

# First example of a preferred *anti* configuration in $\text{RN}=\text{SX}_2$ compounds: *N*-fluoroformyliminotrifluoromethylsulfur fluoride, $\text{FC}(\text{O})\text{N}=\text{S}(\text{F})\text{CF}_3$

R. M. Romano,<sup>1</sup> C. O. Della Védova,<sup>1,2\*†</sup> M. I. Mora Valdez<sup>3</sup> and E. H. Cutín<sup>3†</sup>

<sup>1</sup> CEQUINOR (UNLP, CONICET) Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 esq. 115, 1900 La Plata, Argentina

<sup>2</sup> Laboratorio de Servicios a la Industria y al Sistema Científico, LaSeISiC (UNLP–CIC–CONICET), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional De La Plata, 47 esq. 115, 1900 La Plata, Argentina

<sup>3</sup> Instituto de Química Física, Facultad de Bioquímica, Química y Farmacia, Universidad Nacional de Tucumán, Ayacucho 491, 4000 Tucumán, Argentina

The vibrational spectra, including Raman spectra at different temperatures and resonance Raman spectra, and theoretical calculations of *N*-fluoroformyliminotrifluoromethylsulfur fluoride,  $\text{FC}(\text{O})\text{N}=\text{S}(\text{F})\text{CF}_3$ , were obtained and interpreted. They point to the existence of a predominant *anti-syn* form and in equilibrium at lower concentration a *syn-syn* form (the first related to the nitrogen lone pair with respect to the sulfur lone pair and the second is related to the  $\text{C}=\text{O}$  double bond with respect to the  $\text{N}=\text{S}$  double bond). The general result indicates that it is the first *anti* configuration reported for this type of molecule implying for the energetically most favoured form an *anti* configuration of the lone pairs attached to both the S and N atoms. Copyright © 2000 John Wiley & Sons, Ltd.

## INTRODUCTION

Very few molecules provide vibrational spectra so full of information and are so interesting from the geometrical, conformational and configurational point of view as *N*-fluoroformyliminotrifluoromethylsulfur fluoride,  $\text{FC}(\text{O})\text{N}=\text{S}(\text{F})\text{CF}_3$ . The various possible forms also represent a challenge for the theoretical calculations. Both theoretical and experimental arguments are used in this paper to analyse  $\text{FC}(\text{O})\text{N}=\text{S}(\text{F})\text{CF}_3$ . According to the first inspection of the molecule using the simplest VSEPR model, two main structural questions arise, namely the relative positions of the N and S lone pairs and the conformation of the  $\text{C}=\text{O}$  double bond with respect to the  $\text{N}=\text{S}$  double bond. The analyses of the IR and Raman bands, especially of the carbonylic vibrations, allow the detection

of the structural equilibrium. For the precise prediction of the preferred conformation and configuration, the assistance of theoretical arguments is necessary. Therefore, taking into account our general programme of studying  $\text{FC}(\text{O})\text{N}=\text{SX}_2$  species, this investigation was performed to determine, by application of simple techniques, the structural behaviour of the title molecule.

## EXPERIMENTAL

*N*-Fluoroformyliminotrifluoromethylsulfur fluoride,  $\text{FC}(\text{O})\text{N}=\text{S}(\text{F})\text{CF}_3$ , was prepared by reaction of  $\text{CF}_3\text{SF}_3$  and  $\text{Si}(\text{NCO})_4$ .<sup>1</sup> The liquid product was purified at reduced pressure by several trap-to-trap distillations. Fourier transform (FT) IR (vapour) and Raman (liquid) spectra confirmed the purity of the compound.

Infrared spectra were obtained with a Bruker IFS85 FT spectrometer, with resolution of  $1\text{ cm}^{-1}$ . Raman spectra were obtained with a Jobin-Yvon U-1000 spectrometer equipped with both argon and Krypton ion lasers (Spectra-Physics Model 165) and radiation, of 457.9 and 514.5 nm ( $\text{Ar}^+$ ) was used for excitation. The spectra were measured at ambient temperature, at  $-5^\circ\text{C}$  and at  $45^\circ\text{C}$  with  $4\text{ cm}^{-1}$  resolution. All calculations were performed with the Gaussian 94 suite of programs<sup>2</sup> on a personal computer.

## THEORETICAL CALCULATIONS

The *anti-syn*, *syn-syn*, *anti-anti* and *syn-anti* structures of  $\text{FC}(\text{O})\text{N}=\text{S}(\text{F})\text{CF}_3$  were fully optimised with *ab initio*

\* Correspondence to: C. O. Della Védova, LaSeISiC (UNLP–CIC–CONICET) y CEQUINOR, Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.C. 962, 1900 La Plata, Argentina; e-mail: carlosdv@dalton.quimica.unlp.edu.ar  
† Member of Carrera del Investigador Científico y Técnico of the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina.

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calculations (HF/6-31+G\*). The four structures represent stable structures for which no imaginary wavenumbers occur. They were selected for successive optimizations considering variations in the C2N3S4C7 and N3S4C7F8 dihedral angles (see Fig. 1 for atom numbering and the four different forms of the title compound considered in this work).

According to a brief inspection of the experimental vibrational spectra, at least two structures can occur as suggested by the splitting of the carbonylic band. Thus, not only the energy calculations of the most stable form but also the energy difference with the other stable less favoured energetically forms are interesting in this case. The most stable structure and the existence of configurational equilibrium can be deduced from this analysis. Table 1 lists the calculated energies and energy differences for the four forms of Fig. 1 using *ab initio* and density functional theory approximations. Both calculations (HF/6-31+G\* and B3LYP/6-31+G\*) predict the *anti-syn* form as the most stable (the nitrogen lone pair *anti* with respect to the sulfur lone pair and the C=O double bond *syn* with respect to the N=S double bond) the *syn-syn* form being higher in energy. This result shows no agreement with data reported for other compounds, for which the configuration around the N=S double bond is always *syn* (CIN=SF<sub>2</sub>,<sup>3</sup> CF<sub>3</sub>N=SF<sub>2</sub>,<sup>4</sup> (F. Trautner, D. Christen and H. Oberhammer, to be published), F<sub>3</sub>SN=SF<sub>2</sub>,<sup>5</sup> NCN=SF<sub>2</sub> (R. Haist, E. Lork, R. Mews

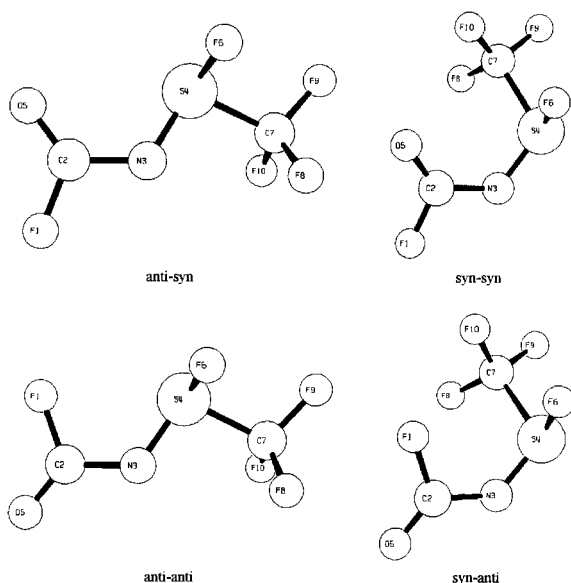
and H. Oberhammer, unpublished results), FC(O)N=SF<sub>2</sub>,<sup>6</sup> and FSO<sub>2</sub>N=SF<sub>2</sub>,<sup>7</sup>). The theoretical calculations reproduce results obtained by analysis of the vibrational spectra (see below) and the geometric structure reported by gas electron diffraction analysis (F. Trautner, E. H. Cutin, C. O. Della Védova, R. Mews and H. Oberhammer, to be published). A smaller basis set (HF/3-21G\*) leads to erroneous prediction of the most stable form for this molecule.

## VIBRATIONAL ANALYSIS

The main interest in the vibrational spectra is the determination of the conformational and configurational properties of the title compound. According to theoretical vibrational data calculated for the four forms of FC(O)N=S(F)CF<sub>3</sub>, the analysis must be concentrated on the C=O stretching ( $\nu_1$ ) and on the C-N stretching ( $\nu_7$ ) vibrations (see Tables 2 and 3), which are expected to show the strongest dependence on the forms of the molecule. In the experimental vibrational spectra shown in Fig. 2 two bands appear in the C=O stretching region, a less intense and a more intense band at higher and lower wavenumbers in both the IR and Raman spectra, respectively, which indicates the presence of two forms. Since theoretical calculations predict  $\nu_{C=O}(\textit{syn-syn}) > \nu_{C=O}(\textit{anti-syn})$ , it can be concluded that the most intense band originates from the *anti-syn* form, i.e. the main structure. Moreover, the expected vibrations for hypothetical *anti-anti* and *syn-anti* forms coincidentally at 1883 cm<sup>-1</sup> are far from the experimental values. These forms can be ruled out in comparison with

**Table 1.** Calculated energies and energy differences with the *anti-syn* form of four stable forms of FC(O)N=S(F)CF<sub>3</sub>

Structure	HF/6-31+G*		B3LYP/6-31+G*	
	E/hartree	$\Delta E/\text{kcal mol}^{-1}$	E/hartree	$\Delta E/\text{kcal mol}^{-1}$
<i>anti-syn</i>	-1099.6909242	0.00	-1103.5492959	0.00
<i>syn-syn</i>	-1099.6861255	3.01	-1103.5476500	1.03
<i>anti-anti</i>	-1099.6847424	3.88	-1103.54470054	1.44
<i>syn-anti</i>	-1099.6847424	6.71	-1103.5450008	2.69



**Figure 1.** Molecular models and atom numberings for four stable structures of FC(O)N=S(F)CF<sub>3</sub> calculated with the HF/6-31+G\*.

**Table 2.** Calculated vibrational wavenumbers for four stable forms of FC(O)N=S(F)CF<sub>3</sub> using the HF/6-31+G\* approximation

Mode	<i>anti-syn</i> <sup>a</sup> $\bar{\nu}/\text{cm}^{-1}$	<i>syn-syn</i> <sup>a</sup> $\bar{\nu}/\text{cm}^{-1}$	<i>anti-anti</i> <sup>a</sup> $\bar{\nu}/\text{cm}^{-1}$	<i>syn-anti</i> <sup>a</sup> $\bar{\nu}/\text{cm}^{-1}$	Tentative assignment (see Table 3)
$\nu_1$	1805	1826	1883	1883	$\nu_{C=O}$
$\nu_2$	1301	1305	1302	1298	$\nu_{as}CF_3$
$\nu_3$	1291	1294	1276	1291	$\nu_{CF}$
$\nu_4$	1265	1242	1244	1246	$\nu_{as}CF_3$
$\nu_5$	1158	1150	1152	1135	$\nu_sCF_3$
$\nu_6$	1091	1119	1065	1091	$\nu_{N=S}$
$\nu_7$	911	865	833	810	$\nu_{CN}$
$\nu_8$	799	801	776	778	CFO oop <sup>b</sup>
$\nu_9$	770	768	769	759	$\delta_sCF_3$
$\nu_{10}$	761	752	751	748	$\nu_{SF}$
$\nu_{11}$	674	629	649	667	$\delta_{FCO}$
$\nu_{12}$	556	556	552	556	$\delta_{as}CF_3$
$\nu_{13}$	547	545	548	543	$\delta_{CF_2}$
$\nu_{14}$	514	503	533	529	$\delta_{NCF}$
$\nu_{15}$	472	455	469	455	$\delta_{SCF}$
$\nu_{16}$	374	382	374	374	$\delta_{NSF}$
$\nu_{17}$	318	329	324	332	
$\nu_{18}$	303	300	300	298	
$\nu_{19}$	229	237	225	241	
$\nu_{20}$	183	211	183	214	
$\nu_{21}$	139	132	137	130	
$\nu_{22}$	92	104	92	101	
$\nu_{23}$	59	65	56	53	
$\nu_{24}$	52	48	43	39	

<sup>a</sup> Scaled by a factor of 0.9.

<sup>b</sup> Out-of-plane.

**Table 3. Experimental (IR and Raman) and theoretical vibrational wavenumbers of FC(O)N=S(F)CF<sub>3</sub>**

IR (gas) <sup>a</sup> $\tilde{\nu}/\text{cm}^{-1}$	Raman (liquid) $\tilde{\nu}/\text{cm}^{-1}$	<i>anti-syn</i> HF/6-31+G* $\tilde{\nu}/\text{cm}^{-1}$	<i>syn-syn</i> HF/6-31+G* $\tilde{\nu}/\text{cm}^{-1}$	Assignment
2265				
2199				
2136				
2007				
1929				
1854 w	1828 <sup>b</sup>		1826	$\nu\text{C}=\text{O}_{\text{syn-syn}}$
1796 vs	1777 <sup>b</sup>	1805		$\nu\text{C}=\text{O}_{\text{anti-syn}}$
1755				
1432				
1368				
1328				
1245 vs		1301	1305	$\nu_{\text{as}}\text{CF}_3$
1236 vs	1217	1291	1294	$\nu\text{CF}$
1144 vs		1265		$\nu_{\text{as}}\text{CF}_3_{\text{anti-syn}}$
1132 vs			1242	$\nu_{\text{as}}\text{CF}_3_{\text{syn-syn}}$
	1123	1158		$\nu_{\text{s}}\text{CF}_3_{\text{anti-syn}}$
			1150	$\nu_{\text{s}}\text{CF}_3_{\text{syn-syn}}$
1105 s	1096 <sup>b</sup>	1091		$\nu\text{N}=\text{S}_{\text{anti-syn}}$
1057 w	1054 <sup>b</sup>		1119	$\nu\text{N}=\text{S}_{\text{syn-syn}}$
904 w	900 <sup>b</sup>	911		$\nu\text{CN}_{\text{anti-syn}}$
854 vw	854 <sup>b</sup>		865	$\nu\text{CN}_{\text{syn-syn}}$
	823			
778 m		799	801	$\text{CFO oop}^c$
	768	770		$\delta_{\text{s}}\text{CF}_3_{\text{anti-syn}}$
	756		768	$\delta_{\text{s}}\text{CF}_3_{\text{syn-syn}}$
720 s	718	761	752	$\nu\text{SF}$
668 w	667	674		$\delta\text{FCO}_{\text{anti-syn}}$
			629	$\delta\text{FCO}_{\text{syn-syn}}$
562 w	564	556	556	$\delta_{\text{as}}\text{CF}_3$
	544	547	545	$\delta\text{CF}_2$
518 w	520	514	503	$\delta\text{NCF}$
480 w	471	472	455	$\delta\text{SCF}$
	366	374	382	$\delta\text{NSF}$
	317	318	329	
	299	303	300	
	235	229	237	
	192	183	211	
	139	139	132	
		92	104	
		59	65	
		52	48	

<sup>a</sup> w = weak, m = medium, s = strong, v = very.

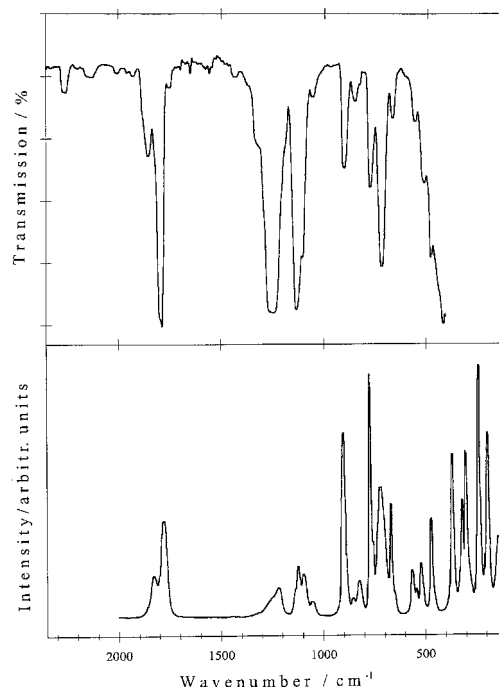
<sup>b</sup> Band showing RR effect.

<sup>c</sup> Out-of-plane.

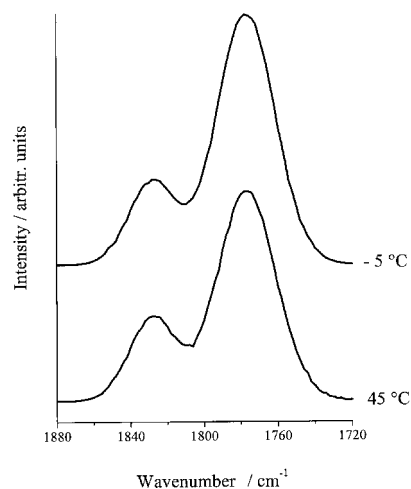
the experimental spectra (the same result was obtained by evaluation of the theoretical relative energies in the theoretical part).

The region corresponding to the C–N stretching vibration shows two definite bands with the band at higher wavenumbers the most intense. According to the Table 2, it is the expected behaviour for the *anti-syn* (more intense C–N stretching band) and *syn-syn* (less intense C–N stretching band) forms of the title compound. The other forms can be excluded as shown in Table 2 because their hypothetical wavenumbers are 833 and 810 cm<sup>-1</sup> for the *anti-anti* and *syn-anti* forms, respectively.

Raman spectra recorded at different temperatures, depicted in the Fig. 3, show that in the carbonylic stretching region the weak band at higher wavenumbers gains intensity with increasing temperature from –5 to



**Figure 2.** Vibrational spectra of FC(O)NS(F)CF<sub>3</sub> at room temperature. Top: gas FTIR spectrum; pressure, 6 Torr; resolution, 1 cm<sup>-1</sup>. Bottom: liquid Raman spectrum; excitation, 514.5 nm (100 mW); resolution, 4 cm<sup>-1</sup>.



**Figure 3.** Raman spectra of liquid FC(O)N=S(F)CF<sub>3</sub> at –5 and at 45 °C. Excitation, 514.5 nm (100 mW); resolution, 4 cm<sup>-1</sup>.

45 °C in accordance with the structural equilibrium and with the assignment of the forms discussed below.

To reinforce the proposed assignments listed in Table 3, resonance Raman spectra were recorded. The intensity of the Raman bands was fixed with respect to the 192 cm<sup>-1</sup> band. When the wavelength of the exciting radiation decreases from 514.5 to 457.9 nm, the intensities of the C=O, N=S and C–N fundamental stretching modes corresponding to two forms in equilibrium increase. The reason for the increase in these modes indicated in Table 3 can be explained as follows. The vibrations involving the C(O)N=S group, which distort the ground-state geometry towards the excited-state structure, will be enhanced most. Clearly, the most enhanced modes are related to the expected chromophore of the molecule, i.e. the region of the  $\pi$  electrons.

The observed vibrations listed in Table 3 were assigned as usual by comparison with data corresponding to related molecules, taking into account the theoretical vibrational spectra as stated by evaluation of the resonance Raman effect. The molecules mainly considered were  $\text{FC(O)=NSF}_2$ ,<sup>8</sup>  $\text{ClSO}_2\text{N=SF}_2$ ,<sup>9</sup>  $\text{CF}_3\text{SO}_2\text{N}_3$ ,<sup>10</sup> and  $\text{CF}_3\text{SO}_2\text{NCO}$ .<sup>11</sup>

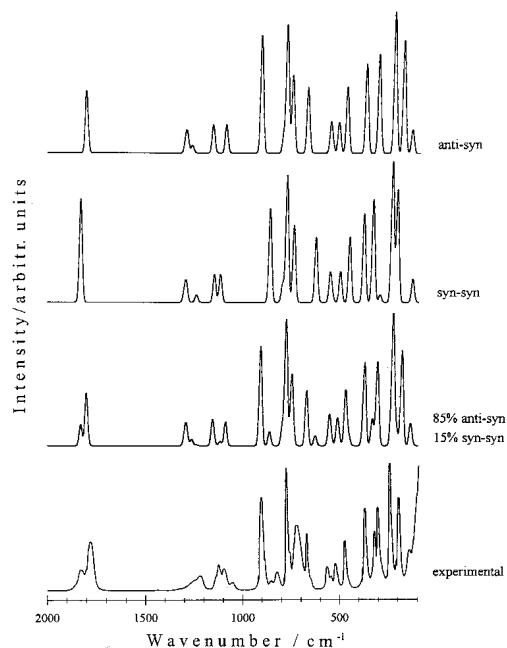
In accordance with the data and assignments in the Table 3, the reported molecules show comparable data. Some features are noteworthy, e.g. the difference between data corresponding to the C=O stretching vibration in the IR (gas) and Raman (liquid) spectra.  $\Delta(\nu_{\text{gas}} - \nu_{\text{liquid}})$  is about 20–25  $\text{cm}^{-1}$  for each conformer and may be rationalized by the formation of intermolecular associations in the liquid. The attractive forces operating in this phase result in a lowering of the C=O bond order as consequence of changes in the electronic distribution due to these interactions. This  $\Delta$  is also considerable for the C–F stretching vibration and for the N=S stretching vibration of the *anti-syn* form. However,  $\Delta$  is lower in the *syn-syn* form, precluding different types of interaction due to their different forms.

The position of the N=S stretching vibration depends strongly on the electronegativities of the substituents attached to the group. The trend is similar to the C=O group which increases its wavenumber with the sum of the substituent electronegativities.<sup>12</sup> The N=S stretching wavenumber is assigned at 1105  $\text{cm}^{-1}$  (IR) for the most stable *anti-syn* form of the  $\text{FC(O)N=S(F)CF}_3$  molecule; the reported value for  $\text{ClSO}_2\text{N=SCl}_2$ <sup>13</sup> is 1101  $\text{cm}^{-1}$  (IR), for  $\text{ClSO}_2\text{N=SF}_2$ <sup>9</sup> 1278  $\text{cm}^{-1}$ , for  $\text{FC(O)N=SF}_2$ <sup>8</sup> 1330  $\text{cm}^{-1}$ , for  $\text{CF}_3\text{N=SCl}_2$ <sup>14</sup> 1314  $\text{cm}^{-1}$  and for  $\text{CF}_3\text{N=SF}_2$ <sup>15</sup> 1388  $\text{cm}^{-1}$ . These data demonstrate the mentioned trend, i.e. the higher the electronegativity sum of the N=S group substituents, the higher is the position of the N=S stretching wavenumber.

The remaining assignments in Table 3 compare very well with data from theoretical calculations (HF/6–31+G\*). The reliability of these calculations should be noted and the agreement for a wide range of compounds gives confidence in the results.

## CONCLUSIONS

All the compounds with general formula  $\text{RN=SX}_2$  whose experimental gas-phase structures are reported show a *syn* orientation of the nitrogen and sulfur lone pairs [ $\text{ClN=SF}_2$ ,<sup>3</sup>  $\text{CF}_3\text{N=SF}_2$ ,<sup>4</sup> (F. Trautner, D. Christen and H. Oberhammer, to be published),  $\text{F}_3\text{SN=SF}_2$ ,<sup>5</sup>  $\text{NCN=SF}_2$  (R. Haist, E. Lork, R. Mews and H. Oberhammer, unpublished results),  $\text{FC(O)N=SF}_2$ ,<sup>6</sup> and  $\text{FSO}_2\text{N=SF}_2$ ,<sup>7</sup>  $\text{CF}_3\text{N=SCl}_2$ <sup>16</sup> and  $\text{ClN=S(CF}_3)_2$ <sup>17</sup>]. The formal substitution of a  $\text{CF}_3$  group by F in  $\text{FC(O)N=SF}_2$  produces large changes in the configurational properties of these compounds. According to our studies, a mixture of the *anti-syn* form and the *syn-syn* form occurs, with the first energetically favoured. These results are in accordance with current gas electron diffraction studies of the molecule (F. Trautner, E. H. Cutin, C. O. Della Védova, R. Mews and H. Oberhammer, to be published).



**Figure 4.** Raman spectra calculated with data from Table 3 and comparison with the experimental spectrum (excitation, 514.5 nm).

Both the relative energy calculations and the prediction of the vibrational spectra are coincident to show structural mixture for the molecule. Figure 4 depicts theoretical spectra of the *anti-syn* and *syn-syn* forms. A mixture of 85% of the *anti-syn* form and 15% of the *syn-syn* form reproduces the experimental spectrum very well, validating the results.

No explanation for the unusual preference of the *anti-syn* form can be given. Systematic studies on a wide range of compounds will be necessary to answer this intriguing question. Moreover,  $\text{FC(O)N=S(CF}_3)_2$  was calculated (F. Trautner, E. H. Cutin, C. O. Della Védova, R. Mews and H. Oberhammer, to be published). The ‘normal’ behaviour was also reported for this molecule, the lone pairs being attached to the N and S atoms in a *syn* position. For the model  $\text{FC(O)N=S(F)H}$  the same result was obtained in this work using for the two forms an HF/6–31+G\* approach.

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