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CF₃CF₂N=S(F)CF₃: Vibrational spectra and conformational properties



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HIGHLIGHTS

- CF₃CF₂N=S(F)CF₃ exists in the gas phase as a mixture of *anticlinal* and *syn* forms.
- Theoretical calculations predict the *anticlinal* form as the global minimum.
- Steric effects govern the conformational preferences showed by CF₃CF₂N=S(F)CF₃.

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ABSTRACT

The structural, conformational, and configurational properties of 1,1,1-trifluoro-N-(1,1,2,2,2-pentafluoroethyl) methanesulfinimidoyl fluoride, CF₃CF₂N=S(F)CF₃ have been studied by vibrational spectroscopy [IR (vapor) and Raman (liquid)] and quantum chemical calculations [B3LYP, MP2 and B3PW91 levels of theory (using the 6-311+G(d) and 6-311+G(2df) basis sets). According to these theoretical approximations, CF₃CF₂N=S(F)CF₃ might be found in the gas phase as a mixture of a favoured *anticlinal* form (C–N bond *anticlinal* with respect to the C–S–F bisector angle) and a less abundant syn conformer showing C_1 symmetry as well ($\Delta G^{\circ} \approx 1.5$ kcal mol⁻¹). However, corresponding vibrational modes for these conformers show only small shifts which would not allow confidently detecting the rather small contribution of this second form in the experimental spectra.

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Introduction

The unusual nature of the sulfur nitrogen bond has attracted the attention of many and diverse research groups since more than fifty years. Its double bond character has been the subject of a controversy, since several experiments do not suit the idea of a classical double bond but of a more polar bonding, which allows an easier bond cleavage in polar media [1]. Recently, there has been much speculation on the possibility of weak non-bonding interactions occurring between second and third row elements that are capable of stabilizing particular small molecules or polymer

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conformations. The role of nitrogen–sulfur nonbonding interactions was found to be weak and noninfluential in the binding phenomena of these systems [2].

It is clear then that being the mere nature of the sulfur nitrogen bond not fully understood, the conformational properties of compounds possessing this entity may also give raise to interesting questions. Taking into account the donor–acceptor model, predicting the conformational properties on the basis of the molecular structure and the diverse orbital interactions feasible for a given configuration must balance a variety of influences. For iminosulfur molecules of the type R–N=SX₂, the configuration around the N=S bond can be rationalized primarily by considering two opposing effects: (1) orbital interactions between lone pairs and opposite σ^* orbitals, and (2) steric repulsions between substituents on nitrogen and on sulfur. Whereas steric repulsions favor *anti* structures, two

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anomeric interactions lp S $\rightarrow \sigma^*$ (N–R) and lp N $\rightarrow \sigma^*$ (SX₂) stabilize the *syn* form (see Scheme 1). Although the S–X bonds are not exactly *anti* to the nitrogen lone pair, orbital overlap is still appreciable. The mentioned anomeric effects overcompensate steric repulsions of the lone pairs of the nitrogen and sulfur atoms with each other, leading to *syn* conformers.

These conformational properties were reported by Protashchuk et al for H–N=SH₂ [3] and confirmed by our studies about the structural, conformational and vibrational properties of other sulfur nitrogen compounds of this type (FC(O)N=SF₂ [4], $C_2F_5N=SF_2$ [5], CF₃C(0)N=SF₂ [6], FC(0)N=SCl₂ [7] and C₂F₅N=SCl₂ [8]). These symmetric sulfur substituted compounds show only a single conformer of *syn* geometry around the N=S bond in the fluid phases. However, our group reported for the first time the unexpected conformational properties of asymmetric sulfur compounds RN=SXY $(FC(O)N=S(F)CF_3 [9]$ and $CF_3C(O)N=S(F)CF_3 [10])$, which show an equilibrium of the anti-syn and syn-syn forms (anti or syn of the C—N bond with respect to the bisector of the F—S—C angle: svn of the carbonyl group with respect to the N=S bond), with the former being more stable (see Fig. 1). This unusual anti orientation around the N=S bond was not unexpected from a sterical viewpoint, but in comparison with the constrained syn preference of the symmetric $-N=SX_2$ compounds.

Taking into account the results obtained for corresponding members of the series $-N=SX_2$ and -N=SXY mentioned above, the title molecule might exhibit conformational properties rather different from its symmetric analogue CF₃CF₂N=SF₂ and closer to those characterizing the -N=SXY derivatives. In order to gain additional experimental and theoretical information about the structural properties of sulfur imides, we report here a study of

CF₃CF₂N=S(F)CF₃ based mainly on its vibrational spectra [IR (vapor) and Raman (liquid)]. It is well known that perfluorination increases the density and viscosity of hydrocarbons, and that perfluorinated alkyl substituents show remarkable thermal stability and resistance towards oxidation [11,12]. We are particularly interested in analyzing the effect of a fully fluorinated carbon chain on the molecular structure. Moreover, quantum chemical calculations have been performed in order to assist the interpretation of the experimental data, and natural bond orbital (NBO) population analyses have been applied to rationalize the effect of electronic interactions on the structural, conformational, and configurational properties of CF₃CF₂N=S(F)CF₃.

Materials and methods

Experimental

1,1,1-Trifluoro-N-(1,1,2,2,2-pentafluoroethyl) methanesulfinimidoyl fluoride, CF₃CF₂N=S(F)CF₃, was synthesized by the reaction of CF₃CN and CF₃SF₃ [13]. The product obtained was purified at reduced pressure by repeated trap-to-trap distillations. A gas phase infrared spectrum at 2 mbar was recorded in the range 4000–400 cm⁻¹ with an FT IR Perkin Elmer 1600 spectrometer (resolution 2 cm⁻¹). Raman spectra of the liquid sample handled in glass capillaries at room temperature were obtained using a FT Bruker IFS 66v spectrometer (spectral resolution of 4 cm⁻¹) equipped with a Nd:YAG laser (1064 nm).

Computational details

All quantum chemical calculations were performed using the Gaussian 03 program [14]. Geometry optimizations were performed with the MP2 [15], B3LYP [16] and B3PW91 [17] approximations using 6-311+G(d) and 6-311+G(2df) basis sets and standard gradient techniques with simultaneous relaxation of all the geometric parameters. Natural population analysis and second-order donor–acceptor interaction energies were estimated by using the NBO [18] analysis as implemented in the Gaussian 03 program.



Fig. 1. Schematic representation of the most stable conformers observed for iminosulfur molecules of the type RN=SX₂ and RN=SXY.

Results and discussion

Quantum chemical calculations

According to Fig. 2, at least two configurations around the N=S double bond of CF₃CF₂N=SF(CF₃) could be expected. Since an anti arrangement of the C-N bond with respect to the X-S-Y bisector angle was preferred for molecules of the type RN=SXY [9,10], this was also expected for the title molecule. To confirm this hypothesis, the study of the potential energy surface was achieved by structure optimizations at fixed dihedral angles $\phi(C-N=S-F)$ in steps of 30° (see Fig. 3). The theoretical approximations confirm the assumption stated above. The global minimum corresponds to a *anticlinal* form, with $\phi(C-N=S-F) \approx 100^\circ$, while the local minimum indicates a syn arrangement of the C-N and the X-S-Y bisector of $\phi(C-N=S-F) \approx 60^{\circ}$ [19]. As it can be observed from the molecular model shown in Fig. 2, the strong repulsion between the fluorine atoms bonded to the sulfur atom and those belonging to the fluoromethyl and trifluoromethyl groups determine a molecular distortion. Consequently, the symmetry plane observed for the symmetric substituted iminosulfur compounds CF₃N=SCl₂ and $CF_3N=SF_2$ is absent in the title molecule, as it was also observed for CF₃CF₂N=SF₂ and CF₃CF₂N=SCl₂.

Subsequent full optimizations and frequency calculations of the stable minima predicts ΔE° (*syn* – *anticlinal*) \approx 1.30 kcal mol⁻¹, see Table 1. From these relative energies we may expect both conformers to be present in the experimental vibrational spectra. The structural parameters of the *anticlinal* form are summarize in Table 2.

As it was mentioned before, the anticlinal conformer is expected to be significantly more stable than the syn form, because the F atom and the bulky CF₃ groups are maximally separated in the former. The existence of the sterically unfavourable syn orientation around the N=S bond can be rationalized by orbital interactions between the lone pairs of N and S and the vicinal antibonding σ^* orbitals. From a natural bond orbital analysis (NBO) of the B3LYP/6-311+G(2df) wavefunction these anomeric effects stabilize the syn orientation by 33 kcal/mol compared to only 22 kcal/mol for the anticlinal orientation. Fig. 4 depicts the molecular orbitals involved in the relevant orbital interactions. These strong orbital interactions apparently override steric repulsions. The deletion of certain NBO's to avoid NBO donor-acceptor interactions allows to determine the energetic effect in the configurations involved as the difference between the original fully-optimized geometry and the NBO-deleted optimized geometry. The role of electronic delocalization can be quantitatively assessed by deleting all non-Lewis (starred) NBO's from the basis set. The resulting natural Lewis structure wavefunction is perfectly localized, with all Lewis-type NBO's doubly occupied. The Lewis-type wavefunction



Fig. 3. Calculated potential functions for rotation around the N=S bond.

has an energy that is higher than the original energy. The net energy difference gives the stabilizing effect of the delocalizing (non-Lewis) contributions. In this case, the localized contribution favors the *anticlinal* form; in contrast, the $\Delta E(NL) = \Delta E(full) - \Delta E(L)$ term strongly favors the *syn* conformer. It is clear then that in the present study the steric effects exert a stronger influence than the orbital interactions in the determination of the structure adopted by the global minimum of the potential energy surface.

Vibrational spectroscopy

According to the calculated relative energy found for the *anticlinal* and *syn* forms of CF₃CF₂N=S(F)CF₃, both conformers might be observed in equilibrium in the fluid phases. Unfortunately, only a few remarkable differences between corresponding vibrational fundamentals were predicted in the calculated spectra which complicate the distinction of the conformers in the spectra registered at room temperature. Besides the low relative abundance of the second form in equilibrium, differences of 4 to 16 cm⁻¹ in calculated wavenumbers (see Table 3) are too low to support the evidence of this equilibrium. Table 3 lists the experimental and calculated frequencies and a tentative assignation of the main vibrational modes on the basis of data reported for CF₃CF₂N=SF₂ [5], CF₃CF₂N=SCl₂ [8], FC(O)N=S(F)CF₃ [9] and CF₃C(O)N=S(F)CF₃ [10] and taking into account theoretical calculations at different levels of theory (MP2/6-311+G(2df) and B3PW91/6-311+G(2df)).



Fig. 2. Molecular models for the most stable forms of CF₃CF₂N=S(F)CF₃.

Table 1

Calculated relative energies, free energies (kcal/mol) ^a and relative abundances (%) at 298 K for the <i>anticlinal</i> and <i>syn</i> forms of CF ₃ CF ₂ N=S(F)CF ₃ .									
Form	B3LYP/6-311+G(2df)			B3PW91/6-311+G(2df)			MP2/6-311+G(d)		
	⊿E°	ΔG°	%	ΔE°	ΔG°	%	ΔE°	ΔG°	%
Anticlinal	0.00	0.00	84.1	0.00	0.00	93.8	0.00	0.00	96.0
Svn	0.97	1.00	15.9	1.64	1.63	6.2	1.29	1.90	4.0

^a Energy differences $\Delta X^{\circ} = X^{\circ}(syn) - X^{\circ}(anticlinal)$, (X = E, G).

Table 2	
Calculated geometric parameters for the	e anticlinal conformer of $CF_2CF_2N=S(F)CF_2^a$.

	MP2 6-311+G(d)	B3LYP 6-311+G(2df)	B3PW91 6-311+G(2df)
C1—F	1.332	1.334	1.330
C2—F	1.356	1.361	1.355
C1-C2	1.544	1.558	1.555
C—N	1.418	1.409	1.406
N=S	1.544	1.535	1.532
S—F	1.707	1.657	1.644
S—C	1.866	1.893	1.882
C3—F	1.323	1.324	1.319
F1-C1-F2,3	108.7	108.7	108.7
F2-C1-F3	109.0	108.8	108.9
F1-C1-C2	110.1	110.0	110.0
F2, 3-C1-C2	110.0	110.3	110.2
F4-C2-F5	107.0	106.4	106.6
F4,5-C2-N	112.5	112.6	112.6
C2-N=S	117.3	119.6	118.9
N=S-F6	111.6	110.3	110.3
N=S-C3	97.3	98.4	98.4
F6—S—C3	89.8	91.2	91.4
S-C3-F7	111.5	111.8	111.7
S-C3-F8,9	107.7	107.6	107.6
C1-C2-N=S	126.4	133.0	132.4
C2-N=S-F6	102.3	101.5	101.8
C2-N=S-C3	-165.0	-164.1	-163.5

^a Bond lengths in Å and angles in degrees. Mean values are given for parameters that are not unique. See Fig. 2 for atom numbering.

Figs. 5 and 6 show experimental infrared and Raman spectra and a graphical comparison of calculated *anticlinal* and *syn* Raman spectra.

The replacement of the fluorine atoms bonded to sulfur for chlorine atoms in the $C_2F_5N=SX_2$ series cause a red shift, from 1340 to 1292 cm⁻¹ of the corresponding N=S stretching modes observed in infrared. Had no change in the conformational preferences occurred in the present study, an intermediate value for the

corresponding vibrational fundamental might have been observed. The N=S stretching belonging to the *anticlinal* form was assigned to the signal centered at 1268 cm^{-1} in the infrared spectra (1261 cm⁻¹, Raman), in agreement with the assignment reported for the FC(O)N=SF₂ [4], FC(O)N=SCl₂ [7] and FC(O)N=S(F)CF₃ [9] series (1330, 1245 and 1105 cm⁻¹, respectively).

The low intensity infrared absorption at 1380 cm⁻¹ in the infrared spectrum (1377 cm⁻¹, Raman) was assigned to the C–C stretching mode in concordance with the literature (1410 and 1380 cm⁻¹ for $C_2F_5N=SF_2$ and $C_2F_5N=SCl_2$, respectively) and theoretical calculations (1417, 1352 and 1369 cm⁻¹ with the MP2, B3LYP and B3PW91 approximations).

As it is expected, the vibrational modes belonging to the C_2F_5 and CF_3 groups lie in the same region of the vibrational spectra and were predicted strongly coupled. The symmetric stretching modes belonging to the sulfur bonded CF_3 group were assigned to the strong signals centered at 1256 and 1151 cm⁻¹ in the infrared spectrum, while the antisymmetric stretching, together with the corresponding vibration for the terminal CF_3 group of the C_2F_5 entity, was observed at 1210 cm⁻¹ (1225 cm⁻¹, Raman). The remaining stretching frequencies of the C1F₃ group were assigned to the signals observed at 1243 and 1110 cm⁻¹. The asymmetric and symmetric stretching modes of the fluoromethylene group were observed at 1170 and 1046 cm⁻¹.

Unfortunately, the calculated wavenumbers for all stronger bands in the IR-gas spectrum show only small differences (<10 cm⁻¹) for the two conformers and the presence of both forms cannot be detected in the experimental spectra. The largest difference in wavenumbers (about 20 cm⁻¹) is predicted for the C—N stretch which possesses a very low IR intensity but the highest intensity in the Raman spectrum. Comparison of calculated and experimental Raman spectra (Fig. 6) for the C—N stretching region clearly demonstrates the presence of both conformers. However, it is not possible to determine the ratio of the mixture, since calculated Raman intensities are very unreliable. The C—N stretching for the *syn* conformer might be assigned to the signal at 768 cm⁻¹



Fig. 4. Relevant NBO orbitals [B3LYP/6-311+G(2df)] for the sulfur imide bond of CF₃CF₂N=S(F)CF₃ in the syn (above) and anticlinal (below) configurations.

Table 3				
Experimental and calculated wavenumbers	of the anticlinal (1) and syn (11) conformers	s of CF ₂ CF ₂ N=S(F)CF ₂ and tentative	assignments of main fundame	ental vibrational modes

Approximate description ^a	Approximate description ^a Experimental ^b		Calculated ^c					
	IR (gas)	Raman (liquid)	MP2/6-311+G(d)		B3LYP/6-311+G(2df)		B3PW91/-311+G(2df)	
			I	Ш	Ι	II	I	II
C—C Stretch.	1380 (13)	1377 (10)	1417 (1)	1432 (2)	1352 (5)	1366 (10)	1369 (5)	1382 (11)
N=S Stretch.	1268 (92)	1261 (17)	1316 (100)	1334 (100)	1270(100)	1291(100)	1290(100)	1313(100)
C3F ₃ Sym. Stretch.	1256 (79)	1235 (17)	1276 (51)	1266 (45)	1240 (56)	1233 (42)	1262 (60)	1257 (43)
C1F ₃ Sym. Stretch.	1243 (88)	-	1255 (35)	1252 (52)	1214 (39)	1211 (54)	1236 (41)	1234 (55)
C3F ₃ Asym. Stretch.	1210 (91)	1225 (16)	1247 (32)	1246 (30)	1211 (24)	1208 (30)	1234 (24)	1229 (30)
C1F ₃ Asym. Stretch.	1210 (91)	1225 (16)	1236 (28)	1230 (23)	1198 (25)	1196 (19)	1220 (24)	1219 (18)
C2F ₂ Asym. Stretch.	1170 sh	-	1178 (27)	1166 (19)	1128 (27)	1122 (29)	1149 (27)	1145 (24)
C3F ₃ Sym. Stretch.	1151(100)	1128 (16)	1151 (62)	1148 (68)	1108 (64)	1109 (62)	1125 (65)	1131 (56)
C1F ₃ Sym. Stretch.	1110 sh	1109 (15)	1131 (26)	1135 (16)	1085 (30)	1092 (17)	1108 (30)	1112 (26)
C2F ₂ Sym. Stretch.	1046 (14)	1027 (12)	1050 (20)	1052 (27)	1027 (16)	1033 (27)	1040 (15)	1044 (26)
C—N Stretch.	-	791 (100)	804 (1)	784 (<1)	789 (2)	768 (2)	800(2)	778 (<1)
C3F ₃ Sym. Def.	-	768 (59)	779(1)	762 (<1)	761 (2)	747 (5)	771 (2)	757 (1)
S—F6 Stretch.	756 (61)	754 (54)	733 (6)	733 (10)	724 (4)	718 (13)	731 (4)	724 (14)
S—C3 Stretch.	-	469 (28)	500 (2)	526 (<1)	495 (1)	514 (<1)	498 (1)	518 (<1)

^a Stretch.: stretching; Def.: deformation; Asym.: antisymmetric; Sym.: symmetric; sh: shoulder. See Fig. 2 for atom numbering.

^b Gas: *P* = 2.0 mbar (glass cell, 200 mm optical path length, Si windows, 0.5 mm thick), relative absorbance at band maximum in parentheses; liquid: room temperature, relative band intensity in parentheses.

^c Relative infrared intensities in parentheses; 100%: 674 [667], 658 [643] and 646 [642] km/mol (*anticlinal* form) with MP2, B3LYP and B3PW91, respectively (between brackets values for the *syn* form are given).



Fig. 5. Vibrational spectra of $CF_3CF_2N=S(F)CF_3$ at room temperature. Top: gas phase infrared spectrum of (P = 2 mbar); (* windows bands). Bottom: Liquid phase Raman spectrum.

(Raman) showing a 23 cm⁻¹ red shift with respect to the most abundant *anticlinal* form in excellent agreement with the predicted theoretical shifts ($\Delta v = 20$, 21 and 22 cm⁻¹, with MP2, B3LYP and



Fig. 6. Graphical comparison of the experimental and theoretical (B3LYP/6-311+G(2df)) Raman spectra in the C–N stretching region of *anticlinal* and *syn* forms of $CF_3CF_2N=S(F)CF_3$.

B3PW91 methods respectively). On the other hand, the symmetric deformations of the mentioned CF₃ group could be assigned to the bands centered at 768 and 754 cm⁻¹ for the *anticlinal* and *syn* forms, respectively (average theoretical shift: $\Delta v = 14 \text{ cm}^{-1}$), although the last frequency was predicted as a very low intensity signal in the Raman spectrum. In that case, the unexpected intensity observed mostly accounts for the contribution of the S—F stretching mode (see below). However, the relative abundance of the second form in equilibrium was predicted too low to account for the strong signals mentioned above for the *syn* conformer, making the assumption of such equilibrium not feasible. The assignation of the 756/754 cm⁻¹ signals of the vibrational spectra to the S—F stretching is in agreement with data reported for FC(O)N=S(F)CF₃[9] and CF₃-C(O)N=S(F)CF₃[10] (720 and 715 cm⁻¹, respectively in the infrared spectra).

Finally, the signal observed at 469 cm⁻¹ in the Raman spectrum was assigned to the S–C stretching in good agreement with the theoretical calculations (500, 495 and 498 cm⁻¹, with MP2, B3LYP and B3PW91, respectively) and data reported for FC(O)N= $S(F)CF_3$ y $CF_3C(O)N=S(F)CF_3$, (471 and 472 cm⁻¹, respectively).

Conclusions

Experimental and theoretical conformational studies of several RN=SF₂ and RN=SCl₂ compounds resulted in sterically unfavorable syn structures and no contribution of an anticlinal conformer was observed. The strong preference for the syn structure is explained by anomeric effects between the nitrogen and sulfur lone pairs with vicinal antibonding σ^* orbitals, which are much higher in the syn than in the anticlinal conformer and override the higher steric repulsions. In contrast to these results, gas electron diffraction, vibrational and guantum chemical studies of the unsymmetrically substituted compounds FC(O)N=S(F)CF₃ and CF₃C(O)N=S(F)CF₃ resulted in a mixture of syn and anticlinal structures around the N=S bond, with preference of the anticlinal conformer. For CF₃CF₂₋ N=S(F)CF₃ quantum chemical calculations also predict a strong preference of the anticlinal form with only small contributions (4–16%) of the syn form. Although anomeric interactions strongly favor the syn conformer also in the unsymmetrically substituted sulfur compounds, these effects no longer fully override the increased steric interactions due to the CF₃ group bonded to sulfur. The vibrational spectra have been assigned for the anticlinal conformer. The presence of the syn conformer is clearly demonstrated in the N–C region of the Raman spectra of the liquid phase. Because of the large uncertainties in calculated Raman intensities it is not possible to derive a ratio of the mixture from the experimental spectra.

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