JOURNAL OF RAMAN SPECTROSCOPY
J. Raman Spectrosc. **31**, 881–885 (2000)

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

R. M. Romano,[1] C. O. Della Védova,[1,2]*† M. I. Mora Valdez[3] and E. H. Cutín[3]†

[1] CEQUINOR (UNLP, CONICET) Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, 47 esq. 115, 1900 La Plata, Argentina
[2] Laboratorio de Servicios a la Industria y al Sistema Científico, LaSeISiC (UNLP–CIC–CONICET), Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional De La Plata, 47 esq. 115, 1900 La Plata, Argentina
[3] Instituto de Química Física, Facultad de Bioquímica, Química y Farmacia, Universidad Nacional de Tucumán, Ayacucho 491, 4000 Tucumán, Argentina

The vibrational spectra, including Raman spectra at different temperatures and resonance Raman spectra, and theoretical calculations of *N*-fluoroformyliminotrifluoromethylsulfur fluoride, FC(O)N=S(F)CF$_3$, were obtained and interpreted. They point to the existence of a predominant *anti–syn* form and in equilibrium at lower concentration a *syn–syn* form (the first related to the nitrogen lone pair with respect to the sulfur lone pair and the second is related to the C=O double bond with respect to the N=S double bond). The general result indicates that it is the first *anti* configuration reported for this type of molecule implying for the energetically most favoured form an *anti* configuration of the lone pairs attached to both the S and N atoms. Copyright © 2000 John Wiley & Sons, Ltd.

INTRODUCTION

Very few molecules provide vibrational spectra so full of information and are so interesting from the geometrical, conformational and configurational point of view as *N*-fluoroformyliminotrifluoromethylsulfur fluoride, FC(O)N=S(F)CF$_3$. The various possible forms also represent a challenge for the theoretical calculations. Both theoretical and experimental arguments are used in this paper to analyse FC(O)N=S(F)CF$_3$. According to the first inspection of the molecule using the simplest VSEPR model, two main structural questions arise, namely the relative positions of the N and S lone pairs and the conformation of the C=O double bond with respect to the N=S double bond. The analyses of the IR and Raman bands, especially of the carbonylic vibrations, allow the detection of the structural equilibrium. For the precise prediction of the preferred conformation and configuration, the assistance of theoretical arguments is necessary. Therefore, taking into account our general programme of studying FC(O)N=SX$_2$ species, this investigation was performed to determine, by application of simple techniques, the structural behaviour of the title molecule.

EXPERIMENTAL

N-Fluoroformyliminotrifluoromethylsulfur fluoride, FC(O)N=S(F)CF$_3$, was prepared by reaction of CF$_3$SF$_3$ and Si(NCO)$_4$.[1] The liquid product was purified at reduced pressure by several trap-to-trap distillations. Fourier transform (FT) IR (vapour) and Raman (liquid) spectra confirmed the purity of the compound.

Infrared spectra were obtained with a Bruker IFS85 FT spectrometer, with resolution of 1 cm^{-1}. Raman spectra were obtained with a Jobin-Yvon U-1000 spectrometer equipped with both argon and Krypton ion lasers (Spectra-Physics Model 165) and radiation, of 457.9 and 514.5 nm (Ar$^+$) was used for excitation. The spectra were measured at ambient temperature, at $-5\,^\circ$C and at $45\,^\circ$C with 4 cm^{-1} resolution. All calculations were performed with the Gaussian 94 suite of programs[2] on a personal computer.

THEORETICAL CALCULATIONS

The *anti–syn*, *syn–syn*, *anti–anti* and *syn–anti* structures of FC(O)N=S(F)CF$_3$ were fully optimised with *ab initio*

---

* Correspondence to: C. O. Della Védova, LaSeISiC (UNLP–CIC–CONICET) y CEQUINOR, Departamento de Química, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, C.C. 962, 1900 La Plata, Argentina; e-mail: carlosdv@dalton.quimica.unlp.edu.ar
† Member of Carrera del Investigador Científico y Técnico of the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), Argentina.

Contract/grant sponsor: Fundación Antorchas.
Contract/grant sponsor: Alexander von Humboldt stiftung.
Contract/grant sponsor: British Council.
Contract/grant sponsor: Deutsche Akademische Austauschdienst (DAAD).
Contract/grant sponsor: Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET); Contract/grant number: PIP 4695.
Contract/grant sponsor: Agencia Nacional de Promoción Científica y Tecnológica; Contract/grant number: PICT 122.
Contract/grant sponsor: Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC).

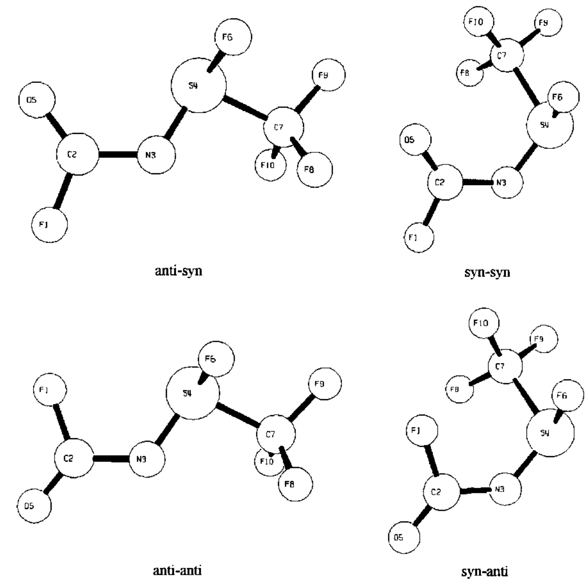
Received 10 January 2000
Accepted 16 March 2000

calculations (HF/6–31+G*). The four structures represent stable structures for which no imaginary wavenumbers occur. They were selected for successive optimizations considering variations in the C2N3S4C7 and N3S4C7F8 dihedral angles (see Fig. 1 for atom numbering and the four different forms of the title compound considered in this work).

According to a brief inspection of the experimental vibrational spectra, at least two structures can occur as suggested by the splitting of the carbonylic band. Thus, not only the energy calculations of the most stable form but also the energy difference with the other stable less favoured energetically forms are interesting in this case. The most stable structure and the existence of configurational equilibrium can be deduced from this analysis. Table 1 lists the calculated energies and energy differences for the four forms of Fig. 1 using *ab initio* and density functional theory approximations. Both calculations (HF/6–31+G* and B3LYP/6–31+G*) predict the *anti–syn* form as the most stable (the nitrogen lone pair *anti* with respect to the sulfur lone pair and the C=O double bond *syn* with respect to the N=S double bond) the *syn–syn* form being higher in energy. This result shows no agreement with data reported for other compounds, for which the configuration around the N=S double bond is always *syn* ($ClN{=}SF_2$,[3] $CF_3N{=}SF_2$[4] (F. Trautner, D. Christen and H. Oberhammer, to be published), $F_5SN{=}SF_2$,[5] $NCN{=}SF_2$ (R. Haist, E. Lork, R. Mews and H. Oberhammer, unpublished results), $FC(O)N{=}SF_2$[6] and $FSO_2N{=}SF_2$[7]). The theoretical calculations reproduce results obtained by analysis of the vibrational spectra (see below) and the geometric structure reported by gas electron diffraction analysis (F. Trautner, E. H. Cutin, C. O. Della Védova, R. Mews and H. Oberhammer, to be published). A smaller basis set (HF/3–21G*) leads to erroneous prediction of the most stable form for this molecule.

Table 1. Calculated energies and energy differences with the *anti–syn* form of four stable forms of $FC(O)N{=}S(F)CF_3$

	HF/6–31+G*		B3LYP/6–31+G*	
Structure	*E*/hartree	Δ*E*/kcal mol^{-1}	*E*/hartree	Δ*E*/kcal mol^{-1}
anti–syn	−1099.6909242	0.00	−1103.5492959	0.00
syn–syn	−1099.6861255	3.01	−1103.5476500	1.03
anti–anti	−1099.6847424	3.88	−1103.54470054	1.44
syn–anti	−1099.6847424	6.71	−1103.5450008	2.69



anti-syn syn-syn

anti-anti syn-anti

Figure 1. Molecular models and atom numberings for four stable structures of $FC(O)N{=}S(F)CF_3$ calculated with the HF/6–31+G*.

VIBRATIONAL ANALYSIS

The main interest in the vibrational spectra is the determination of the conformational and configurational properties of the title compound. According to theoretical vibrational data calculated for the four forms of $FC(O)N{=}S(F)CF_3$, the analysis must be concentrated on the C=O stretching (ν_1) and on the C–N stretching (ν_7) vibrations (see Tables 2 and 3), which are expected to show the strongest dependence on the forms of the molecule. In the experimental vibrational spectra shown in Fig. 2 two bands appear in the C=O stretching region, a less intense and a more intense band at higher and lower wavenumbers in both the IR and Raman spectra, respectively, which indicates the presence of two forms. Since theoretical calculations predict $\nu_{C=O}(syn\text{–}syn) > \nu_{C=O}(anti\text{–}syn)$, it can be concluded that the most intense band originates from the *anti–syn* form, i.e. the main structure. Moreover, the expected vibrations for hypothetical *anti–anti* and *syn–anti* forms coincidentally at 1883 cm^{-1} are far from the experimental values. These forms can be ruled out in comparison with

Table 2. Calculated vibrational wavenumbers for four stable forms of $FC(O)N{=}S(F)CF_3$ using the HF/6–31+G* approximation

Mode	*anti–syn*[a] $\tilde{\nu}$/cm^{-1}	*syn–syn*[a] $\tilde{\nu}$/cm^{-1}	*anti–anti*[a] $\tilde{\nu}$/cm^{-1}	*syn–anti*[a] $\tilde{\nu}$/cm^{-1}	Tentative assignment (see Table 3)
ν_1	1805	1826	1883	1883	νC=O
ν_2	1301	1305	1302	1298	$\nu_{as}CF_3$
ν_3	1291	1294	1276	1291	νCF
ν_4	1265	1242	1244	1246	$\nu_{as}CF_3$
ν_5	1158	1150	1152	1135	ν_sCF_3
ν_6	1091	1119	1065	1091	νN=S
ν_7	911	865	833	810	νCN
ν_8	799	801	776	778	CFO oop[b]
ν_9	770	768	769	759	δ_sCF_3
ν_{10}	761	752	751	748	νSF
ν_{11}	674	629	649	667	δFCO
ν_{12}	556	556	552	556	$\delta_{as}CF_3$
ν_{13}	547	545	548	543	δCF_2
ν_{14}	514	503	533	529	δNCF
ν_{15}	472	455	469	455	δSCF
ν_{16}	374	382	374	374	δNSF
ν_{17}	318	329	324	332	
ν_{18}	303	300	300	298	
ν_{19}	229	237	225	241	
ν_{20}	183	211	183	214	
ν_{21}	139	132	137	130	
ν_{22}	92	104	92	101	
ν_{23}	59	65	56	53	
ν_{24}	52	48	43	39	

[a] Scaled by a factor of 0.9.
[b] Out-of-plane.

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

IR (gas)[a] $\tilde{\nu}$/cm^{-1}	Raman (liquid) $\tilde{\nu}$/cm^{-1}	*anti–syn* HF/6–31+G* $\tilde{\nu}$/cm^{-1}	*syn–syn* HF/6–31+G* $\tilde{\nu}$/cm^{-1}	Assignment
2265				
2199				
2136				
2007				
1929				
1854 w	1828[b]		1826	νC=O$_{syn-syn}$
1796 vs	1777[b]	1805		νC=O$_{anti-syn}$
1755				
1432				
1368				
1328				
1245 vs		1301	1305	ν_{as}CF$_3$
1236 vs	1217	1291	1294	νCF
1144 vs		1265		ν_{as}CF$_{3anti-syn}$
1132 vs			1242	ν_{as}CF$_{3syn-syn}$
	1123	1158		ν_sCF$_{3anti-syn}$
			1150	ν_sCF$_{3syn-syn}$
1105 s	1096[b]	1091		νN=S$_{anti-syn}$
1057 w	1054[b]		1119	νN=S$_{syn-syn}$
904 w	900[b]	911		νCN$_{anti-syn}$
854 vw	854[b]		865	νCN$_{syn-syn}$
	823			
778 m		799	801	CFO oop[c]
	768	770		δ_sCF$_{3anti-syn}$
	756		768	δ_sCF$_{3syn-syn}$
720 s	718	761	752	νSF
668 w	667	674		δFCO$_{anti-syn}$
			629	δFCO$_{syn-syn}$
562 w	564	556	556	δ_{as}CF$_3$
	544	547	545	δCF$_2$
518 w	520	514	503	δNCF
480 w	471	472	455	δSCF
	366	374	382	δNSF
	317	318	329	
	299	303	300	
	235	229	237	
	192	183	211	
	139	139	132	
		92	104	
		59	65	
		52	48	

[a] w = weak, m = medium, s = strong, v = very.
[b] Band showing RR effect.
[c] Out-of-plane.

the experimental spectra (the same result was obtained by evaluation of the theoretical relative energies in the theoretical part).

The region corresponding to the C–N stretching vibration shows two definite bands with the band at higher wavenumbers the most intense. According to the Table 2, it is the expected behaviour for the *anti–syn* (more intense C–N stretching band) and *syn–syn* (less intense C–N stretching band) forms of the title compound. The other forms can be excluded as shown in Table 2 because their hypothetical wavenumbers are 833 and 810 cm^{-1} for the *anti–anti* and *syn–anti* forms, respectively.

Raman spectra recorded at different temperatures, depicted in the Fig. 3, show that in the carbonylic stretching region the weak band at higher wavenumbers gains intensity with increasing temperature from −5 to 45 °C in accordance with the structural equilibrium and with the assignment of the forms discussed below.

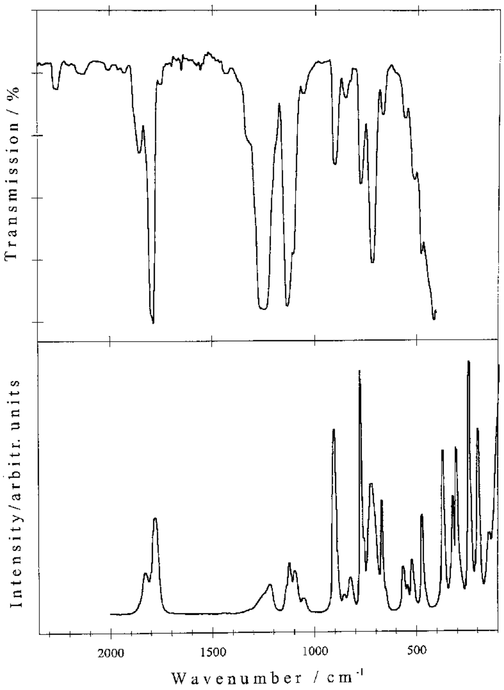


Figure 2. Vibrational spectra of FC(O)NS(F)CF$_3$ at room temperature. Top: gas FTIR spectrum; pressure, 6 Torr; resolution, 1 cm^{-1}. Bottom: liquid Raman spectrum; excitation, 514.5 nm (100 mW); resolution, 4 cm^{-1}.

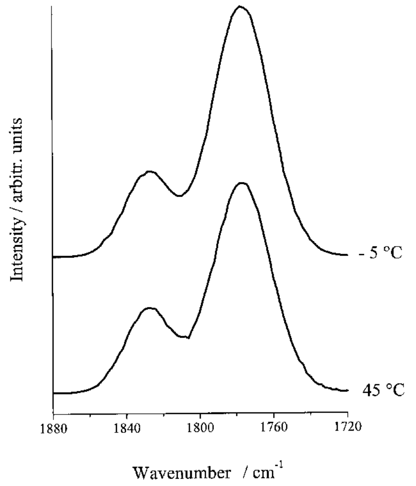


Figure 3. Raman spectra of liquid FC(O)N=S(F)CF$_3$ at −5 and at 45 °C. Excitation, 514.5 nm (100 mW); resolution, 4 cm^{-1}.

To reinforce the proposed assignments listed in Table 3, resonance Raman spectra were recorded. The intensity of the Raman bands was fixed with respect to the 192 cm^{-1} band. When the wavelength of the excitating radiation decreases from 514.5 to 457.9 nm, the intensities of the C=O, N=S and C–N fundamental stretching modes corresponding to two forms in equilibrium increase. The reason for the increase in these modes indicated in Table 3 can be explained as follows. The vibrations involving the C(O)N=S group, which distort the ground-state geometry towards the excited-state structure, will be enhanced most. Clearly, the most enhanced modes are related to the expected chromophore of the molecule, i.e. the region of the π electrons.

The observed vibrations listed in Table 3 were assigned as usual by comparison with data corresponding to related molecules, taking into account the theoretical vibrational spectra as stated by evaluation of the resonance Raman effect. The molecules mainly considered were $FC(O)=NSF_2$,[8] $ClSO_2N=SF_2$,[9] $CF_3SO_2N_3$,[10] and CF_3SO_2NCO.[11]

In accordance with the data and assignments in the Table 3, the reported molecules show comparable data. Some features are noteworthy, e.g. the difference between data corresponding to the C=O stretching vibration in the IR (gas) and Raman (liquid) spectra. $\Delta(\nu_{\text{gas}} - \nu_{\text{liquid}})$ is about 20–25 cm^{-1} for each conformer and may be rationalized by the formation of intermolecular associations in the liquid. The attractive forces operating in this phase result in a lowering of the C=O bond order as consequence of changes in the electronic distribution due to these interactions. This Δ is also considerable for the C–F stretching vibration and for the N=S stretching vibration of the *anti–syn* form. However, Δ is lower in the *syn–syn* form, precluding different types of interaction due to their different forms.

The position of the N=S stretching vibration depends strongly on the electronegativities of the substituents attached to the group. The trend is similar to the C=O group which increases its wavenumber with the sum of the substituent electronegativities.[12] The N=S stretching wavenumber is assigned at 1105 cm^{-1} (IR) for the most stable *anti–syn* form of the $FC(O)N=S(F)CF_3$ molecule; the reported value for $ClSO_2N=SCl_2$[13] is 1101 cm^{-1} (IR), for $ClSO_2N=SF_2$[9] 1278 cm^{-1}, for $FC(O)N=SF_2$[8] 1330 cm^{-1}, for $CF_3N=SCl_2$[14] 1314 cm^{-1} and for $CF_3N=SF_2$[15] 1388 cm^{-1}. These data demonstrate the mentioned trend, i.e. the higher the electronegativity sum of the N=S group substituents, the higher is the position of the N=S stretching wavenumber.

The remaining assignments in Table 3 compare very well with data from theoretical calculations (HF/6–31+G*). The reliability of these calculations should be noted and the agreement for a wide range of compounds gives confidence in the results.

CONCLUSIONS

All the compounds with general formula $RN=SX_2$ whose experimental gas-phase structures are reported show a *syn* orientation of the nitrogen and sulfur lone pairs [$ClN=SF_2$,[3] $CF_3N=SF_2$[4] (F. Trautner, D. Christen and H. Oberhammer, to be published), $F_5SN=SF_2$,[5] $NCN=SF_2$ (R. Haist, E. Lork, R. Mews and H. Oberhammer, unpublished results), $FC(O)N=SF_2$,[6] and $FSO_2N=SF_2$,[7] $CF_3N=SCl_2$[16] and $ClN=S(CF_3)_2$[17]]. The formal substitution of a CF_3 group by F in $FC(O)N=SF_2$ produces large changes in the configurational properties of these compounds. According to our studies, a mixture of the *anti–syn* form and the *syn–syn* form occurs, with the first energetically favoured. These results are in accordance with current gas electron diffraction studies of the molecule (F. Trautner, E. H. Cutin, C. O. Della Védova, R. Mews and H. Oberhammer, to be published).

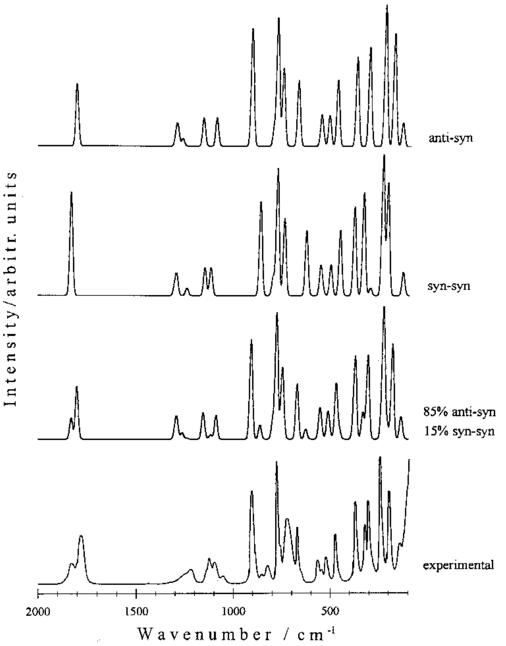


Figure 4. Raman spectra calculated with data from Table 3 and comparison with the experimental spectrum (excitation, 514.5 nm).

Both the relative energy calculations and the prediction of the vibrational spectra are coincident to show structural mixture for the molecule. Figure 4 depicts theoretical spectra of the *anti–syn* and *syn–syn* forms. A mixture of 85% of the *anti–syn* form and 15% of the *syn–syn* form reproduces the experimental spectrum very well, validating the results.

No explanation for the unusual preference of the *anti–syn* form can be given. Systematic studies on a wide range of compounds will be necessary to answer this intriguing question. Moreover, $FC(O)N=S(CF_3)_2$ was calculated (F. Trautner, E. H. Cutin, C. O. Della Védova, R. Mews and H. Oberhammer, to be published). The 'normal' behaviour was also reported for this molecule, the lone pairs being attached to the N and S atoms in a *syn* position. For the model $FC(O)N=S(F)H$ the same result was obtained in this work using for the two forms an HF/6–31+G* approach.

Acknowledgements

C.O.D.V. thanks Professor Dr P. J. Aymonino (Lanais EFO) for valuable discussions, the Fundación Antorchas (Argentina), Alexander von Humboldt Stiftung, the British Council and DAAD (Deutsche Akademische Austauschdienst, Germany) for financial support and for the DAAD–Fundación Antorchas and Alexander von Humboldt Stiftung–Fundación Antorchas Awards to the German–Argentine cooperation and the British Council–Fundación Antorchas award to the British–Argentinean cooperation. He also thanks the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) (PIP 4695), the Agencia Nacional de Promoción Científica y Tecnológica (PICT 122) and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC), Argentina, for financial support. He is indebted to the Facultad de Ciencias Exactas, Universidad Nacional de La Plata, República Argentina, for financial support and to the Fundación Antorchas for a National Award for Argentinean cooperation.

REFERENCES

1. Duncan LC. *Inorg. Chem.* 1970; **9**: 987.
2. Frisch MJ, Trucks GW, Schlegel HB, Gill PMW, Johnson BG, Robb MA, Cheeseman JR, Keith TA, Petersson GA, Montgomery JA, Raghavachari K, Al-Laham A, Zkrewski VG, Ortiz JV, Foresman JB, Ciolowski J, Stefanov BB, Nanayakkara A, Challacombe M, Peng CY, Ayala PY, Chen W, Wong MW, Andres JL, Repogle ES, Gomperts R, Martin RL, Fox DJ, Binkley JS, Defrees DJ, Baker J, Stewart JP, Head-Gordon M, Gonzalez C, Pople JA. *GAUSSIAN 94*. Gaussian: Pittsburgh, PA, 1995.
3. Haase J, Oberhammer H, Zeil W, Glemser O, Mews R. *Z. Naturforsch., Teil A* 1970; **23**: 153.
4. Karl RR, Bauer SH. *Inorg. Chem.* 1975; **14**: 1859.
5. White RM, Baily SR, Graybeal JD, Trasher JS, Palmer MH. *J. Mol. Spectrosc.* 1988; **129**: 243.
6. Leibold C, Cutin EH, Della Védova CO, Mack H-G, Mews R, Oberhammer H. *J. Mol. Struct.* 1996; **375**: 207.
7. Haist R, Cutin EH, Della Védova CO, Oberhammer H. *J. Mol. Struct.* 1999; **484**: 249.
8. Álvarez RMS, Cutin EH, Romano RM, Della Védova CO. *Spectrochim. Acta, Part A* 1996; **52**: 667.
9. Álvarez RMS, Cutin EH, Romano RM, Mack H-G, Della Védova CO. *J. Mol. Struct.* 1998; **443**: 155.
10. Álvarez RMS, Cutin EH, Romano RM, Mack H-G, Della Védova CO. *Spectrochim. Acta, Part A* 1998; **54**: 605.
11. Álvarez RMS, Cutin EH, Mack H-G, Romano RM, Della Védova CO. *J. Raman Spectrosc.* 1997; **28**: 277.
12. Kagarise RE. *J. Am. Chem. Soc.* 1955; **77**: 1377.
13. Álvarez RMS, Cutin EH, Romano RM, Mack H-G, Della Védova CO. *J. Raman Spectrosc.* 1998; **29**: 257.
14. Álvarez RMS, Cutin EH, Romano RM, Della Védova CO. *Spectrochim. Acta, Part A* 1999; **55**: 2615.
15. Griffiths J, Sturman D. *Spectrochim. Acta, Part A* 1969; **25**: 1355.
16. Haist R, Cutin EH, Della Védova CO, Oberhammer H. *J. Mol. Struct.* 1999; **475**: 273.
17. Oberhammer H, Kumar RC, Knerr GD, Shreeve JM. *Inorg. Chem.* 1981; **20**: 3871.