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

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The vibrational spectra, including Raman spectra at different temperatures and resonance Raman spectra, and theoretical calculations of N-fluoroformyliminotrifluoromethylsulfur fluoride, FC(O)N=S(F)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 C=O double bond with respect to the N=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, FC(O)N=S(F)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 FC(O)N=S(F)CF$_3$. According to the first inspection of the molecule 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 C=O double bond with respect to the N=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 FC(O)N=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, FC(O)N=S(F)CF$_3$, was prepared by reaction of CF$_3$SF$_2$ and Si(NCO)$_4$. 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 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 (Ar$^+$) was used for excitation. The spectra were measured at ambient temperature, at −5°C and at 45°C with 4 cm$^{-1}$ resolution. All calculations were performed with the Gaussian 94 suite of programs$^2$ on a personal computer.

**THEORETICAL CALCULATIONS**

The anti–syn, syn–syn, anti–anti and syn–anti structures of FC(O)N=S(F)CF$_3$ were fully optimised with ab initio
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 carboxylic 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=SF3,3 CF,N=SF3,4 (F. Trautner, D. Christen and H. Oberhammer, to be published), F3SN=SF3,5 NCN=SF3 (R. Haist, E. Lork, R. Mews and H. Oberhammer, unpublished results), FC(O)N=SF,6 and FSO2N=SF2,7). 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)CF3, the analysis must be concentrated on the C=O stretching (νC=O) and on the C–N stretching (νC–N) 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 νC=C=C=syn+syn) νC=C=syn–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⁻¹ 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)CF3 |
|-----------------|-----------------|-----------------|-----------------|
| Structure       | HF/6–31+G*       | B3LYP/6–31+G*   |
|                 | ΔE/hartree       | ΔE/hartree      |
| anti–syn        | -1099.6099242    | -1103.5492959   |
| syn–syn         | -1099.6861255    | -1103.5476500   |
| anti–anti       | -1099.6847424    | -1103.5470054   |
| syn–anti        | -1099.6847424    | -1103.5450008   |

![Figure 1](https://example.com/figure1.png)

Figure 1. Molecular models and atom numberings for four stable structures of FC(O)N=S(F)CF3 calculated with the HF/6–31+G* approximation.

| Table 2. Calculated vibrational wavenumbers for four stable forms of FC(O)N=S(F)CF3 using the HF/6–31+G* approximation |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Mode            | anti–syn        | anti–syn        | anti–syn        | anti–syn        | syn–syn         | syn–syn         |
|                 | νC=O            | νC=O            | νC=O            | νC=O            | νC=O            | νC=O            |
| νvCF3           | 1301            | 1305            | 1302            | 1298            | 1301            | 1305            |
| νυN=S           | 1321            | 1294            | 1276            | 1291            | 1321            | 1294            |
| νvCF3           | 1325            | 1242            | 1244            | 1246            | 1325            | 1242            |
| νC=O            | 1158            | 1150            | 1152            | 1135            | 1158            | 1150            |
| νυN=S           | 1091            | 1119            | 1065            | 1091            | 1091            | 1119            |
| νυN=S           | 911             | 865             | 833             | 810             | 911             | 865             |
| νυCF3           | 799             | 801             | 776             | 778             | 799             | 801             |
| νυCF3           | 770             | 768             | 769             | 759             | 770             | 768             |
| νυCF3           | 761             | 752             | 751             | 748             | 761             | 752             |
| νυCF3           | 674             | 629             | 649             | 667             | 674             | 629             |
| νυCF3           | 556             | 556             | 552             | 556             | 556             | 556             |
| νυCF3           | 547             | 545             | 548             | 543             | 547             | 545             |
| νυCF3           | 514             | 503             | 533             | 529             | 514             | 503             |
| νυCF3           | 472             | 455             | 469             | 455             | 472             | 455             |
| νυCF3           | 374             | 382             | 374             | 374             | 374             | 374             |
| νυCF3           | 318             | 329             | 324             | 332             | 318             | 329             |
| νυCF3           | 303             | 300             | 300             | 298             | 303             | 300             |
| νυCF3           | 229             | 237             | 225             | 241             | 229             | 237             |
| νυCF3           | 183             | 211             | 183             | 214             | 183             | 211             |
| νυCF3           | 139             | 132             | 157             | 130             | 139             | 132             |
| νυCF3           | 92              | 104             | 92              | 101             | 92              | 104             |
| νυCF3           | 59              | 65              | 56              | 53              | 59              | 65              |
| νυCF3           | 52              | 48              | 43              | 39              | 52              | 48              |

a Scaled by a factor of 0.9.
b 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\(^{-1}\) 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 \(45^\circ\)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\(^{-1}\) 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.

**Table 3. Experimental (IR and Raman) and theoretical vibrational wavenumbers of FC(O)N=S(F)CF\(_3\)**

| Mode | IR (gas) \(i/\text{cm}^{-1}\) | Raman (liquid) \(i/\text{cm}^{-1}\) | anti–syn | syn–syn | Assignment |
|------|----------------|----------------|----------|----------|-----------|
| \(\nu_{\text{CF}}\) | | | 1305 | 1305 | \(\nu_{\text{CF}}\) |
| \(\nu_{\text{CF}}\) | | 1294 | 1294 | 1294 | \(\nu_{\text{CF}}\) |
| \(\nu_{\text{C}–\text{N}}\) | | 1150 | 1150 | 1150 | \(\nu_{\text{C}–\text{N}}\) |
| \(\nu_{\text{N=S}}\) | 1091 | 1091 | 1091 | 1091 | \(\nu_{\text{N=S}}\) |
| \(\nu_{\text{C}–\text{N}}\) | | 1123 | 1123 | 1123 | \(\nu_{\text{C}–\text{N}}\) |
| \(\nu_{\text{C}–\text{N}}\) | | 799 | 799 | 799 | \(\nu_{\text{C}–\text{N}}\) |
| \(\nu_{\text{C}–\text{N}}\) | | 768 | 768 | 768 | \(\nu_{\text{C}–\text{N}}\) |
| \(\nu_{\text{C}–\text{N}}\) | | 766 | 766 | 766 | \(\nu_{\text{C}–\text{N}}\) |
| \(\nu_{\text{C}–\text{N}}\) | | 720 | 720 | 720 | \(\nu_{\text{C}–\text{N}}\) |
| \(\nu_{\text{C}–\text{N}}\) | | 668 | 668 | 668 | \(\nu_{\text{C}–\text{N}}\) |
| \(\nu_{\text{C}–\text{N}}\) | | 562 | 562 | 562 | \(\nu_{\text{C}–\text{N}}\) |
| \(\nu_{\text{C}–\text{N}}\) | | 518 | 518 | 518 | \(\nu_{\text{C}–\text{N}}\) |
| \(\nu_{\text{C}–\text{N}}\) | | 480 | 480 | 480 | \(\nu_{\text{C}–\text{N}}\) |

\(\nu = \text{weak, m = medium, s = strong, v = very.}\)

\(\text{Band showing RR effect.}\)

\(\text{Out-of-plane.}\)
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 FC(O)═NSF2,8 CISO2N═SF2,9 CF3SO2N3,10 and CF3SO2NCO.11

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. ∆(νgas − νliquid) is about 20–25 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 ∆ is also considerable for the C−F stretching vibration and for the N═S stretching vibration of the anti–syn form. However, ∆ 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.12 The N═S stretching wavenumber is assigned at 1105 cm⁻¹ (IR) for the most stable anti–syn form of the FC(O)N═S(F)CF3 molecule; the reported value for CISO2N═SCl13 is 1101 cm⁻¹ (IR), for CISO2N═SF2,9 1278 cm⁻¹, for FC(O)N═SF2,9 1330 cm⁻¹, for CF3N═SCl14 1314 cm⁻¹ and for CF3N═SF2,15 1388 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 RN═SX2 whose experimental gas-phase structures are reported show a syn orientation of the nitrogen and sulfur lone pairs [CN═SF2,3 CF3N═SF2,4 (F. Trautner, D. Christen and H. Oberhammer, to be published), F3SN═SF2,9 NCSN═ SF2 (R. Haist, E. Lork, R. Mews and H. Oberhammer, unpublished results), FC(O)N═SF2,9 and FSO2N═SF2,7 CF3N═SCl16 and CN═S(CF3)2]. The formal substitution of a CF3 group by F in FC(O)N═SF2 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).

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, FC(O)N═S(F)CF3 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 FC(O)N═S(F)CF3 the same result was obtained in this work using for the two forms an HF/6–31+G* approach.

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