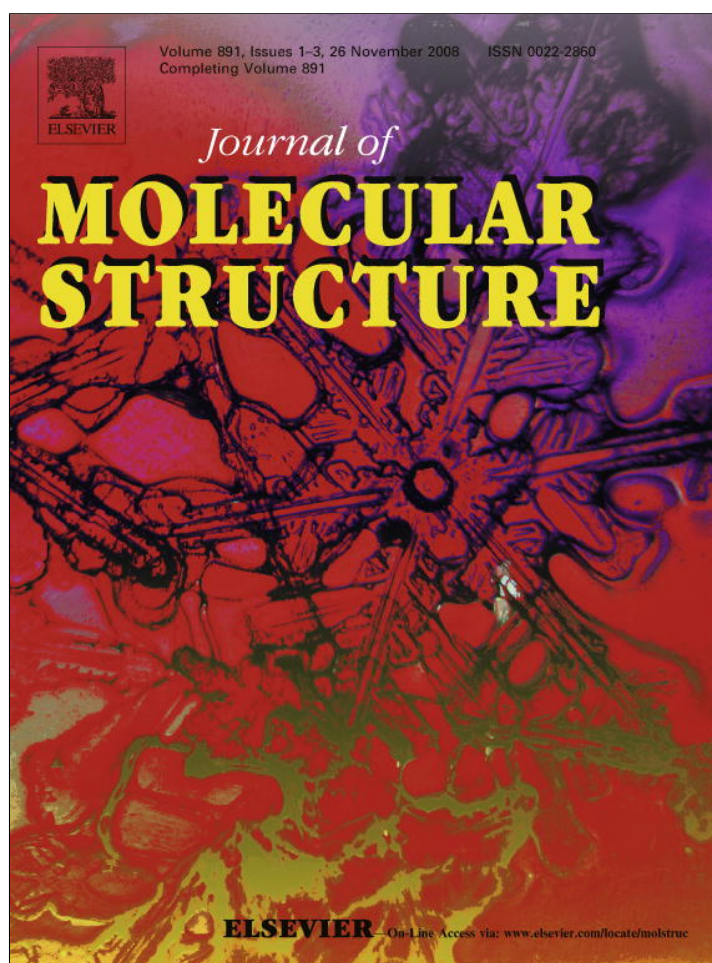


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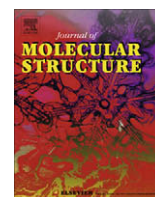
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journal homepage: www.elsevier.com/locate/molstrucStructure and conformations of *N*-(chloroformyl) iminosulfur dichloride, ClC(O)N=SCl_2 Norma L. Robles^{a,1}, Edgardo H. Cutin^{a,2}, Rosa M.S. Álvarez^{a,*,2}, Heinz Oberhammer^{b,*}^a Instituto de Química Física, Facultad de Bioquímica, Química y Farmacia, Universidad Nacional de Tucumán, San Lorenzo 456, 4000 Tucumán, Argentina^b Institut für Physikalische und Theoretische Chemie, Universität Tübingen, 72076 Tübingen, Germany

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ABSTRACT

Vibrational spectra [FT IR (gas and liquid); FT Raman (liquid)] and quantum chemical calculations at different levels of theory (HF, B3LYP and MP2 using 6-31G(d), 6-311 + G(2df) and cc-pVTZ base sets) demonstrate that *N*-(chloroformyl) iminosulfur dichloride (ClC(O)N=SCl_2) is present in the fluid phases as a mixture of *syn-syn* and *syn-anti* forms (*syn* orientation of the C–N bond with respect to the Cl–S–Cl bisector; *syn* or *anti* orientation of the carbonyl group with respect to the N=S bond). From the relative IR intensities of the C=O stretching bands the contribution of the *syn-anti* form is calculated to be 6(2)% in the gas, corresponding to a Gibbs free energy difference $\Delta G^\circ = G^\circ_{\text{syn-anti}} - G^\circ_{\text{syn-syn}} = 1.6(3)$ kcal/mol. This value is reproduced very well by quantum chemical calculations which include electron correlation effects ($\Delta G^\circ = 1.59\text{--}1.91$ kcal/mol). The HF approximation overestimates this energy difference ($\Delta G^\circ = 4.45$ kcal/mol). On the basis of theoretical calculations and reported data for other iminosulfur dichlorides, a complete assignment of the fundamental modes for ClC(O)N=SCl_2 is proposed.

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1. Introduction

The study of the conformational properties of 1,3-conjugated systems is still of great interest due to the fact that unexpected configurations might be found as a consequence of different electronic or steric effects. Particularly, special interest was devoted to molecules of the type XC(O)N=SR_2 and $\text{XC(O)N=SRR}'$ ($X = \text{F}; R, R' = \text{F, Cl, CF}_3$) [1–3]. The conformational properties of these compounds depend strongly on the substituents at the sulfur atom. For example, iminosulfur difluoride, FC(O)N=SF_2 [1], is present in the fluid phases as a single *syn-syn* conformer (*syn* orientation of the C–N bond with respect to the R–S–R bisector angle and *syn* orientation of the carbonyl group with respect to the N=S bond. See Scheme 1). On the other hand, the dichloride analogue, FC(O)N=SCl_2 [2], shows a conformational equilibrium between the *syn-syn* and *syn-anti* forms, with the former one being the energetically preferred structure ($\Delta E = E_{\text{syn-anti}} - E_{\text{syn-syn}} = 3.51, 1.49$ and 1.73 kcal/mol according to the HF, B3LYP and MP2 methods, respectively, using the 6-31G(d) basis set). Since the *syn* orien-

tation around the N=S bond is sterically not favoured, anomeric effects involving lone-pair orbitals at the nitrogen and sulfur atoms and opposite $\sigma^*_{\text{S-F}}$, $\sigma^*_{\text{S-Cl}}$ and $\sigma^*_{\text{C-N}}$ orbitals were proposed to explain the preference of these conformations.

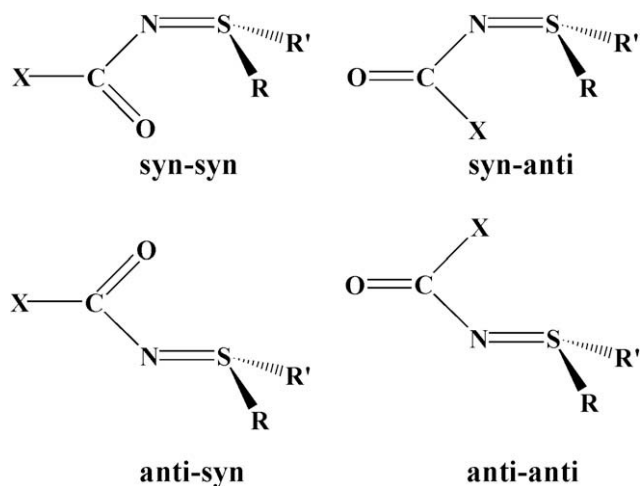
Taking into account these results, an unexpected behaviour was reported for FC(O)N=S(F)CF_3 [3]. In this case, even though the *syn-syn* form is present in the fluid phases, it is not the predominant conformer. According to vibrational spectroscopy and gas electron diffraction (GED) the sterically favoured *anti-syn* structure is more stable than the *syn-syn* configuration by $\Delta G^\circ = 0.94(35)$ kcal/mol (mean value of vibrational spectroscopy and GED). This is reproduced qualitatively by HF, MP2 and B3LYP calculations with 6-31G(d) basis sets which predict energy differences of 2.41, 0.64 and 0.28 kcal/mol, respectively.

Besides quantum chemical calculations, the molecular structures of all mentioned examples were studied by GED. In all cases, vibrational spectroscopy also proved to be a powerful tool to derive qualitative, (in some cases even quantitative), information about the presence of different forms in the fluid phases. This turns vibrational spectroscopy into a reliable technique to prove the presence of more than one form in the fluid phases. Quantum chemical calculations can supply unknown experimental information and it is interesting to observe here that in all mentioned studies theoretical approximations including electron correlation effects improved the description of the different forms.

So far, influence due to modifications in the substitution at the sulfur atom has been analysed. However, the presence of a bulkier

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Scheme 1.

and less electronegative atom bonded to the carbonyl group could affect the conformational properties as well. In this work we report a structural, conformational and vibrational study of (*N*-chloroformyl) iminosulfur dichloride, ClC(O)N=SCl_2 , based on its vibrational spectra [FT-IR (gas and liquid); Raman (liquid)] and on quantum chemical calculations at different levels of theory (HF, B3LYP and MP2 methods using the 6-31G(d), 6-311 + G(2df) and cc-pVTZ basis sets). Results reported for other molecules containing the N=SCl_2 moiety, as well as theoretical simulations of the vibrational spectra of ClC(O)N=SCl_2 were considered to propose a complete assignment of the fundamental modes. A Natural Bond Orbital analysis (NBO) was performed in order to understand the effects involved in the stabilization of the different forms.

2. Quantum chemical calculations

In a first approach, ClC(O)N=SCl_2 can adopt any conformation depicted in Scheme 1. Fig. 1 shows the potential curves for internal rotation around the C–N bond calculated at fixed torsional angles $\phi(\text{C–N})$ (using HF/6-311 + G(2df), B3LYP/6-311 + G(2df) and MP2/6-31G(d)) approximations. These curves were calculated for *syn* orientation of the C–N bond with respect to the Cl–S–Cl bisector ($\phi(\text{N=S}) = 0^\circ$). Besides the global minimum for the *syn-syn* confor-

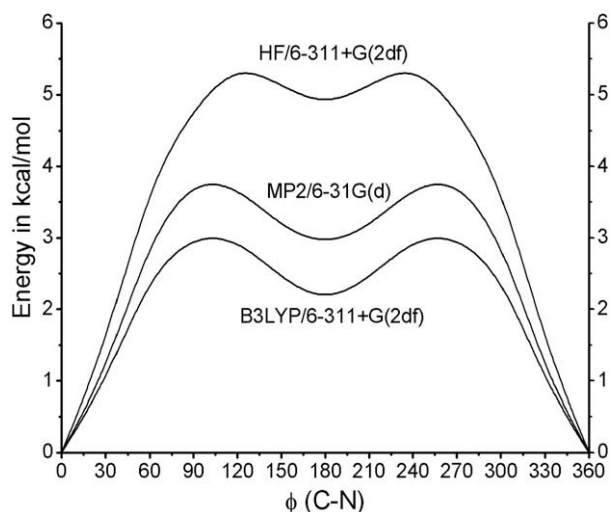


Fig. 1. Calculated potential functions for rotation around the C–N bond.

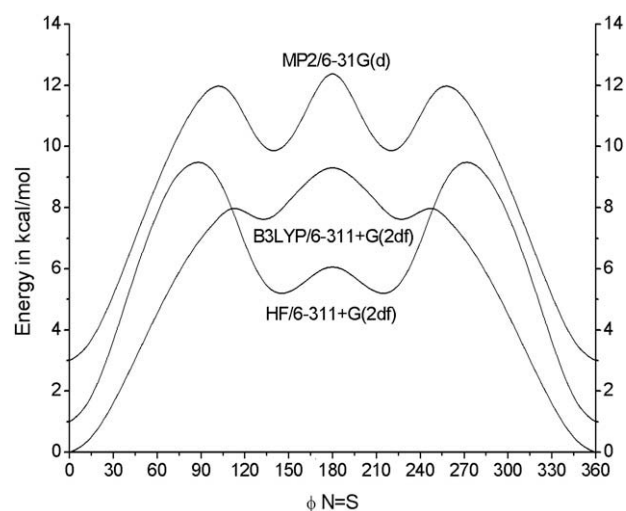


Fig. 2. Calculated potential functions for rotation around the N=S bond. The HF and MP2 curves are shifted by 1 and 3 kcal/mol, respectively.

mation at $\phi(\text{C–N}) = 0^\circ$, a second minimum exits for the *anti* orientation of the C=O bond relative to N=S ($\phi(\text{C–N}) = 180^\circ$). Similarly, Fig. 2 shows the potential curves for rotation around the N=S bond with the C=O bond in the favoured *syn* orientation relative to the N=S bond ($\phi(\text{C–N}) = 0^\circ$). These curves were calculated by the same approximations mentioned above. In this case, the minimum of each curve corresponds again to *syn-syn* configuration with $\phi(\text{N=S}) = 0^\circ$, while the additional minima correspond to C_1 structures with *anticlinal* orientation of the C–N bond with respect to the Cl–S–Cl bisector instead of the expected *anti* configuration. The exact *anti-syn* structure with C_s symmetry corresponds to a transition state. Similar curves are obtained for *anti* orientation of the C=O bond relative to N=S bond (data not shown).

Subsequent frequency calculations at the minima demonstrated the existence of four stable configurations: *syn-syn* and *syn-anti* forms proposed in Scheme 1 (C_s symmetry); and two structures with C_1 geometry corresponding to the *anticlinal-syn* and *anticlinal-anti* forms. Although all methods predicted the *syn-syn* configuration as the most stable form, some discrepancies were found when considering the structure of the second most stable conformer. While the Hartree–Fock approach predicted an *anticlinal-syn* conformation, methods including electron correlation effects favour the *syn-anti* form as second most stable conformer. The comparison between the calculated relative energies predicted by the different methods (see Table 1), in agreement with experimental evidence of conformational equilibrium (see Section 4) suggests that the Hartree–Fock method is an inappropriate approach to perform conformational studies for molecules of this kind. A similar conclusion was derived by the studies of FC(O)N=SCl_2 [2] and ClC(O)N=C=O [4].

Since energy differences predicted by approximations which include electron correlation are considered to be more reliable, it is possible to postulate the existence of a conformational equilibrium between the *syn-syn* and *syn-anti* structures. Both configurations belong to the C_s symmetry group with the symmetry plane containing the Cl3, O, C, N and S atoms. (For atom numbering see Fig. 3).

Table 2 shows the theoretical geometric parameters of the *syn-syn* conformer. All quantum chemical calculations were performed using the GAUSSIAN 03 program package [5]. An NBO analysis (see Section 5) was performed using the NBO program [6] included in the GAUSSIAN 03 program package with the B3LYP/6-311 + G(2df) approximation.

Table 1
Calculated relative energies and free energies (kcal/mol),^a relative abundances at 298 K (%) and wavenumbers (cm⁻¹) of the stretching C=O mode (values in parentheses are calculated IR intensities in km/mol) for the *syn-syn*, *syn-anti* and *anticondinal-syn* conformers of ClC(O)N=SCl₂

Form	HF/6-311 + G(2df)				B3LYP/6-311 + G(2df)				MP2/cc-pVTZ			
	ΔE	ΔG°	%	$\nu(\text{C=O})^b$	ΔE	ΔG°	%	$\nu(\text{C=O})$	ΔE	ΔG°	%	$\nu(\text{C=O})$
<i>syn-syn</i>	0.00	0.00	99.8	1769 (327)	0.00	0.00	96.1	1801 (228)	0.00	0.00	93.4	1793 (159)
<i>syn-anti</i>	4.83	4.45	0.1	1812 (803)	2.09	1.91	3.9	1827 (567)	2.00	1.59	6.6	1816 (462)
<i>anticondinal-syn</i>	4.23	3.88	0.1	1724 (460)	6.92	6.62	0.0	1758 (320)	6.58	6.14	0.0	1744 (214)
<i>anticondinal-anti</i>	7.79	6.93	0.0	1819 (889)	7.29	7.13	0.0	1864 (639)	7.02	6.90	0.0	1857 (540)

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

^b Scaled by a factor of 0.9.

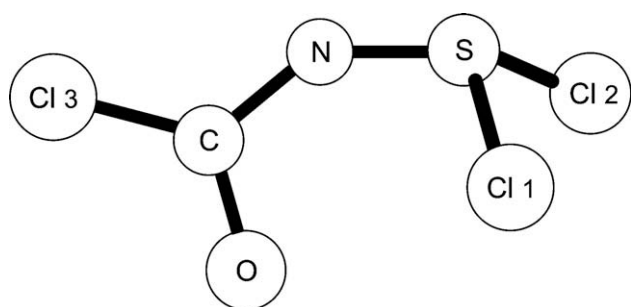


Fig. 3. Molecular model for the *syn-syn* conformer of ClC(O)N=SCl₂.

Table 2
Calculated geometric parameters for the *syn-syn* conformer of ClC(O)N=SCl₂^a

	HF 6-311 + G(2df)	B3LYP 6-311 + G(2df)	MP2 cc-pVTZ
N=S	1.515	1.528	1.533
S-Cl1	2.038	2.120	2.090
S-Cl2	2.038	2.120	2.090
C-N	1.371	1.386	1.401
C=O	1.168	1.187	1.195
C-Cl3	1.747	1.773	1.752
C-N=S	124.5	127.9	122.9
N-C=O	128.2	127.9	127.6
N-C-Cl3	110.5	109.5	109.1
N-S-Cl1	110.5	110.8	110.8
N-S-Cl2	110.5	110.8	110.8
Cl3-C-N=S	180.0	180.0	180.0
O=C-N=S	0.0	0.0	0.0

^a Bond lengths in Å and angles in degrees. See Fig. 3 for atom numbering.

3. Experimental

ClC(O)N=SCl₂ was synthesized by the reaction between FC(O)N=SF₂ and PCl₅ according to the technique reported by Roisky et al. [7].

The gas and the liquid FT-IR spectra of this compound were registered with a Bruker IFS 66v FT-IR spectrometer. A Bruker RFS 100/S FT-Raman spectrometer was used to obtain the liquid Raman spectra of the title molecule.

4. Vibrational spectra

Table 3 shows a tentative assignment of the 15 vibrational fundamental modes expected for the *syn-syn* conformer of ClC(O)N=SCl₂, whose vibrational spectra are shown in Figs. 4 and 5. All vibrational modes were assigned in comparison with reported data for molecules containing the N=SCl₂ moiety (FC(O)N=SCl₂ [2], CF₃N=SCl₂ [8], ClSO₂N=SCl₂ [9] and preliminary theoretical calculations for ClC(O)N(SO₂F)₂ [10]). Quantum chemical calculations at different levels of theory as well as data reported

for molecules containing the FC(O)N=S entity (FC(O)N=SF₂ [1], and FC(O)N=S(F)CF₃ [3]), were also taken into account with the same purpose.

As it was proposed in previous articles [1–3], the carbonyl band can be used to evaluate conformational equilibrium in molecules possessing the FC(O)N=S entity. A *syn* configuration of the C=O double bond with respect to the N=S double bond results in a lower wavenumber for this vibrational stretching mode with respect to the corresponding one in an *anti* configuration. A closer analysis of the effects involved, demonstrates that a *syn* orientation allows strong electronic delocalization from the nitrogen lone-pair to the $\sigma^*_{\text{C=O}}$ orbital, causing weakening of the C=O bond strength. The experimental and theoretical frequency difference between *syn* and *anti* orientations of the C=O bond relative to the N=S bond is in the 30–50 cm⁻¹ range. The carbonyl band in the gas FT-IR spectrum of the title molecule (see Fig. 4, inset A) agrees with the behaviour reported. The stretching mode of the C=O group (*syn-syn* conformer) was assigned to the strong band placed at 1748 cm⁻¹, while the same mode for the *syn-anti* configuration could be assigned to the medium-weak intensity band at 1775 cm⁻¹. In the Raman spectrum this splitting is absent: the asymmetric band centered at 1730 cm⁻¹ in the carbonyl region was assigned to this mode for both conformers, (see Fig. 5). The calculated values predicted by the different approximations agree with this assignment (1769/1812 cm⁻¹; 1801/1827 cm⁻¹; 1793/1816 cm⁻¹ for the *syn-syn* and *syn-anti* forms, respectively, according to the HF/6-311 + G(2df), B3LYP/6-311 + G(2df) and MP2/cc-pVTZ approximations). The same vibrational mode was reported at 1818 cm⁻¹ (1791 cm⁻¹, Raman) for the *syn-syn* conformer of FC(O)N=SCl₂ [2], while for ClC(O)N(SO₂F)₂ the reported infrared spectrum described an intense band centered at 1795 cm⁻¹ (1870 and 1868 cm⁻¹, according to HF/6-31G(d) and B3LYP/6-31G(d) approximations, respectively) [10]. It is interesting to add here that the liquid FT-IR spectrum of ClC(O)N=SCl₂ shows a single asymmetric band with a shoulder towards lower wavenumbers values in the carbonyl region. Since the electronic effects mentioned above reasonably well explain the assignment proposed, this unusual shape is considered to be caused by intermolecular interaction in the liquid phase.

An additional evidence of the presence of the second conformer in the fluid phases is given by the bands assigned to the N=S stretching mode. According to vibrational data reported for imino-sulfurous compounds possessing halogen atoms as substituents at the sulfur atom, this vibrational fundamental occurs in the 1400–1100 cm⁻¹ range. For the title molecule, the strong band in the infrared spectrum and the medium-weak intensity band in the Raman spectrum, both centered at 1165 cm⁻¹ were assigned to this mode in the *syn-syn* form. The less intense feature placed at 1250 cm⁻¹ in the infrared spectra (see Fig. 4, inset B) would belong to the same vibration in the *syn-anti* conformer. The experimental shift is in good agreement with the calculated values (1181/1282 cm⁻¹; 1223/1311 cm⁻¹; 1234/1326 cm⁻¹ for the *syn-syn*

Table 3
Experimental and calculated wavenumbers of the *syn-syn* conformer and tentative assignments

Mode	Approximate description ^a	Experimental ^b		Calculated ^c		
		IR (gas)	Raman (liquid)	HF 6-311 + G (2df) ^d	B3LYP 6-311 + G (2df)	MP2 cc-pVTZ
$\nu_1(A')$	(C=O) stretch.	1748 (84)	1730 (16)	1769 (26)	1801 (26)	1793 (17)
$\nu_2(A')$	(S=N) stretch.	1165 (100)	1165 (19)	1181 (100)	1223 (100)	1234 (100)
$\nu_3(A')$	(C–Cl) stretch.	941 (72)	943 (4)	957 (9)	951 (29)	982 (32)
$\nu_4(A')$	(C–N) stretch.	754 (79)	754 (25)	770 (60)	751 (27)	774 (23)
$\nu_5(A'')$	(NCO) oop def.	675 (66)	671 (3)	711 (4)	691 (3)	691 (3)
$\nu_6(A')$	(CICO) def.	490 (24)	490 (70)	494 (<1)	483 (<1)	503 (<1)
$\nu_7(A'')$	(SCl ₂) sym. stretch.	461 sh (26)	446 (100)	482 (13)	434 (14)	452 (16)
$\nu_8(A')$	(SCl ₂) asym. stretch.	436 (34)	420 sh (66)	469 (10)	418 (18)	438 (19)
$\nu_9(A')$	(SCl ₂) wagging	–	392 (46)	392 (3)	393 (5)	399 (4)
$\nu_{10}(A'')$	(SCl ₂) twisting	–	305 (42)	314 (<1)	297 (<1)	306 (<1)
$\nu_{11}(A')$	(SCl ₂) scissoring	–	266 (66)	270 (<1)	258 (<1)	273 (<1)
$\nu_{12}(A')$	(CICN) def.	–	193 (80)	198 (<1)	174 (<1)	191 (<1)
$\nu_{13}(A')$	(CNS) def.	–	122 (82)	118 (<1)	102 (<1)	113 (<1)
$\nu_{14}(A'')$	(S=N) torsion	–	95 (74)	89 (<1)	70 (<1)	86 (<1)
$\nu_{15}(A'')$	(C–N) torsion	–	–	46 (<1)	40 (<1)	40 (<1)

^a Stretch.: stretching; def.: deformation; oop: out-of-plane; asym.: asymmetric; sym.: symmetric.

^b Relative absorbance at band maximum in parentheses; liquid: room temperature, relative band intensity in parentheses; sh.: shoulder.

^c Relative infrared band strength in parentheses; 100%: 1272, 888 and 914 km/mole calculated at the HF, B3LYP and MP2 methods, respectively.

^d Scaled by a factor of 0.9.

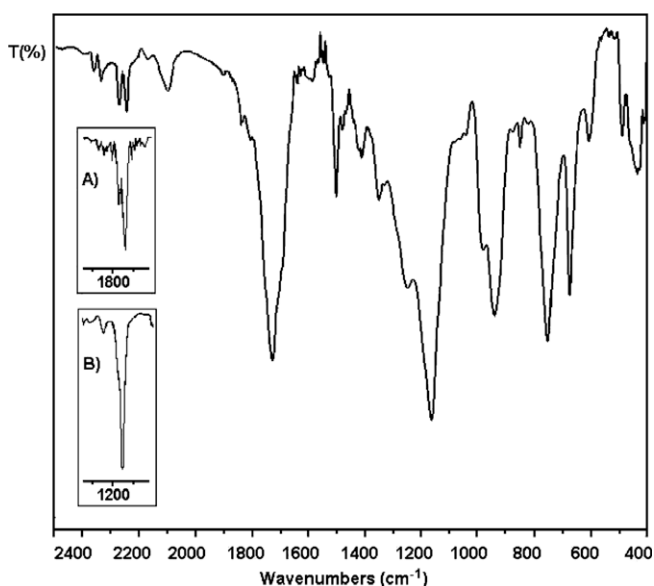


Fig. 4. Infrared spectrum of liquid ClC(O)N=SCl_2 . Insets (A) and (B) depict the C=O and N=S stretching signals in the gaseous spectrum, respectively.

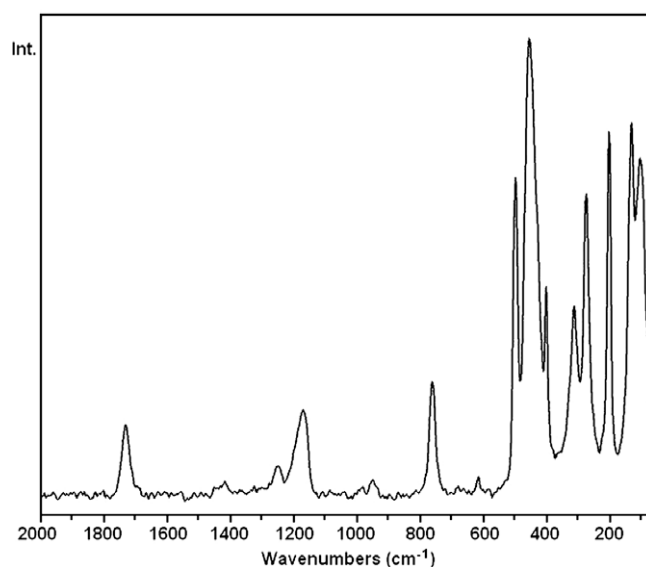


Fig. 5. Raman spectrum of liquid ClC(O)N=SCl_2 at room temperature (resolution 4 cm^{-1}).

and *syn-anti* forms, respectively, according to HF/6-311 + G(2df), B3LYP/6-311 + G(2df) and MP2/cc-pVTZ approximations.

The C–Cl stretching mode was assigned to the medium band centered at 941 cm^{-1} in the liquid infrared spectra. This assignment was proposed on the basis of the comparison among infrared spectra recorded during the preparation of the substance: the strong band belonging to the C–F stretching of the intermediate FC(O)N=SCl_2 disappears as the product ClC(O)N=SCl_2 is obtained. The similar band found at 988 cm^{-1} in the reported infrared spectrum of $\text{ClC(O)N(SO}_2\text{F)}_2$ (875 and 815 cm^{-1} according to the HF/6-31G(d) and B3LYP/6-31G(d) approximations, respectively) supports the proposed assignment [10].

In comparison with data reported for several molecules containing the N=SCl_2 moiety [2,8,9], as well as theoretical simulations of the vibrational modes, the symmetric stretching of the SCl_2 group was assigned to the band centered at 446 cm^{-1} in the

Raman spectrum (the same mode would correspond to the shoulder observed at 461 cm^{-1} in the infrared spectrum). The asymmetric stretching would be observed at lower wavenumbers values: 436 cm^{-1} in the infrared spectrum (420 cm^{-1} , shoulder of the most intense Raman band). The assignment proposed is in excellent agreement with the theoretical predictions ($482/469 \text{ cm}^{-1}$, HF/6-311 + G(2df); $434/418 \text{ cm}^{-1}$, B3LYP/6-311 + G(2df); $452/438 \text{ cm}^{-1}$, MP2/cc-pVTZ, for the symmetric and asymmetric modes, respectively).

Quantum chemical calculations predicted the C–N stretching mode at 770 , 751 and 774 cm^{-1} (HF, B3LYP and MP2 methods, respectively). Thus, the band centered at 754 cm^{-1} was assigned to this mode, although this vibration occurs at a considerably higher wavenumber (843 cm^{-1} , IR) in FC(O)N=SCl_2 [2]. Substitution of fluorine by chlorine in the carbonyl group is expected to exert a strong influence on the C–N wavenumbers.

Among all deformations modes for this molecule, out-of-plane NCO and symmetric CICO bendings were the most interesting features to take into account. The former mode was assigned to the medium intensity band centered at 675 cm^{-1} in the infrared spectrum (671 cm^{-1} , Raman); the CICO deformation would be observed at 490 cm^{-1} in both vibrational spectra. In comparison with the assignment proposed for $\text{FC}(\text{O})\text{N}=\text{SCl}_2$ [2], the NCO deformation is now an asymmetric mode, while the CICO would be symmetric with respect to the symmetry plane of the molecule.

5. Discussion

The prevailing conformer of $\text{ClC}(\text{O})\text{N}=\text{SCl}_2$ possesses a *syn-syn* structure in the gas and liquid phases. The observed absorbance ratio of the two bands is $A(\text{syn-anti})/A(\text{syn-syn}) = 0.48(9)$. Taking into account the ratio of their calculated intensities (square of the transition moments) $I(\text{syn-anti})/I(\text{syn-syn}) = 2.7(3)$, which is the mean value of B3LYP/6-311 + (2df) (2.49) and MP2/cc-pVTZ (2.91), the contribution of the *syn-anti* form is 6(2)%. The uncertainty is derived from the estimated uncertainties in the absorbance ratio and in the calculated intensities. This contribution corresponds to $\Delta C^\circ = 1.6(3)\text{ kcal/mol}$. This experimental value is reproduced closely by quantum chemical calculations which include electron correlation (1.59 and 1.91 kcal/mol, respectively).

The preference for the sterically strongly unfavourable *syn* orientation around the N=S bond can be rationalized by orbital interactions between the n_σ lone pairs of N and S and the vicinal antibonding σ^* orbitals. From a natural bond orbital (NBO) analysis of the B3LYP/6-311(2df) wave function these anomeric effects stabilize the *syn* orientation by 36.8 kcal/mol ($n_\sigma(\text{S}) \rightarrow \sigma^*(\text{N}-\text{C}) = 9.4\text{ kcal/mol}$ and $n_\sigma(\text{N}) \rightarrow \sigma^*(\text{S}-\text{Cl}) = 13.7 + 13.7\text{ kcal/mol}$), compared to only 11.2 kcal/mol ($n_\sigma(\text{S}) \rightarrow \sigma^*(\text{N}-\text{C}) = 1.5\text{ kcal/mol}$ and $n_\sigma(\text{N}) \rightarrow \sigma^*(\text{S}-\text{Cl}) = 8.5 + 1.2\text{ kcal/mol}$) for the *anticlinal* orientation. These strong orbital interactions apparently override steric repulsions. A strong steric repulsion occurring in the *syn-syn* conformer is evident from the calculated (B3LYP) C=N=S angle which increases from 115.4° in *anticlinal-syn* to 127.9° in *syn-syn*. Orbital interactions do not provide such a straightforward explanation for the preference of the *syn* orientation around the N=C bond. In this case anomeric effects ($n_\sigma(\text{N}) \rightarrow \sigma^*(\text{C}=\text{O}) = 8.1\text{ kcal/mol}$ in *syn-syn* conformer and $n_\sigma(\text{N}) \rightarrow \sigma^*(\text{C}-\text{Cl}) = 13.0\text{ kcal/mol}$ in *syn-anti* conformer) actually favour the *anti* orientation of the C=O bond relative to the N=S bond. Apparently, strong steric repulsion between the chlorine atoms of the $\text{C}(\text{O})\text{Cl}$ and SCl_2 groups override the ano-

meric effect and lead to a preference of the *syn* orientation. This steric repulsion is again evident from the calculated C=N=S angle, which increases from 127.9° in *syn-syn* to 139.2° in *syn-anti*.

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