

(1,1-Dichloro-2,2,2-trifluoroethylimino)sulfur dichloride, $\text{CF}_3\text{CCl}_2\text{N}=\text{SCl}_2$: Vibrational spectra and quantum chemical calculations

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ARTICLE INFO

Article history:

Received 26 February 2009

Received in revised form 27 April 2009

Accepted 28 April 2009

Available online 6 May 2009

Keywords:

Vibrational spectroscopy
Quantum chemical calculations
(1,1-Dichloro-2,2,2-trifluoroethylimino)sulfur dichloride

ABSTRACT

The vibrational spectra of (1,1-dichloro-2,2,2-trifluoroethylimino)sulfur dichloride, $\text{CF}_3\text{CCl}_2\text{N}=\text{SCl}_2$, were recorded in the gas phase with IR spectroscopy and in the liquid state with Raman spectroscopy. Quantum chemical calculations at the HF, B3LYP (6-311+G(d) and 6-311+G(2df) basis sets) and MP2 levels of theory (6-31+G(d) and 6-311+G(df) basis sets) were performed. According to all calculations the lowest energy conformer possesses C_1 symmetry with *syn* orientation of the SCl_2 group relative to the N–C bond and near-trans orientation of the CF_3 group relative to the N=S bond. Calculations predict the presence of a second stable conformer with *anticlinal* orientation of the SCl_2 group which, however, possesses considerably higher energy and is therefore not observed in the analysis of the experimental vibrational spectra. The vibrational spectra were assigned for a single conformer in accordance with these calculations.

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1. Introduction

Only a limited number of structural, conformational, and configurational studies of iminosulfur molecules $\text{R}=\text{N}=\text{SX}_2$ have been reported in the literature and little is known about the factors which affect these properties. In principle, depending on the orientation of the R–N bond with respect to the X–S–X bisector two molecular forms, *syn* and *anti*, can be expected (See Scheme 1).

Vibrational spectroscopy, gas electron diffraction (GED), X-ray crystallography, and quantum chemical calculations have been shown to be powerful tools to determine the structural properties of this class of molecules. Thus, for systems of the type $\text{R}=\text{N}=\text{SF}_2$, $\text{R}=\text{CF}_3$ [1], $\text{FC}(\text{O})$ [2], $\text{CF}_3\text{C}(\text{O})$ [3], CF_3CF_2 [4], FSO_2 [5], and of the type $\text{R}=\text{N}=\text{SCl}_2$, $\text{R}=\text{CF}_3$ [6], $\text{FC}(\text{O})$ [7], CF_3CF_2 [8], $\text{ClC}(\text{O})$ [9] it could be demonstrated that the *syn* configuration (*syn* of the R–N bond with respect to the X–S–X bisector) is the most stable structure, although it is sterically rather unfavorable. It is interesting to note that in molecules with different substituents attached to the sulfur atom, i.e. molecules of the type $\text{R}=\text{N}=\text{SXY}$, such as $\text{FC}(\text{O})\text{N}=\text{S}(\text{F})\text{CF}_3$ [10] and $\text{CF}_3\text{C}(\text{O})\text{N}=\text{S}(\text{F})\text{CF}_3$ [11], the most stable form turns out to be *anti* (R–N bond *anti* with respect to the X–S–Y bisector).

The preference of the *syn* configuration in molecules with symmetrical substitution at the sulfur atom can be explained by orbital interactions of the electron lone pairs at S and N with antibonding orbitals of vicinal N–R and S–X bonds, respectively. These ano-

meric effects strongly stabilize the sterically unfavorable *syn* structure. Numerical values for these interaction energies have been reported for $\text{ClC}(\text{O})\text{N}=\text{SCl}_2$ [9]. Nevertheless, the effect of various substituents at nitrogen has not yet been fully understood.

In order to obtain additional experimental and theoretical information about the effects of such substituents on structural, conformational and vibrational properties of sulfur imides, we report in the present study results for $\text{CF}_3\text{CCl}_2\text{N}=\text{SCl}_2$. This compound allows for the first time to analyze the influence of an alkyl group with fluorine and chlorine substituents at the carbon atoms on the molecular properties.

2. Experimental

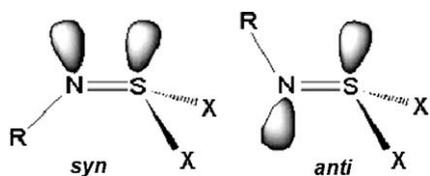
(1,1-Dichloro-2,2,2-trifluoroethylimino)sulfur dichloride was synthesized by the reaction of CF_3CN and SCl_2 . The product was purified at reduced pressure by repeated trap-to-trap distillations [12]. A gas phase infrared spectrum at 5 mbar was recorded in the range $4000\text{--}400\text{ cm}^{-1}$ with an FTIR Perkin Elmer 1600 spectrometer (resolution 2 cm^{-1}). Raman spectra of liquid $\text{CF}_3\text{CCl}_2\text{N}=\text{SCl}_2$ between 2000 and 50 cm^{-1} were obtained using a FT Bruker IFS 66v spectrometer (spectral resolution of 4 cm^{-1}) equipped with a Nd:YAG laser (1064 nm). The liquid samples were handled in glass capillaries at room temperature.

3. Quantum chemical calculations

Calculations at different levels of theory (HF and B3LYP with 6-311+G(d) and 6-311+G(2df) basis sets and MP2 with 6-31+G(d)

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Scheme 1.

and 6-311+G(df) basis sets) were performed using the Gaussian 03 program package [13]. In the first step the potential functions for internal rotation around the N=S and N=C bonds were derived with the smaller basis sets. Fig. 1 shows the potential curves for internal rotation around the N=S bond.

The orientation of the SCl₂ group relative to the N=C bond is described by the dihedral angle between the N=C bond and the S-X direction with X being a dummy atom on the SCl₂ bisector. The potential curves were derived by structure optimizations at fixed dihedral angles $\varphi(\text{C-N-S-X})$ in steps of 30°. With rotation around the N=S bond also the orientation of the CF₃ group ($\varphi(\text{C-C-N=S})$) changes appreciably. To obtain the lowest-energy path for full rotation from 0° to 360° around the N=S bond which corresponds to a symmetrical potential function, the CF₃ group has to be forced to possess the same orientation for $\varphi(\text{C-N-S-X}) = 180\text{--}360^\circ$ as for $\varphi(\text{C-N-S-X}) = 0\text{--}180^\circ$. Otherwise a higher-energy path is obtained. This potential curve demonstrates that the global minimum occurs for *syn* orientation with $\varphi(\text{C-N-S-X}) \approx 10^\circ$. Strong repulsion between the chlorine atoms bonded to the sulfur and carbon atoms causes distortion of this structure from C_s to C₁ symmetry. The presence of a second stable form with near *anti* orientation of the SCl₂ group ($\varphi(\text{C-C-N=S}) \approx 150^\circ$) and about 5–8 kcal/mol higher in energy is predicted. The potential function for internal rotation around the N=C bond was derived by geometry optimizations for fixed $\varphi(\text{C-C-N=S})$ dihedral angles in steps of 20°. These potential functions (not shown) possess a double minimum shape near-*trans* orientation of the CF₃ group relative to the N=S bond with minima of $\varphi(\text{C-C-N=S})$ between 150° and 160° (200° and 210°, respectively). The barrier between the two equivalent near-*trans* forms is predicted to be less than 0.5 kcal/mol. The MP2 method predicts an additional shallow minimum for a *gauche* orientation of the CF₃ group ($\varphi(\text{C-C-N=S}) \approx 50^\circ$ and 310°) and about 2.5 kcal/mol higher in energy. On the other hand potential functions derived with HF and B3LYP approximations possess only

shoulders in this region. Additional calculations were performed for the barrier to internal rotation of the CF₃ group around the C-C bond. The values derived for this barrier (9.4, 7.2 and 9.2 kcal/mol according to HF, B3LYP and MP2 approximations) are much higher than usual. Intermediate barriers were predicted for CF₃CF₂N=SCl₂ [8].

In the last step the structures of the two structures, *syn-trans* and *anti-trans* were optimized with the larger basis sets. The relative energy of the *anti-trans* form is calculated to be 4.9 (HF), 7.3 (B3LYP) and 8.0 kcal/mol (MP2). From these relative energies we conclude that only the *syn-trans* configuration shown in Fig. 2 is present at room temperature and it determines the experimental vibrational spectra. The structural parameters of this form are summarized in Table 1 and the vibrational frequencies in Table 2.

5. Vibrational spectra

Observed and calculated wavenumbers and approximate descriptions of the fundamental modes are listed in Table 2. For this molecule $3N - 6 = 27$ normal modes of vibration are expected. The observed features in the IR and Raman spectra are consistent with the existence of a single conformer (see Figs. 3 and 4).

Calculations (MP2) predict a splitting of the N=S stretch of 24 cm⁻¹ between *syn* and *anti* conformers. No such splitting is observed in the experimental spectra. Thus, the *syn* structure possessing C₁ symmetry, as derived by theoretical calculations was used in the analysis of the vibrational spectra. The expected normal modes of vibration have been assigned on the basis of characteristic wavenumbers and taking into account the calculated vibrational frequencies and intensities for this compound. Furthermore, wavenumbers of related molecules, such as CF₃N=SCl₂ [6], CF₃CF₂N=SCl₂ [8], CF₃CF₂N=SF₂ [4], CF₃CF₂N=S(F)CF₃ [14] and CF₃CF₂N=S(Cl)CF₃ [14], were used in the analysis of the fundamental modes.

In general, good agreement exists between the experimental and calculated values. Wavenumbers obtained with approximations including electron correlation (B3LYP/6-311+G(2df) and MP2/6-311+G(df)) reproduce experimental values slightly better than the scaled HF method. Some experimental wavenumbers are reproduced closer by the B3LYP method, others by the MP2 approximation.

According to reported data of most imidosulfur compound containing a CF₃ substituent, the region between 1400 and 900 cm⁻¹ contains the C-C, N=S, C-Cl and C-F stretching modes belonging to the CF₃ group. Thus, the presence of several intense and narrow bands in this region of the IR spectrum and weak and broad bands in the Raman spectrum is directly related to these vibrational modes. Considering that the C-C stretching mode of CF₃CF₂N=SF₂ and of CF₃CF₂N=SCl₂ (1410 and 1380 cm⁻¹ in the IR spectrum, respectively) was assigned to the signal of highest frequency in the vibrational spectra, the band of medium intensity located at

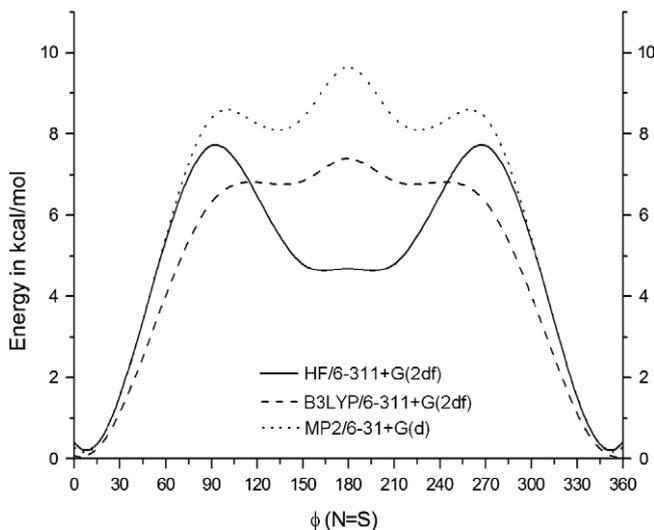


Fig. 1. Calculated potential functions for rotation around the N=S bond.

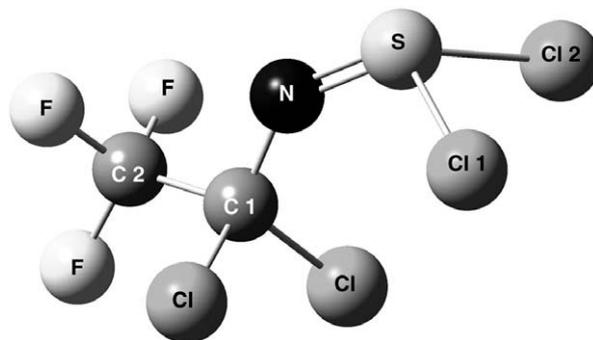
Fig. 2. Molecular model for the *syn* conformer of CF₃CCl₂N=SCl₂.

Table 1
Calculated geometric parameters for the *syn* conformer of $\text{CF}_3\text{CCl}_2\text{N}=\text{SCL}_2$.^a

	HF 6-311+G(2df)	B3LYP 6-311+G(2df)	MP2 6-311+G(df)
<i>Bond lengths</i>			
C1–F ^b	1.304	1.334	1.322
C1–C2	1.549	1.565	1.552
C2–Cl ^b	1.782	1.806	1.768
C2–N	1.401	1.403	1.417
N=S	1.481	1.504	1.509
S–Cl ^b	2.063	2.144	2.108
<i>Angles</i>			
C1–C2–N	106.8	107.3	105.7
C2–N=S	137.1	138.7	134.0
N=S–Cl ^b	111.7	112.1	112.3
C1–S–Cl2	96.4	96.4	96.4
$\varphi(\text{C1–C2–N=S})$	–154.4	–160.1	–147.7
$\varphi(\text{C2–N=S–X})$	11.6	10.5	10.0

^a Bond lengths in Å and angles in degrees. For atom numbering, see Fig. 2.

^b For parameters that are not unique, average values are given.

1395 cm^{-1} in the infrared spectrum and at 1410 cm^{-1} in the Raman spectrum of $\text{CF}_3\text{CCl}_2\text{N}=\text{SCL}_2$ is also assigned to this fundamental mode.

The frequency of the N=S stretching vibration has been shown to be directly related to the electron withdrawing properties of the substituents attached to nitrogen and sulfur atoms [15]. Increasing electron withdrawing properties of the substituents attached to any of these atoms strengthens this bond. Taking into account that the N=S stretch of $\text{CF}_3\text{N}=\text{SCL}_2$ [6] (1314 cm^{-1} IR and 1300 cm^{-1} Raman) and of $\text{CF}_3\text{CF}_2\text{N}=\text{SCL}_2$ [8] (1292 cm^{-1} IR and 1286 cm^{-1} Raman) and that group electronegativities of CF_3 , CF_3CF_2 and CF_3CCl_2 are similar, the band placed at 1303 cm^{-1} (1304 cm^{-1} Raman) was assigned to the N=S stretching vibration of this compound.

The symmetric and antisymmetric stretching modes belonging to the CF_3 group were assigned to the bands localized at 1250 and 1238 cm^{-1} in the infrared spectrum. This assignment is differ-

ent from that reported for $\text{CF}_3\text{CF}_2\text{N}=\text{SCL}_2$, where both stretching modes were assigned to a band at 1235 cm^{-1} in the infrared spectrum (1218 cm^{-1} Raman). Possibly the presence of the CCl_2 group causes a splitting of these stretching modes of the CF_3 group. The totally symmetric mode was assigned to the band located at 948 cm^{-1} in the infrared spectrum, in agreement with the theoretical frequencies obtained by different approaches (950, 957 and 985 cm^{-1} , according to methods HF, B3LYP and MP2, respectively). With respect to the CCl_2 group, all quantum chemical calculations predict strong coupling of the totally symmetric stretching modes of the CF_3 and CCl_2 groups. Antisymmetric and symmetric stretching modes belonging to the CCl_2 group were assigned to the bands centred at 915 and 833 cm^{-1} (909 and 837 cm^{-1} , Raman), respectively. All these modes were described considering local C_s symmetry of the $\text{CF}_3\text{CCl}_2\text{N}$ moiety (see Fig. 2).

The C–N stretching mode was assigned to the medium intensity bands placed at 725 and 722 cm^{-1} in the IR and Raman spectra, respectively. Theoretical values for this mode (HF 719 cm^{-1} ; B3LYP 719 cm^{-1} and MP2 746 cm^{-1}) together with reported frequencies for related molecules support this assignment.

According to theoretical wavenumbers, the band observed at 567 cm^{-1} in the IR spectrum and at 556 cm^{-1} in the Raman spectrum can be assigned to the symmetric deformation of the CF_3 group. This band has a lower wavenumber with respect to the observed signals for $\text{CF}_3\text{CF}_2\text{N}=\text{SCL}_2$ (709 cm^{-1} IR) [8] and $\text{CF}_3\text{CF}_2\text{N}=\text{SF}_2$ (732 cm^{-1} [4]). The presence of the CCl_2 group may modify considerably the vibrational properties of the CF_3 group.

The SCL_2 antisymmetric and symmetric stretching modes appear in the 500–400 cm^{-1} region of the vibrational spectra. By comparison with $\text{CF}_3\text{N}=\text{SCL}_2$ [6] and $\text{CF}_3\text{CF}_2\text{N}=\text{SCL}_2$ [8] and taking into account the results obtained from theoretical calculations, the band observed at 469 cm^{-1} in the infrared spectra (446 cm^{-1} shoulder, Raman) can be assigned to the symmetric stretching of the SCL_2 group. The antisymmetric stretching, displaced to lower frequencies in both reference molecules, is assigned to the band located in 428 cm^{-1} in the IR spectra (430 cm^{-1} Raman) of

Table 2
Experimental and calculated wavenumbers (cm^{-1}) of the *syn* conformer and tentative assignment.

Approximate description ^a	IR (gas)	Raman (liquid)	HF ^b 6-311+G(2df)	B3LYP 6-311+G(2df)	MP2 6-311+G(df)
C2–C1 stretch.	1395	1410	1330	1345	1391
N=S stretch.	1303	1304	1270	1239	1314
CF_3 sym. stretch.	1250	1250	1256	1207	1291
CF_3 asym. stretch.	1238	1204	1245	1190	1285
CF_3 sym. stretch.	948	–	950	957	985
CCl_2 sym. stretch.	915	909	914	893	962
CCl_2 asym. stretch.	833	837	844	794	912
C1–N stretch.	725	722	719	719	746
CF_3 sym. def.	579	–	565	563	586
CF_3 sym. def.	567	556	554	549	576
CF_3 asym. def.	537	538	529	525	556
SCL_2 sym. stretch.	469	446 sh	470	453	466
SCL_2 asym. stretch.	428	430	452	422	433
CCl_2 asym. def.	–	–	419	393	410
SCL_2 sym. def.	–	384	390	381	393
CF_3 sym. def.	–	–	362	355	381
CF_3 asym. def.	–	349	350	342	363
CCl_2 sym. def.	–	261	259	257	275
CF_3CCl_2 sym. def.	–	243	244	238	250
SCL_2 asym. def.	–	212	217	203	217
SCL_2 sym. def.	–	197	198	187	195
CF_3CCl_2 asym. def.	–	166	166	160	167
C1–C2–N def.	–	147	144	138	145
C2–N=S def.	–	114	113	104	118
CF_3 torsion	–	85	81	77	86
SCL_2 torsion	–	–	66	63	66
C2–N torsion	–	–	23	14	20

^a stretch., stretching; def., deformation; sym., symmetric; asym., antisymmetric; sh., shoulder. For atom numbering, see Fig. 2.

^b Scaled by the factor 0.9.

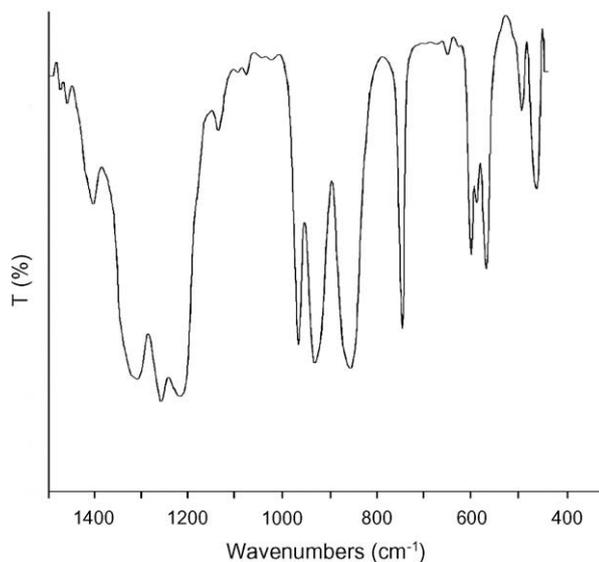


Fig. 3. Gas phase infrared spectrum of $\text{CF}_3\text{CCl}_2\text{N}=\text{SCl}_2$ ($P = 5$ mbar).

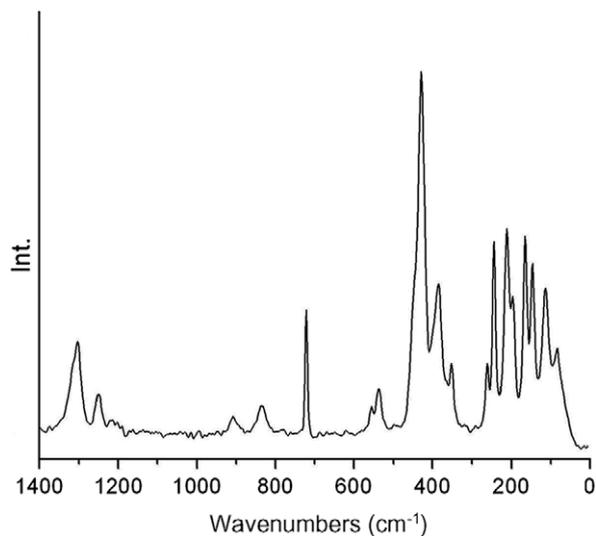


Fig. 4. Liquid phase Raman spectrum of $\text{CF}_3\text{CCl}_2\text{N}=\text{SCl}_2$.

$\text{CF}_3\text{CCl}_2\text{N}=\text{SCl}_2$. Both experimental wavenumbers are in good agreement with calculated values.

6. Conclusions

The applied quantum chemical methods demonstrate to be a powerful tool for the determination of the structural and conformational properties of this kind of molecules. Although these

calculations predict the presence of two stable conformers for $\text{CF}_3\text{CCl}_2\text{N}=\text{SCl}_2$, *syn* and *anti* configuration of the $\text{C}=\text{N}=\text{SCl}_2$ moiety and *trans* orientation of the CF_3 group, only the *syn* configuration has to be considered in the interpretation of the experimental vibrational spectra. The *anti* conformer is predicted to be considerably higher in energy. The number of bands observed in the spectra confirms the presence of single species. The theoretical vibrational modes agree very well with the observed ones. This agreement together with the reported data for analogous molecules confirms the assignment of the 27 fundamental modes of the title compound.

Acknowledgments

Financial support by the Volkswagen Stiftung (1/78 724) and DAAD (Deutscher Akademischer Austauschdienst, Germany) is gratefully acknowledged. The Argentinean authors acknowledge CONICET (Consejo Nacional de Investigaciones Científicas y Técnicas) and UNT (Universidad Nacional de Tucumán). We thank also Prof. R. Mews, University of Bremen, for providing facilities for experimental work.

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