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Structural, conformational and vibrational properties of 1,1,1-Trifluoro-N-(1,1,2,2,2-pentafluoroethyl) methanesulfinimidoyl chloride, $\text{CF}_3\text{CF}_2\text{-N}=\text{S}(\text{Cl})\text{CF}_3$

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SpectrochimicaActa A: Molecular and Biomolecular Spectroscopy**Full Article****Structural, conformational and vibrational properties of 1,1,1-Trifluoro-
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Structural, conformational and vibrational properties of 1,1,1-Trifluoro-N-(1,1,2,2,2-pentafluoroethyl) methanesulfinimidoyl chloride,
 $\text{CF}_3\text{CF}_2\text{-N=S(Cl)CF}_3$

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Abstract

The structural, conformational, and configurational properties of 1,1,1-Trifluoro-N-(1,1,2,2,2-pentafluoroethyl) methanesulfinimidoyl chloride, $\text{CF}_3\text{CF}_2\text{-N=S(Cl)CF}_3$ 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), 6-311+G(df) and 6-311+G(2df) basis sets]. According to these theoretical approximations, $\text{CF}_3\text{CF}_2\text{-N=S(Cl)CF}_3$ exists in the gas phase as a mixture of a favored *anticlinal* form (C–N bond *anticlinal* with respect to the C–S–Cl bisector) with C_1 symmetry and a less abundant *syn* conformer showing C_1 symmetry as well ($\Delta G^\circ \approx 1.20 \text{ kcal mol}^{-1}$). Due to the small contribution only a few corresponding vibrational modes of the *syn* conformer could be assigned confidently in the experimental spectra. Compared to $\text{CF}_3\text{CF}_2\text{-N=S(F)CF}_3$, the replacement of F by Cl produces a clear change in N=S bond length and the corresponding stretching frequency, without affecting the conformational properties.

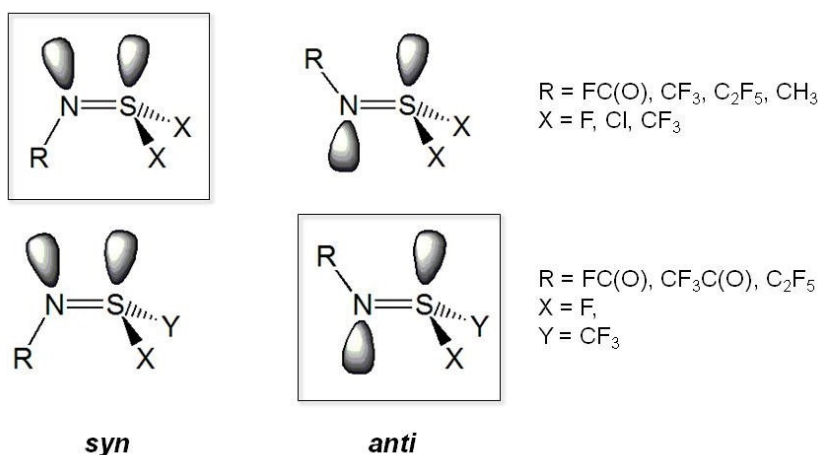
Keywords

Vibrational spectroscopy; Quantum chemical calculations; Conformational equilibrium; 1,1,1-Trifluoro-N-(1,1,2,2,2-pentafluoroethyl) methanesulfinimidoyl chloride

Introduction

Structural, conformational and vibrational properties of molecules of the type $R-N=SX_2$ have been studied extensively by gas electron diffraction, vibrational spectroscopy and quantum chemical calculations. A few representative examples are $FC(O)-N=SF_2$ [1], $FC(O)-N=SCl_2$ [2], $CF_3-N=SF_2$ [3], $CF_3-N=SCl_2$ [4], $CF_3CF_2-N=SF_2$ [5] and $CF_3CF_2-N=SCl_2$ [6]. These compounds with symmetric halogen substitution at the sulfur atom possess interesting conformational properties, since for all compounds only the sterically unfavorable *syn* structure ($R-N$ bond *syn* with respect to the $X-S-X$ bisector) was observed in the experiments (see first framed structure in Scheme I). According to quantum chemical calculations (B3LYP/6-311+G(2df)) the *anti* conformer of both compounds is appreciably higher in energy than the *syn* form, by 5.1 kcal/mol in the case of $CF_3-N=SF_2$ and by 8.5 kcal/mol for $CF_3-N=SCl_2$. Orbital interactions between the electron lone pairs of nitrogen and sulfur with vicinal antibonding orbitals, $lp(N) \rightarrow \sigma^*(S-X)$ and $lp(S) \rightarrow \sigma^*(N-C)$, strongly favor the *syn* conformers. The interaction energies of these anomeric effects in the *syn* form are higher by 15 kcal/mol in $CF_3-N=SF_2$ and by 31 kcal/mol in $CF_3-N=SCl_2$ and thus override the stronger steric interactions in these conformers. The replacement of halogen atoms bonded to sulfur by bulkier groups, such as in $CH_3-N=S(CF_3)_2$ [7], does not affect these conformational preferences. Also in this compound the *syn* form is lower in energy by 5.2 kcal/mol, according to calculations. Again, higher orbital interactions (27 kcal/mol) favor the sterically highly unfavorable *syn* conformer. This indicates that steric effects are of minor importance. However, substitution

of one fluorine atom bonded to sulfur in the corresponding $R-N=SF_2$ molecules by a CF_3 group yields unexpected results. For the compounds $FC(O)-N=S(F)CF_3$ [8], $CF_3C(O)-N=S(F)CF_3$ [9] and $CF_3CF_2-N=S(F)CF_3$ [10] an equilibrium of *anti* and *syn* conformers has been observed, but with the *anti* form being more stable (see second framed structure in Scheme I). This demonstrates that replacing one of the fluorine atoms bonded to sulfur by a CF_3 group leads to a remarkable change of the conformational properties of the involved compounds.



Scheme I

Fluorine has long attracted attention as a useful substituent to modify the properties of organic compounds. Its small size, high electronegativity and the high carbon-fluorine bond strength induce significant changes in polarity, solubility, reactivity and metabolic stability with minimal steric effects. While the introduction of fluorine may not change the size of a molecule appreciably, it can have a profound impact on its shape and interactions with its neighboring groups. Fluorine participates in a number of subtle effects that modify the conformational preferences of organic compounds, suggesting that the C–F bond is potentially useful as a molecular design tool [11]. Consequently, more effort has been invested to replace different atoms or functional groups by fluorine atoms than vice versa.

On one hand, it was pointed out above that steric strain present in symmetrically substituted iminosulfur molecules does not prevent the adoption of *syn* configurations; on the other hand, as soon as asymmetric substitution on the sulfur atom is present, the global minimum of the potential energy surface corresponds to the expected sterically least hindered *anti* conformation. In all studied compounds, fluorine replacement was involved. Now the question arises whether substitution of a chlorine atom in $\text{XN}=\text{SCI}_2$ compounds by a CF_3 group would also induce such conformational changes. We report here a conformational study of 1,1,1-Trifluoro-N-(1,1,2,2,2-pentafluoroethyl)methanesulfinimidoylchloride ($\text{CF}_3\text{CF}_2-\text{N}=\text{S}(\text{Cl})\text{CF}_3$), based on its vibrational spectra [IR (vapor) and Raman (liquid)] and quantum chemical calculations at different levels of theory. Natural bond orbital (NBO) population analyses have been applied to rationalize the effect of electronic interactions on the structural, conformational, and configurational properties of $\text{CF}_3\text{CF}_2-\text{N}=\text{S}(\text{Cl})\text{CF}_3$.

Materials and Methods

Experimental

1,1,1-Trifluoro-N-(1,1,2,2,2-pentafluoroethyl)methanesulfinimidoylchloride, $\text{CF}_3\text{CF}_2-\text{N}=\text{S}(\text{Cl})\text{CF}_3$, was synthesized by the reaction of $\text{CF}_3\text{CF}_2-\text{N}=\text{S}(\text{F})\text{CF}_3$ and PCl_5 [12]. The product obtained was purified at reduced pressure by repeated trap-to-trap distillations. A gas phase FT-IR spectrum at 2 mbar was recorded in the region $4000 - 400 \text{ cm}^{-1}$ at room temperature using a Perkin-Elmer GX1 Fourier Transform infrared instrument (4 cm^{-1} spectral resolution) using a 10 cm path-length cell equipped with KRS-5 windows. The Raman spectrum of the liquid was recorded at room temperature in the range $3000 - 50 \text{ cm}^{-1}$ by employing a diode-pump, solid state 532 nm green laser with 9.2 mW power at the sample for excitation in a ThermoScientific DXR Smart Raman instrument equipped with CCD detector. The resolution was between $2.7 - 4.2 \text{ cm}^{-1}$ with a grating groove density of 900 lines/mm. A confocal aperture of $25 \mu\text{m}$

pinhole was used and 40 exposures of 8 s were accumulated for the sample in order to achieve sufficient signal to noise ratio.

Computational Details

All quantum chemical calculations were performed using the GAUSSIAN 03 program [13]. Geometry optimizations were performed with the MP2 [14], B3LYP [15] and B3PW91 [16] approximations using 6-311+G(d), 6-311+G(df) and 6-311+G(2df) basis sets and standard gradient techniques with simultaneous relaxation of all geometric parameters. Natural population analysis and second order donor-acceptor interaction energies were estimated by using the Natural Bond Orbital analysis (NBO) [17] as implemented in the GAUSSIAN 03 program with the B3LYP/6-311+G (d) approximation.

Results and Discussion

Quantum chemical calculations

From Figure 1 it is clear that at least two configurations around the N=S double bond of $\text{CF}_3\text{CF}_2\text{-N=S(Cl)CF}_3$ are feasible. However, according to the results reported for molecules of the type R-N=S(F)CF_3 [8–10], an *antiperiplanar* arrangement of the C–N bond with respect to the X–S–Y bisector was preferred. Figure 2 shows the potential energy curve for rotation around the N=S bond calculated by structure optimizations at fixed dihedral angles $\phi(\text{C-N=S-Cl})$ in steps of 30° and confirms the assumption inferred above. The global minimum corresponds to an *antiperiplanar* form, with $\phi(\text{C-N=S-Cl}) \approx 260^\circ$, while a second minimum corresponds to a *syn* arrangement of the C–N and the X–S–Y bisector with $\phi(\text{C-N=S-Cl}) \approx 60^\circ$.

Figure 1, near here

Figure 2, near here

The strong repulsion between the chlorine atom and the trifluoromethyl group bonded to the sulfur atom and the fluorine atoms belonging to the pentafluoroethyl group cause a molecular distortion. Consequently, the exact *syn* and *anti* conformations observed for the symmetrically substituted iminosulfur compounds $\text{CF}_3\text{-N=SCl}_2$ and $\text{CF}_3\text{N=SF}_2$ do not exist for the title molecule, as it was also observed for $\text{CF}_3\text{CF}_2\text{-N=SF}_2$, $\text{CF}_3\text{CF}_2\text{-N=SCl}_2$ and $\text{CF}_3\text{CF}_2\text{-N=S(F)CF}_3$. From the relative free energies obtained by subsequent full optimizations and frequency calculations of the two stable minima, ΔG° (*syn* – *anticlinal*) \approx 1 kcal mol⁻¹ or slightly larger (see Table 1), we expect both conformers to be present in the experimental vibrational spectra. The structural parameters of the *anticlinal* form are summarized in Table 2. As it was mentioned before, the *anticlinal* conformer is expected to be more stable than the *syn* form, because in the *anticlinal* form the chlorine atom and the bulky CF_3 group bonded to sulfur are further away from the C_2F_5 group bonded to nitrogen than in the *syn* conformer.

Table 1, near here**Table 2, near here**

The difference in conformational properties of symmetrical R-N=SX_2 compounds, in which the *syn* form is strongly favored, and the unsymmetrical R-N=S(Cl)CF_3 derivative, in which an *anticlinal* structure is slightly favored, is predominately due to anomeric effects. Whereas these orbital interactions favor the *syn* conformer in the symmetrical compounds $\text{CF}_3\text{N=SF}_2$, $\text{CF}_3\text{N=SCl}_2$ and $\text{CH}_3\text{N=S(CF}_3)_2$ by 15, 31 and 27 kcal/mol, respectively, and override the larger steric repulsions in this form (see Introduction), the difference of these interaction energies in the two conformers of $\text{CF}_3\text{CF}_2\text{-N=S(Cl)CF}_3$ is much smaller. From a natural bond orbital analysis (NBO) of the B3LYP/6-311+G(2df) wavefunction the anomeric effects stabilize the *syn* orientation by 64 kcal/mol compared to 59 kcal/mol for

the *anticlinal* orientation. Therefore, the anomeric effects still favor the *syn* conformer by 5 kcal/mol, but this difference is too small to override the higher steric interactions in this form. Figure 3 depicts the molecular orbitals involved in the relevant orbital interactions in both conformers. 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 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 $\Delta E(NL) = \Delta E(\text{full}) - \Delta E(L)$ 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.

Figure 3, near here

Vibrational analysis

The small energy difference predicted between the *anticlinal(I)* and *syn(II)* forms indicate a conformational equilibrium of both structures and therefore signals belonging to both conformers should be observed in the fluid phases. Unfortunately, only a few vibrational fundamentals are predicted to be split enough to distinguish between both conformers. Figures 4 and 5 show a graphical comparison of experimental infrared and Raman spectra with calculated spectra (B3LYP/6-311+G(2df)) taking into account a mixture of both conformers as predicted by the DFT method. A tentative assignment of the $3N - 6 = 36$ experimental and calculated (B3LYP/6-311+G (2df), B3PW91/6-311+G (2df) and MP2/6-311+G (df)) vibrational modes was performed, considering data reported for $C_2F_5-N= SX_2$ (X = F [5], Cl [6]) and $C_2F_5-N=S(F)CF_3$ [10] (see Table 3). The DFT calculations predict the experimental frequencies considerably closer than the MP2 approximation.

Figure 4, near here

Figure 5, near here

Table 3, near here

The N=S stretching signal was observed at 1340 and 1292 cm^{-1} , respectively, in the infrared spectra of $\text{C}_2\text{F}_5\text{-N=SF}_2$ and $\text{C}_2\text{F}_5\text{-N=SCl}_2$. The frequency lowering observed as a consequence of a decrease in the electron withdrawing properties of the atoms bonded to sulfur was followed by the expected bond length elongation, according to values obtained with the B3LYP/6-311+G(2df) approximation (1.491 and 1.510 Å, respectively).

The N=S bond length and corresponding stretching mode of *anticlinal* conformer of $\text{C}_2\text{F}_5\text{-N=S(F)CF}_3$ were reported at 1.535 Å (B3LYP/6-311+G(2df)) and 1268 cm^{-1} (IR), respectively. In the present study, a 1.550 Å bond length was predicted and a signal with the same characteristics was observed at 1238 cm^{-1} in the infrared spectrum of $\text{C}_2\text{F}_5\text{-N=S(Cl)CF}_3$. From these findings we postulate that as long as conformational preferences change or different substituents are bonded to the sulfur atom, it is the electron withdrawing effect which governs the vibrational frequency shift, allowing us a confident assignment of the 1238 cm^{-1} signal to the N=S stretching of the title compound.

Taking into account data reported for $\text{CF}_3\text{CF}_2\text{-N=SX}_2$ ($X = \text{F, Cl}$) the symmetric and asymmetric stretching modes of the CF_3 of the perfluoroethyl substituent was assigned to the signals observed at 1265 and 1210 cm^{-1} , respectively, in the infrared spectrum of the *anticlinal* conformer of the title compound. The totally symmetric mode was assigned to the strong feature at 1115 cm^{-1} . The shoulder observed towards lower frequencies might be assigned to the corresponding vibration of the *syn* conformer, being the first evidence of its presence in the fluid phases. This assumption is consistent with the theoretical frequency shift predicted by all theoretical calculations ($\Delta\nu \approx 6 \text{ cm}^{-1}$). In agreement with data reported for $\text{CF}_3\text{CF}_2\text{-N=S(F)CF}_3$, the asymmetric band placed at 1238 cm^{-1} in the infrared spectrum might contain the highest frequency symmetric stretchings of the trifluoromethyl group bonded to the sulfur atom, while the totally symmetric mode was observed as a distinct

signal at 1153 cm^{-1} . With regard to the stretching modes belonging to the CF_2 group, the asymmetric stretching was assigned to the signal observed at 1129 cm^{-1} while the corresponding symmetric mode was attributed to the feature at 1008 cm^{-1} . All theoretical calculations performed predict the CF_2 symmetric stretching of the *syn* form little blue shifted with respect to the *anticlinal* configuration. Therefore, the signal placed at 1023 cm^{-1} in the infrared spectrum and the shoulder at higher frequencies of the signal centered at 1002 cm^{-1} in the Raman spectrum constitute additional evidence of the second form in equilibrium at room temperature. Finally, to finish with the assignment of the stretching modes of the perfluoroethyl group, the C–C stretching was assigned to the feature at 1374 and 1375 cm^{-1} in the infrared and Raman spectrum, respectively, in close agreement with the assignment proposed for $\text{CF}_3\text{CF}_2\text{--N=S(F)CF}_3$ (1380 and 1377 cm^{-1}), $\text{CF}_3\text{CF}_2\text{--N=SCl}_2$, (1380 and 1378 cm^{-1}) and $\text{CF}_3\text{CF}_2\text{--N=SF}_2$ (1410 and 1408 cm^{-1}).

The C–N stretching in the *anticlinal* form was predicted at higher frequencies ($\Delta\nu \approx 21\text{ cm}^{-1}$) than the corresponding mode for the *syn* configuration. Therefore, the signals observed at 787 and 766 cm^{-1} in the infrared spectrum (788 and 767 cm^{-1} , Raman) were attributed to those vibrations for the *syn* and *anticlinal* configurations, respectively. The S–C stretching was assigned to the band centered at 493 cm^{-1} in the infrared spectrum in agreement with data reported for FC(O)--N=S(F)CF_3 [8], $\text{CF}_3\text{C(O)--N=S(F)CF}_3$ [9] and $\text{CF}_3\text{CF}_2\text{--N=S(F)CF}_3$ [10] (480 , 472 and 469 cm^{-1} , respectively). Finally, the S–Cl stretching was assigned to the band centered at 452 and 450 cm^{-1} in the infrared and Raman spectra, respectively.

Conclusion

For all compounds of the type RN=SF_2 and RN=SCl_2 reported so far [1–6], the experimental and theoretical conformational studies determined sterically unfavorable

*syn*structures as the global minimum of each potential energy surface and no contribution of *anticlinal* configurations. The unexpected 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 quantum chemical studies of the unsymmetrically substituted compounds FC(O)N=S(F)CF_3 and $\text{CF}_3\text{C(O)N=S(F)CF}_3$ and lately $\text{CF}_3\text{CF}_2\text{N=S(F)CF}_3$, resulted in a mixture of *syn* and *anticlinal* structures around the N=S bond, with preference of the *anticlinal* conformer. For $\text{CF}_3\text{CF}_2\text{N=S(F)CF}_3$ and $\text{CF}_3\text{CF}_2\text{N=S(Cl)CF}_3$ quantum chemical calculations also predict a preference of the *anticlinal* form with only small contributions (4% to 17%) of the *syn* form. Even though anomeric interactions favor the *syn* conformer also in the asymmetrically substituted sulfur compounds, their contribution exerts a less strong effect than in the RN=SF_2 and RN=S(Cl)_2 compounds and these anomeric effects no longer fully override the increased steric interactions due to the CF_3 group bonded to sulfur. For a few corresponding vibrational fundamentals, the features observed in the vibrational spectra might account for the presence of the *syn* conformer. Unfortunately, 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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Figure Captions

Fig 1. Molecular models for the most stable forms of $\text{CF}_3\text{CF}_2\text{-N=S(Cl)CF}_3$.

Fig 2. Calculated potential functions for rotation around the N=S bond.

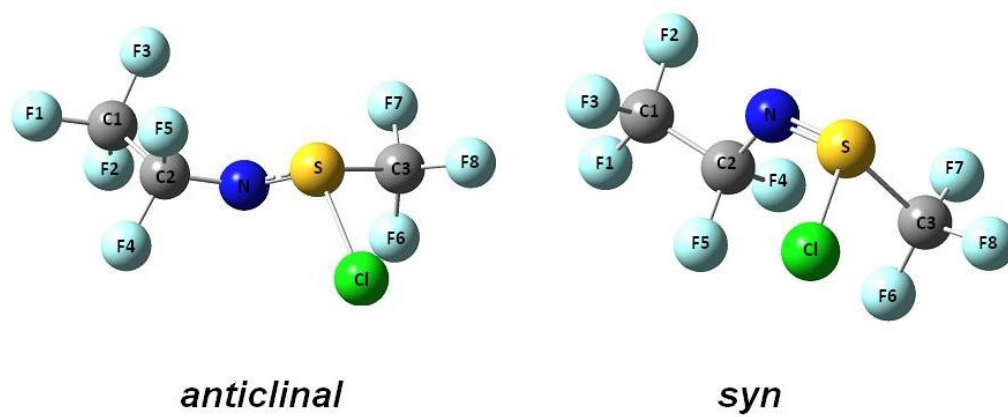
Fig. 3. Relevant NBO orbitals [B3LYP/6-311+G(2df)] for the sulfur imide bond of $\text{CF}_3\text{CF}_2\text{-N=S(Cl)CF}_3$ in the *syn* (above) and *anticlinal* (below) configurations.

Fig. 4. Graphical comparison of the experimental and theoretical mixture of the *anticlinal* and *syn* (B3LYP/6-311+G(2df)) infrared spectra of $\text{CF}_3\text{CF}_2\text{-N=S(Cl)CF}_3$.

Fig. 5. Graphical comparison of the experimental and theoretical mixture of the *anticlinal* and *syn* (B3LYP/6-311+G(2df)) Raman spectra of $\text{CF}_3\text{CF}_2\text{-N=S(Cl)CF}_3$.

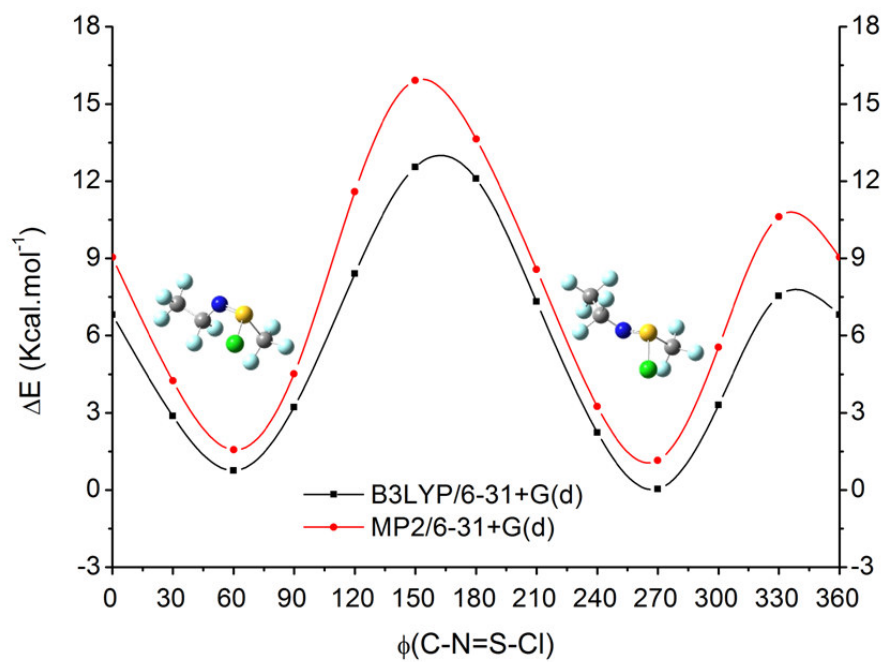
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Figure 1



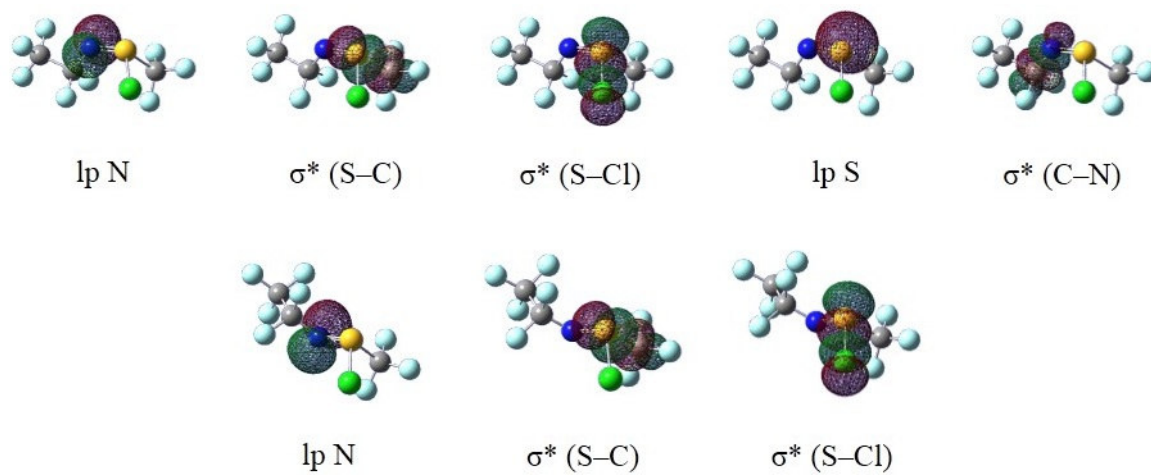
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Figure 2



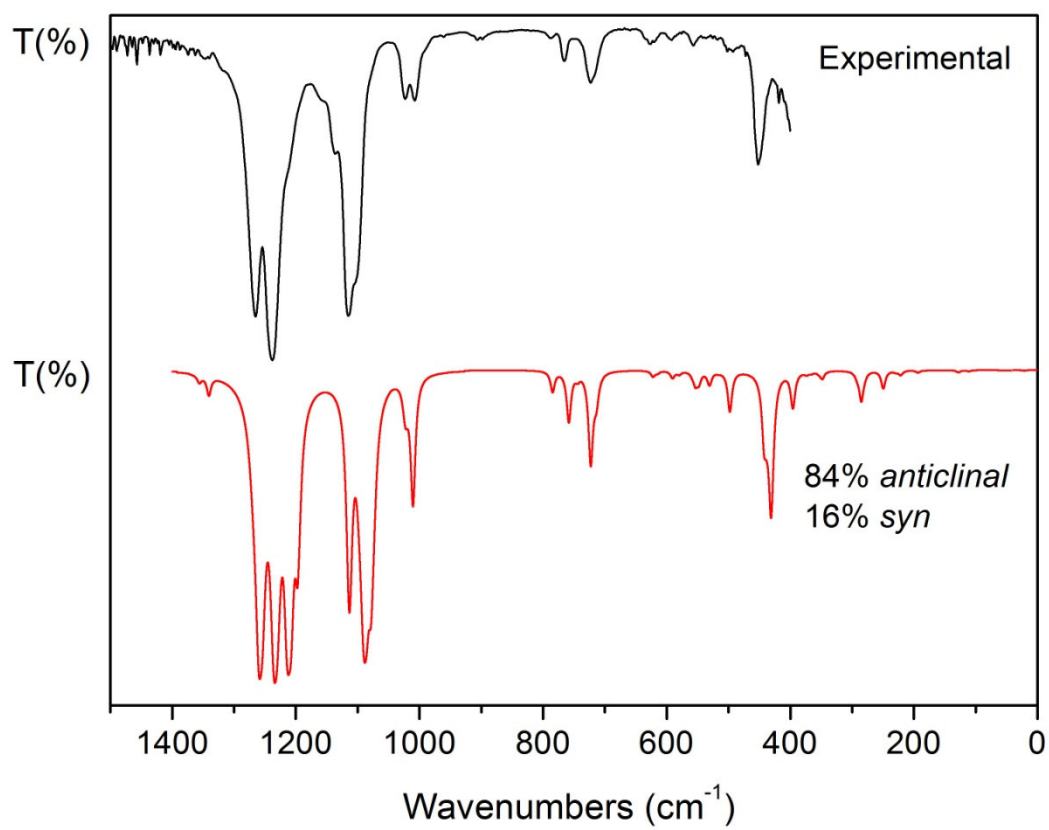
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Figure 3



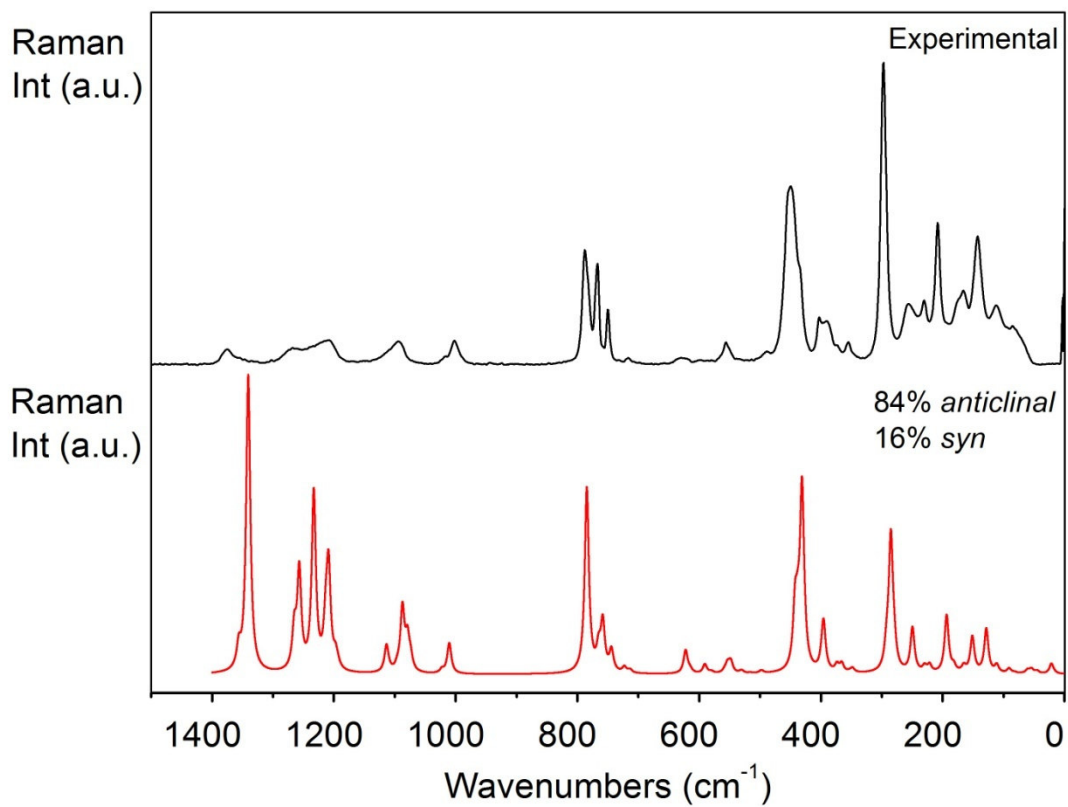
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Figure 4



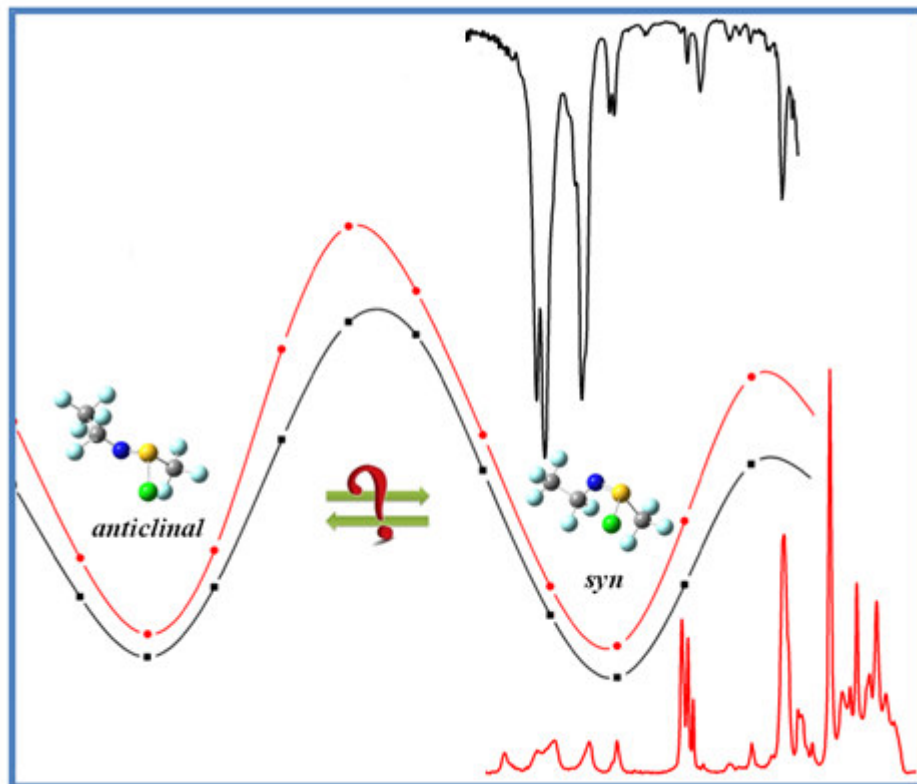
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Figure 5



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Graphical Abstract



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Table 1. Calculated relative energies, free energies (Kcal/mol)^a and relative abundances (%) at 298 K for the *anticlinal* and *syn* forms of CF₃CF₂-N=S(Cl)CF₃.

Form	B3LYP/ 6-311+G(2df)			B3PW91/ 6-311+G(2df)			MP2/6-311+G(df)		
	ΔE°	ΔG°	%	ΔE°	ΔG°	%	ΔE°	ΔG°	%
<i>anticlinal</i>	0.00	0.00	84.1	0.00	0.00	93.8	0.00	0.00	83.2
<i>syn</i>	0.97	1.00	15.9	1.64	1.63	6.2	0.14	0.96	16.8

^aEnergy differences $\Delta X^\circ = X^\circ(\textit{syn}) - X^\circ(\textit{anticlinal})$, (X= E[°], G[°]).

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Table 2. Calculated geometric parameters for *anticlinal* conformer of $\text{CF}_3\text{CF}_2\text{-N=S(Cl)CF}_3$ ^a.

	MP2 6-311+G(df)	B3LYP 6-311+G(2df)	B3PW91 6-311+G(2df)
C1–F	1.323	1.334	1.329
C2–F	1.348	1.362	1.356
C1–C2	1.546	1.559	1.556
C–N	1.412	1.406	1.404
N=S	1.553	1.550	1.546
S–Cl	2.113	2.157	2.124
S–C	1.867	1.902	1.890
C3–F	1.312	1.322	1.318
F1–C1–F2,3	108.9	108.8	108.7
F2–C1–F3	109.2	108.6	108.9
F1–C1–C2	110.4	110.6	110.6
F2,3–C1–C2	109.8	110.0	110.0
F4–C2–F5	106.6	106.3	106.4
F4,5–C2–N	112.9	112.7	112.3
C2–N=S	116.0	119.0	118.4
N=S–Cl	114.2	113.2	113.2
N=S–C3	110.0	97.2	97.2
C1–S–C3	97.1	94.4	94.3
S–C3–F7	111.7	112.2	112.1
S–C3–F8,6	107.6	107.3	107.2
C1–C2–N=S	144.8	134.7	134.3
C2–N=S–Cl	97.5	95.2	95.5

^a Bond lengths in Å and angles in degrees. For atom numbering see Fig. 1. Mean values are given for parameters that are not unique.

Table 3. Experimental and calculated wavenumbers of the *anticlinal (I)* and *syn (II)* conformers of $\text{CF}_3\text{CF}_2\text{-N}=\text{S}(\text{Cl})\text{CF}_3$ and tentative assignment of main fundamental vibrational modes.

Approximate Description ^a	Experimental ^b		Calculated ^b					
	IR ^c (gas)	Raman ^d (liquid)	MP2/ 6-311+G(df)		B3LYP/ 6-311+G(2df)		B3PW91/ 6-311+G(2df)	
			<i>I</i>	<i>II</i>	<i>I</i>	<i>II</i>	<i>I</i>	<i>II</i>
C–C Stretch.	1374 (7)	1375 (9)	1431 (1) [62]	1440 (<1) [38]	1341 (1)[100]	1373 (3)[60]	1358 (1)[100]	1373 (3)[60]
C1F ₃ Sym. Stretch.	1265 (87)	1268 (10)	1329 (61) [15]	1324 (100) [94]	1257 (87)[31]	1287 (100)[100]	1279 (82)[27]	1287 (100)[100]
N=S Stretch.	1238 (100)	1241 sh	1309 (100) [38]	1307 (41) [25]	1233 (100)[56]	1258 (26)[10]	1255 (100)[53]	1258 (26)[10]
C3F ₃ Sym. Stretch.	-	-	1300 (32) [2]	1300 (18) [13]	1213 (40) [12]	1233 (39)[4]	1235 (42)[20]	1233 (39)[4]
C1F ₃ Asym. Stretch.	1210 sh	1209 (29)	1291 (64) [42]	1290 (20) [6]	1209 (26) [31]	1229 (25)[10]	1232 (26)[27]	1229 (25)[10]
C3F ₃ Asym. Stretch.	1210 sh	1209 (29)	1274 (15) [65]	1279 (4) [31]	1197 (17)[3]	1218 (8)[15]	1220 (16)[4]	1218 (8)[15]
C3F ₃ Sym. Stretch.	1153 (24)	-	1198 (27) [12]	1201 (18) [6]	1114 (27) [9]	1133 (19)[5]	1135 (26)[7]	1133 (19)[5]
CF ₂ Asym. Stretch.	1129 (40)	-	1162 (77) [31]	1170 (33) [38]	1087 (74) [19]	1118 (37)[10]	1105 (75)[20]	1118 (37)[10]
C1F ₃ Sym. Stretch. (<i>I</i>)	1115 (87)	-	1158 (25) [38]		1079 (23)[9]		1100 (19)[10]	
C1F ₃ Sym. Stretch. (<i>II</i>)	1105 sh	1094 (12)		1152 (28) [38]		1092 (30)[30]		1092 (30)[30]
CF ₂ Sym. Stretch. (<i>II</i>)	1023 (23)	1021 (7)		1062 (16) [38]		1034 (17)[10]		1034 (17)[10]
CF ₂ Sym. Stretch. (<i>I</i>)	1008 (24)	1002 (12)	1059 (14) [46]		1010 (13)[9]		1024 (12)[10]	
C–N Stretch. (<i>II</i>)	787 (6)	788 (3)	823 (1) [65]		785 (2)[53]		796 (2)[53]	
C–N Stretch. (<i>I</i>)	766 (13)	767 (36)		801 (<1) [63]		775 (<1)[35]		775 (<1)[50]
C1F ₃ Sym. Def.	-	750 (22)	796 (3) [15]	780 (1) [56]	758 (4)[12]	754 (2)[50]	769 (4)[13]	754 (2)[50]
C3F ₃ Sym. Def.	723 (19)	-	751 (9) [1]	742 (8) [6]	723 (8)[1]	720 (11)[5]	730 (8)[2]	720 (11)[5]
C3F ₃ Def.	627 (7)	630 (6)	645 (<1) [8]	636 (<1) [13]	622 (<1)[6]	619 (1)[10]	628 (<1)[7]	619 (1)[10]
C3F ₃ Def.	592 (6)	598 (3)	617 (<1) [2]	607 (1) [6]	591 (<1)[3]	585 (1)[5]	596 (1)[3]	585 (1)[5]
CF ₃ CF ₂ Def.	556 (8)	556 (11)	575 (1) [2]	579 (<1) [6]	553 (1)[3]	563 (1)[5]	558 (1)[3]	563 (1)[5]

C3F ₃ Def.	536 (5)	-	570 (<1) [2]	568 (1) [13]	548 (<1)[3]	552 (1)[5]	554 (1)[3]	552 (1)[5]
CF ₃ CF ₂ Def.	-	-	548 (1) [1]	552 (2) [<1]	530 (1)[<1]	537 (1)[1]	534 (1)[1]	537 (1)[1]
S–C Stretch.	493 (10)	489 (8)	520 (1) [1]	533 (<1) [1]	498 (3)[1]	520 (<1)[1]	502 (4)[1]	520 (<1)[1]
S–Cl Stretch.	452 (43)	450 (61)	476 (4) [12]	460 (9) [81]	442 (5)[16]	456 (12)[80]	450 (10)[37]	456 (12)[80]
CF ₃ CF ₂ Def.	-	434 sh	444 (20) [100]	445 (4) [100]	431 (13)[47]	431 (2)[15]	447 (9)[33]	431 (2)[15]
CF ₃ CF ₂ Def.	-	403 (19)	412 (1) [12]	413 (2)[25]	396 (2)[12]	402 (1)[15]	399 (2)[10]	402 (1)[15]
CF ₃ CF ₂ Def.	-	390 (18)	379 (<1) [4]	396 (<1) [19]	366 (<1)[3]	380 (1)[15]	368 (<1)[3]	380 (1)[15]
CF ₃ CF ₂ Def.	-	375 sh	366 (<1) [1]	371 (<1) [<1]	348 (<1)[1]	356 (<1)[2]	351 (<1)[1]	356 (<1)[2]
CF ₃ CF ₂ Def.	-	355 (11)	311 (<1) [4]	307 (<1) [13]	293 (<1)[3]	292 (<1)[15]	294 (<1)[5]	292 (1)[15]
N=S-Cl Def.	-	297 (100)	306 (3) [50]	304 (1) [75]	285 (2)[34]	287 (<1)[35]	292 (2)[30]	287 (1)[35]
CF ₃ CF ₂ Def.	-	257 (23)	255 (2) [15]	241 (<1) [16]	250 (1)[12]	231 (<1)[15]	251 (1)[10]	231 (<1)[10]
CF ₃ CF ₂ Def.	-	231 (24)	231 (<1) [8]	230 (<1) [<1]	222 (<1)[12]	219 (<1)[1]	221 (<1)[3]	219 (<1)[<1]
C–C–N Def.	-	209 (49)	210 (<1) [12]	199 (<1) [19]	193 (<1)[16]	183 (<1)[10]	196 (<1)[13]	183 (<1)[10]
C–C Torsion	-	166 (27)	159 (<1) [8]	180 (<1) [6]	151 (<1)[9]	167 (<1)[10]	152 (<1)[7]	167 (<1)[10]
C–S–Cl Def.	-	143 (44)	142 (<1) [15]	132 (<1) [20]	128 (<1)[9]	128 (<1)[10]	132 (1)[10]	128 (<1)[10]
C–N=S Def.	-	112 (23)	117 (<1) [4]	110 (<1) [9]	111 (<1) [3]	91 (<1)[10]	112 (<1)[3]	91 (<1)[10]
N=S Torsion	-	86 (16)	72 (<1) [1]	88 (<1) [11]	61 (<1) [1]	81 (<1)[10]	61 (<1)[1]	81 (<1)[2]
ClF ₃ Torsion	-	-	61 (<1) [<1]	81 (<1) [15]	55 (<1) [1]	72 (<1)[1]	55 (<1)[1]	72 (<1)[<1]
SC3F ₃ Torsion	-	-	47 (<1) [<1]	60 (<1) [2]	45 (<1) [1]	51 (<1)[1]	45 (<1)[1]	51 (<1)[1]
C–N Torsion	-	-	13 (<1) [2]	28 (<1) [2]	21 (<1) [1]	16 (<1)[1]	22 (<1)[3]	16 (<1)[1]

^a Stretch.: stretching ; Def.: deformation ; asym.: asymmetric ; sym.: symmetric; sh: shoulder. See Fig. 1 for atom numbering. ^b Gas: P = 2.0 mbar (glass cell, 200 mm optical path length, KRS-5 windows, 0.5 mm thick), relative absorbance at band maximum in parentheses; liquid: room temperature, relative band intensity in parentheses. ^c Infrared intensities. ^d Raman intensities.

- $\text{CF}_3\text{CF}_2\text{N}=\text{S}(\text{Cl})\text{CF}_3$ exists in the gas phase as a mixture of *anticlinal* and *syn* forms.
- Theoretical calculations predict the *anticlinal* form as the global minimum.
- $\text{CF}_3\text{CF}_2\text{N}=\text{S}(\text{X})\text{CF}_3$ compounds ($\text{X} = \text{F}, \text{Cl}$) show similar conformational properties.

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