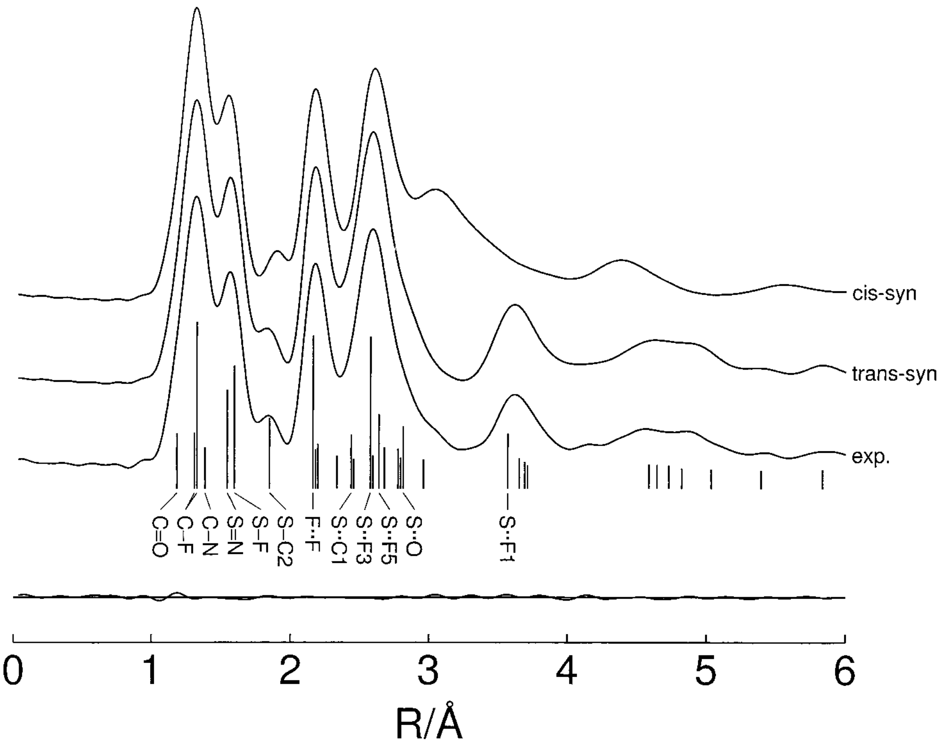

Figure 1. Calculated RDF's for cis-syn and trans-syn conformers along with the experimental RDF curve. The difference curve refers to a mixture of 79% trans-syn and 21% cis-syn. Interatomic distances of the trans-syn conformer are indicated by vertical bars.

Table 3. Experimental and Calculated Vibrational Amplitudes of the Trans-Syn Conformer of $FC(O)N{=}S(F)CF_3$[a]

		amplitude					amplitude		
	dist, Å	GED[b]		B3LYP		dist, Å	GED		B3LYP
C1=O	1.19	0.034		0.034	N···F5	2.79	0.206(48)	l_4	0.174
C−F	1.32−1.33	0.046		0.046	N···F4	2.96	0.206(48)	l_4	0.186
C1−N	1.39	0.049		0.049	C1···F2	3.47	0.082(13)	l_3	0.128
S=N	1.55	0.044		0.044	S···F1	3.60	0.065		0.065
S−F	1.60	0.049		0.049	F2···F4	3.65	0.085		0.085
C2−S	1.85	0.057		0.057	N···F3	3.71	0.078		0.078
F···F	2.16	0.061(3)	l_1	0.059	O···F2	3.73	0.221		0.221
N···F1	2.19	0.061(3)	l_1	0.061	C1···C2	3.85	0.085		0.085
F1···O	2.21	0.061(3)	l_1	0.054	C1···F4	4.08	0.177		0.177
N···O	2.34	0.061(3)	l_1	0.056	C1···F5	4.18	0.170		0.170
C1···S	2.45	0.069		0.069	C2···O	4.49	0.167(31)	l_5	0.113
C2···F2	2.46	0.099		0.099	F1···F2	4.56	0.167(31)	l_5	0.135
C2···N	2.56	0.085		0.085	F1···C2	4.66	0.167(31)	l_5	0.113
S···F3	2.58	0.072(4)	l_2	0.078	F1···F4	4.73	0.254		0.254
S···F4	2.58	0.072(4)	l_2	0.080	F1···F5	4.74	0.241		0.241
F2···N	2.59	0.089		0.089	O···F4	4.77	0.184		0.184
S···F5	2.64	0.072(4)	l_2	0.074	C1···F3	4.91	0.103(28)	l_6	0.086
F2···F3	2.67	0.189		0.189	O···F5	5.03	0.124(41)	l_7	0.151
F2···F5	2.79	0.206(48)	l_4	0.243	O···F3	5.37	0.124(41)	l_7	0.144
S···O	2.80	0.082(13)	l_3	0.118	F1···F3	5.87	0.103(28)	l_6	0.095

[a] For atom numbering, see Figure 2. [b] Amplitudes l_1−l_7 were refined in the least-squares analysis. Amplitudes with the same number were refined in a group.

parameters) and Table 3 (vibrational amplitudes). Molecular models for both conformers are shown in Figure 2.

Vibrational Spectra

The vibrational spectra of $FC(O)N{=}S(F)CF_3$ are described in detail in ref 14. In the present investigation, only the region of the C=O vibration that is most characteristic for the conformational properties is considered. In both the Raman spectrum of the liquid and the IR spectrum of gas, two bands are observed in this region. In the IR (gas) spectrum, a strong band occurs at 1796 cm^{-1} and a weak band at 1864 cm^{-1}. The corresponding vibrational frequencies calculated with the B3LYP method for the trans-syn and cis-syn conformers are 1843 and 1862 cm^{-1}. From the relative intensities of the two bands in the IR (gas) spectrum and from the calculated ratio of the transition moments, $\mu_{\mathrm{trans-syn}}^2/\mu_{\mathrm{cis-syn}}^2 = 1.13$, a composition of 86(8)%:14(8)% is derived. The error limit is estimated from uncertainties in the measured intensity ratio and from uncertainties in the calculated transition moments. This composition corresponds to $\Delta G° = 1.09(35)$ kcal mol^{-1}, in agreement with the GED result.

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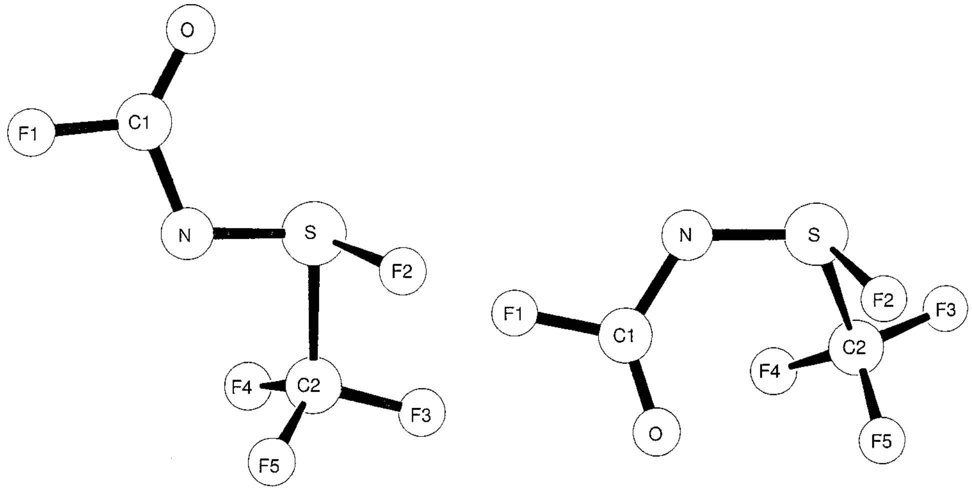

Figure 2. Molecular models with atom labeling for trans-syn (left) and cis-syn (right) conformers.

Discussion

The GED analysis for FC(O)N═S(F)CF_3 results in a mixture of trans-syn and cis-syn conformers. The presence of a mixture of conformers in the gas phase is also confirmed by IR (gas) spectra. All three computational methods predict the trans-syn conformer to be lower in energy (see Table 1). The energy difference $\Delta E = E(\text{cis-syn}) - E(\text{trans-syn})$ predicted by the HF approximation (2.41 kcal mol^{-1}) is larger than the experimental $\Delta G°$ values, and the MP2 and B3LYP methods result in energy differences (0.64 and 0.28 kcal mol^{-1}, respectively) which are smaller than $\Delta G°$. Differences between ΔE and $\Delta G°$ are estimated to be less than 0.2 kcal mol^{-1}. ^{19}F NMR spectra of the neat liquid at −60 °C which have been reported[10] do not show any splitting due to the presence of two conformers. Such spectra of a 1:2 mixture of FC(O)N═S(F)CF_3 and CD_2Cl_2 at low temperatures show evidence for two conformers in a 1:1 ratio at −85 °C. The interconversion of the two forms is incomplete at −100 °C (ratio 1:8). Above −50 °C, no evidence for the presence of more than one conformer is observed. However, there is also evidence for at least one further conformer in the variable-temperature NMR spectra, for which additional studies are being undertaken and will be reported later. These spectra indicate that at room temperature the trans-syn and cis-syn forms interconvert rapidly on the NMR time scale by internal rotation around the N═S double bond. The barriers for this rotation are calculated to be 7.1 kcal mol^{-1} (B3LYP) and 9.3 kcal mol^{-1} (MP2).

The experimental geometric parameters of the trans-syn conformer are compared to calculated values in Table 2. Considering the experimental uncertainties and systematic differences between experimental r_a and calculated r_e values, MP2 and B3LYP calculations reproduce all bond lengths and angles satisfactorily, with the exception of the S−F bond length. Both computational methods predict this bond too long by about 0.06 Å. The dihedral angles Φ(C1−N═S−C2) and Φ(C1−N═S−F2) are not well determined in the GED experiment, and the difference between the experimental and calculated values may be caused at least to some extent by large-amplitude vibrational effects.

The conformational properties of FC(O)N═S(F)CF_3 for which a trans configuration around the S═N bond is preferred are unexpected. As mentioned in the Introduction, all imidosulfur compounds of the type RN═SX_2 whose structures have been determined in the gas phase possess a cis configuration. The configuration around the S═N bond can be rationalized primarily by considering two opposing effects: (1) orbital interactions between lone pairs and opposite σ^* orbitals (general anomeric effect) and (2) steric repulsions between substituents on nitrogen and on sulfur. Whereas steric repulsions favor a trans structure, the two anomeric interactions $n_S \rightarrow \sigma^*(N-R)$ and $n_N \rightarrow \sigma^*(SX_2)$ stabilize the cis configuration (see Chart 1). The S−X bonds are not exactly trans to the nitrogen lone pair, but orbital overlap is still appreciable. Both anomeric effects cause shortening of the S═N bond. In all compounds of the type RN═SF_2 that are mentioned in the Introduction, the anomeric effects overcompensate steric repulsions, leading to cis configurations. In FC(O)N═S(F)CF_3, apparently, steric interactions are stronger than anomeric effects and thus the trans configuration is slightly preferred. In this configuration, orbital interactions no longer cause shortening of the S═N bond, which is considerably longer (1.549(5) Å) than those in imidosulfur difluorides having the cis configuration (1.48 ± 0.02 Å). The theoretical calculations predict the S═N bond in the less stable cis configuration to be about 0.02 Å shorter than that in the trans form. Anomeric interactions can also explain the different frequencies for the C═O vibrations in trans and cis configurations. In the trans-syn form (see Chart 2), the $n_N \rightarrow \sigma^*(C=O)$ interaction weakens the C═O bond and lowers $\nu(C=O)$ to 1796 cm^{-1}. A similar orbital interaction occurs also in the cis-syn conformer, but now the FC(O) group competes with the S(F)-CF_3 group for the nitrogen lone pair and this leads to a higher $\nu(C=O)$ of 1864 cm^{-1}.

It is not possible to predict quantitatively the influence of various R and X substituents on the strength of anomeric effects or on steric repulsions and to give a straightforward explanation for the change of configuration in FC(O)N═S(F)CF_3. To obtain more information about the influence of various substituents at nitrogen and/or sulfur on the conformational properties of imidosulfur compounds, additional theoretical calculations were performed for $CF_3N{=}SF_2$, $CF_3N{=}S(CF_3)_2$, $CF_3N{=}S(F)CF_3$, FC(O)N═SF_2, and FC(O)N═$S(CF_3)_2$. These compounds differ in their substituent at nitrogen (CF_3 or FC(O)) and in their substituents at sulfur (F_2, $(CF_3)_2$, or (F)CF_3). The geometric parameters for cis and trans configurations around the N═S bond were fully optimized. In all cases, the syn orientation of the FC(O) group (C═O syn to N═S) is favored. The energies of the cis configurations relative to the trans forms are listed in Table 4. If the CF_3 group at nitrogen is replaced by the FC(O) group, the relative energy of the cis form is increased by about 1 kcal mol^{-1}. A larger effect on the energy difference is

Table 4. Calculated (B3LYP/6-31G*) Energies (kcal mol^{-1}) of the Cis Configurations Relative to the Trans Configurations for Imidosulfur Compounds

compd	*E*(cis)	*E*(trans)
$CF_3N{=}SF_2$	−5.6	0.0
$CF_3N{=}S(CF_3)_2$	−2.0	0.0
$CF_3N{=}S(F)CF_3$	−0.5	0.0
$FC(O)N{=}SF_2$	−4.5	0.0
$FC(O)N{=}S(CF_3)_2$	−1.0	0.0
$FC(O)N{=}S(F)CF_3$	+0.3	0.0

observed for different substituents at sulfur. Replacement of the two fluorine atoms by CF_3 groups increases the energy of the cis conformer by about 3.5 kcal mol^{-1} relative to the trans form. However, for both compounds, $CF_3N{=}S(CF_3)_2$ and $FC(O)N{=}S(CF_3)_2$, the cis conformer is predicted to be still lower in energy. Mixed substitution at sulfur with one fluorine atom and one CF_3 group results in a further increase of about 1.5 kcal mol^{-1} in the energy difference. The combined substitution effects of the FC(O) group at nitrogen and mixed substitution at sulfur lead to preference of the trans configuration around the N=S bond in $FC(O)N{=}S(F)CF_3$. This is qualitatively in agreement with the experiments which result in larger $\Delta G°$ values of 0.79(36) and 1.09(35) kcal mol^{-1}.

Experimental Section

$FC(O)N{=}S(F)CF_3$ was synthesized by the reaction of (trifluoromethyl)sulfur trifluoride, CF_3SF_3, and silicon tetraisocyanate, $Si(NCO)_4$.[10] The compound was purified by repeated vacuum distillations. Since decomposition occurs at room temperature, the sample was stored and transported in liquid nitrogen. The IR (gas) spectrum was recorded between 4000 and 400 cm^{-1} (resolution 2 cm^{-1}) with a Perkin-Elmer 1600 spectrometer using a 10 cm cell equipped with KBr windows. Raman spectra of the liquid between 2000 and 100 cm^{-1} were obtained with a Spex Ramalog spectrometer provided with an Ar^+ laser (Spectra-Physics model 165). The 457.9 and 514.5 nm lines were used for excitation with a power of 100 mW. The resolution was 5 cm^{-1}. The liquid samples were handled in 6 mm glass tubes at room temperature.

The GED intensities were recorded with a KD-G2 gas diffractograph[15] at 50 and 25 cm nozzle-to-plate distances and with an accelerating voltage of ca. 60 kV. The sample was kept at −4 °C and the nozzle was at room temperature. The photographic plates were analyzed with the usual methods.[16] Averaged molecular intensities in the *s* ranges 2−18 and 8−35 Å^{-1} in intervals of $\Delta s = 0.2$ Å^{-1} are presented in Figure 3.

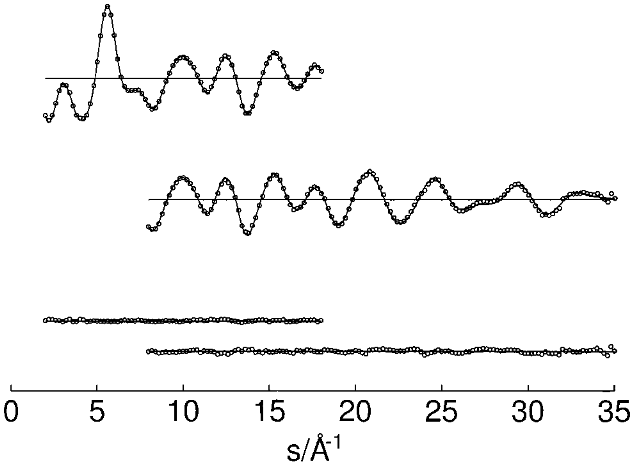

Figure 3. Averaged molecular intensities for long (above) and short (below) nozzle-to-plate distances and residuals.

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