Journal of Molecular Structure 976 (2010) 3–10

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Conformational properties of thiazyldifluoride imidosulfurdifluoride, $N{\equiv}SF_2{-}N{=}SF_2$, and thiazyldifluoride imidosulfuryldifluoride, $N{\equiv}SF_2{-}N{=}S(O)F_2$: Vibrational spectra and quantum chemical calculations

Andrea Flores Antognini [a], Norma L. Robles [a], Edgardo H. Cutin [a], Heinz Oberhammer [b,*]

[a] INQUINOA (CONICET-UNT) 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

ARTICLE INFO

Article history:
Received 6 July 2009
Received in revised form 14 September 2009
Accepted 14 September 2009
Available online 19 September 2009

Keywords:
Thiazyldifluoride imidosulfurdifluoride
Thiazyldifluoride imidosulfuryldifluoride
Conformational properties
Vibrational spectra
Quantum chemical calculations

ABSTRACT

Thiazyldifluoride imidosulfurdifluoride, $N{\equiv}SF_2{-}N{=}SF_2$, and thiazyldifluoride imidosulfuryldifluoride, $N{\equiv}SF_2{-}N{=}S(O)F_2$ were studied by vibrational spectroscopy (FT IR (gas) and Raman (liquid)) and by quantum chemical calculations (B3LYP and MP2 with 6-31G(d) and 6-311+G(2df) basis sets). Depending on the computational method two, three or four stable conformers are predicted for $N{\equiv}SF_2{-}N{=}SF_2$, whereas all methods predict the existence of four stable conformers for $N{\equiv}SF_2{-}N{=}S(O)F_2$. The most stable conformer of both compounds possesses *cis–syn* structure (*cis* configuration of the N≡S—N=S skeleton and *syn* orientation of the terminal SF_2 and $S(O)F_2$ groups relative to the N—S single bond). The experimental vibrational spectra were assigned on the basis of reported data for analogous compounds and calculated wavenumbers for the most stable conformers. The NS triple, double and single bond lenghts are discussed and compared to such bonds in other compounds.

1. Introduction

It was pointed out recently by Mews et al. [1] that multifunctional systems possessing single, double and triple N—S bonds, which can be considered to be derivatives of $N{\equiv}SF_3$, show unusual bonding properties due to the substitution of fluorine atom(s) bonded to sulfur. In fact, the N≡S distance and the A—N≡S angle in adducts of the type $A{\cdot}N{\equiv}SF_2{-}N{=}S(O)F_2$ (with A = AsF_5, SbF_5 and BF_3) where one fluorine atom of $N{\equiv}SF_3$ has been replaced by an $N{=}S(O)F_2$ group, were found to depend unexpectedly on negative hyperconjugation between the thiazyl nitrogen lone pair and σ^*(S—F) orbitals. These observations suggest that the donor properties of these multifunctional systems increase whereby the thiazyl nitrogen is most affected. However, compounds possessing an N≡S—N=S backbone formed by triple, single and double bonds might exhibit different structural properties as free ligands.

Regardless of these interesting geometrical observations, it is also important to analyze the conformational and vibrational properties of such systems, whose characteristics have not been studied so far, probably due to their low thermal stability.

In our group we have been interested for many years in the structural, conformational and vibrational properties of compounds of the type $R{-}N{=}SF_2$ and $R{-}N{=}S(O)F_2$. In the case of the S(IV) derivatives, vibrational and conformational properties for compounds with R = CF_3 [2], FSO_2 [3], FC(O) [4], CN [5] and $CF_3C(O)$ [6] have been reported. For all compounds only structures with *syn* orientation of the SF_2 group relative to the N—R bond have been observed (see Chart 1). According to quantum chemical calculations stable conformers with *anti* orientation of the SF_2 group exist for most derivatives, which, however, are considerably higher in energy and, thus, not observed experimentally. Similarly, for most S(VI) compounds with R = Cl [7], CN [8], FSO_2 [9], FC(O) [10], O=C(N=S(O)F_2) [11] and SF_5 [12] the *syn* orientation of SF_2 (see Chart 2) is strongly preferred. In the case of $FC(O)N{=}S(O)F_2$ and $SF_5N{=}S(O)F_2$ small amounts (14(8)% and 11(5)%, respectively), of a second conformer with *anti* orientation around the S=N bond were observed.

In the present study, we report the assignment of vibrational spectra combined with theoretical calculations for thiazyldifluoride imidosulfurdifluoride, $N{\equiv}SF_2{-}N{=}SF_2$, and thiazyldifluoride imidosulfuryldifluoride, $N{\equiv}SF_2{-}N{=}S(O)F_2$. These compounds are of special interest, since they contain triple and double sulfur nitrogen bonds connected by a single S—N bond. It is expected that the conformational properties of these compounds are more complex, since in addition to the orientation of the terminal SF_2 and $S(O)F_2$ groups also the molecular N≡S—N=S skeleton can adopt *cis*, *gauche* or *trans* configurations. The first syntheses of these

* Corresponding author. Tel.: +49(0) 7071 29 76907; fax: +49(0) 7071 29 5490.
E-mail address: heinz.oberhammer@uni-tuebingen.de (H. Oberhammer).

0022-2860/$ - see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2009.09.020

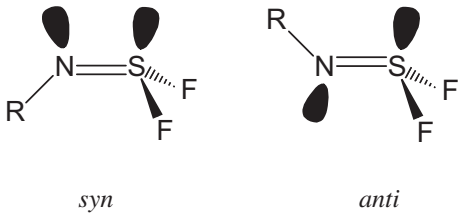

Chart 1.

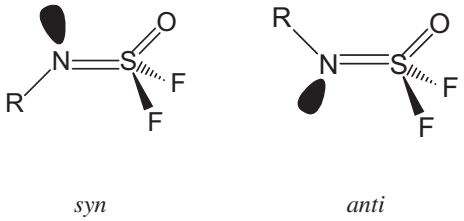

Chart 2.

compounds were reported by Glemser and Höfer [13,14]. Preliminary vibrational spectra and NMR data did not provide any indication about the conformations of these imidosulfur and imidosulfuryl compounds.

2. Experimental

$N{\equiv}SF_2{-}N{=}SF_2$ and $N{\equiv}SF_2{-}N{=}S(O)F_2$ were obtained and purified according the methods reported in the literature [13,14]. The liquid samples of both compounds decompose readily at room temperature. Therefore, the complete Raman spectra could not be obtained and only a limited range of the spectra were measured just before decomposition occurred. The Raman spectra were recorded using a Jobin Ivon V 1000 spectrometer equipped with an argon ion laser (Spectra Physics model 165). On the other hand, the IR spectra of both compounds in the gas phase could be measured at low pressures (5 mbar and 3 mbar, respectively) with an FT IR Perkin Elmer Paragon 500 spectrometer, using a gas cell equipped with KBr windows.

2.1. Quantum chemical calculations

Calculations for both compounds were performed with B3LYP and MP2 approximations and 6-31G(d) and 6-311+G(2df) basis sets using the GAUSSIAN03 program package [15].

$N{\equiv}SF_2{-}N{=}SF_2$: Due to internal rotation around the S—N single and N=S double bonds this molecule can adopt different conformations depending on the structure of the N≡S—N=S skeleton and on the orientation of the terminal SF_2 group. The conformation of the N≡S—N=S skeleton around the S—N single bond may be *cis*, *trans* or *gauche*. The terminal SF_2 group may be oriented *syn* or *anti* around the N=S double bond, with *syn* implying *synperiplanar* or *synclinal* and *anti* implying *antiperiplanar* or *anticlinal* [16]. The orientation of the SF_2 group is described by the dihedral angle ϕ (S—N=S—X) with X being a dummy atom at the F—S—F bisector. Four feasible conformations are shown in Chart 3.

In the first step the potential functions for rotation around the N=S double bond for *cis* conformation of the N≡S—N=S skeleton were derived by optimizing the geometries for fixed ϕ (S—N=S—X) dihedral angles in steps of 30°. All potential curves derived with the four methods (Fig. 1) possess the global minimum for *syn* (ϕ (S—N=S—X) = 0°) orientation and an additional minimum for *anti* orientation of the terminal SF_2 group (ϕ(S—N=S—X) = 180°). This

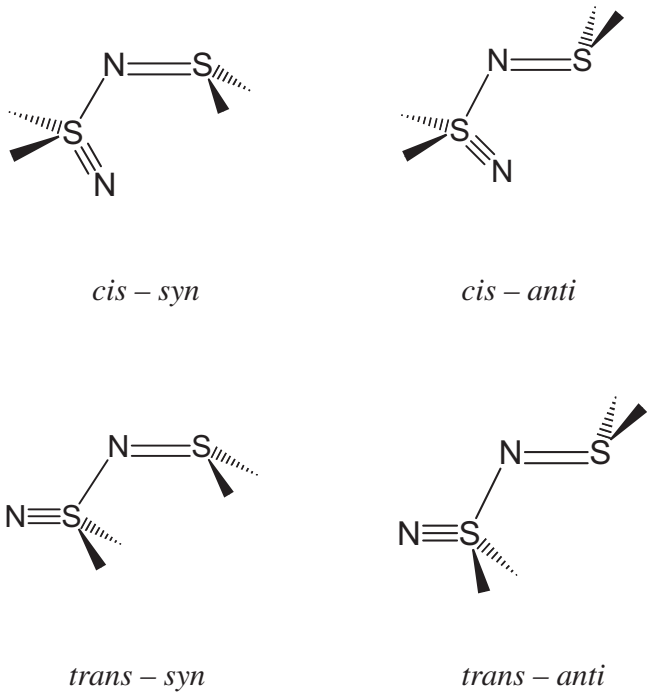

Chart 3.

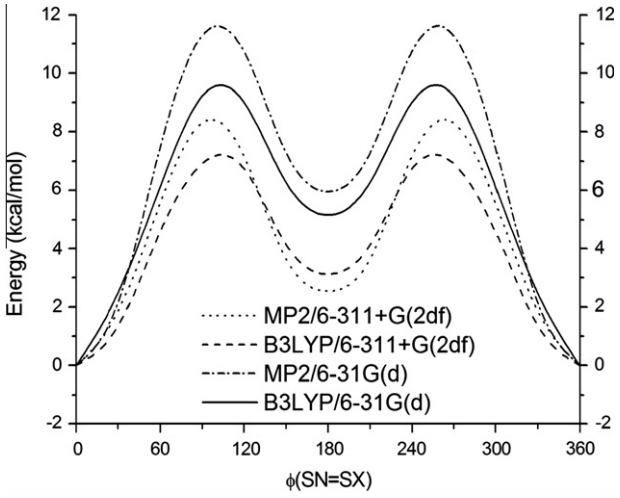

Fig. 1. $N{\equiv}SF_2{-}N{=}SF_2$: Calculated potential curves for internal rotation around the N=S bond for *cis* orientation of the N≡S—N=S skeleton.

second conformer is predicted to be higher in energy by 5.2–6.0 kcal/mol (6-31G(d)) and 2.5–3.1 kcal/mol (6-311+G(2df)), depending on the computational method. The strong preference for the *syn* orientation is in agreement with previous studies for $R{-}N{=}SF_2$ compounds (see Section 1).

In the next step the potential functions for internal rotation around the S—N single bond for *syn* and *anti* orientation of the SF_2 group were calculated by geometry optimizations with fixed ϕ(N≡S—N=S) dihedral angles in steps of 30°. Figs. 2 and 3 show the potential functions for *syn* and *anti* orientation of the SF_2 group, respectively. The shape of both potential curves depends strongly on the computational method and on basis sets. For the favored *syn* orientation of the SF_2 group (Fig. 2) all methods predict the global minimum for *cis* orientation of the N≡S—N=S skeleton (ϕ (N≡S—N=S) = 0°). Potential functions derived with small basis

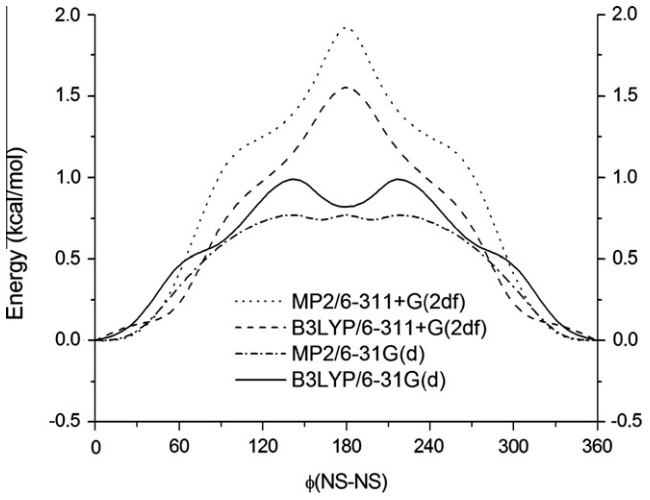

Fig. 2. N≡SF_2—N=SF_2: Calculated potential curves for internal rotation around the S—N bond for *syn* orientation of the terminal SF_2 group.

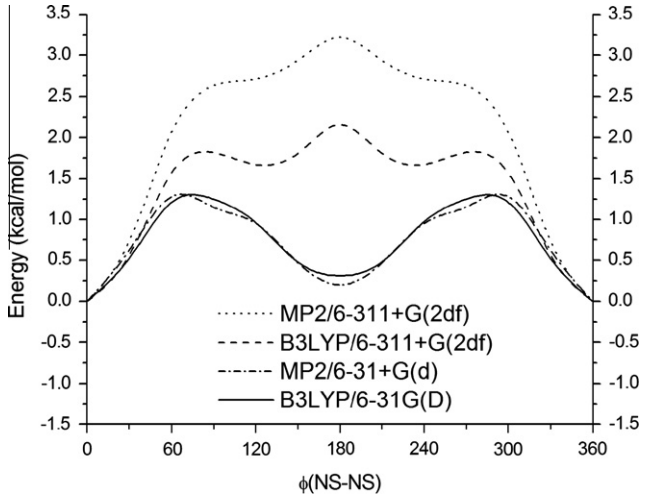

Fig. 3. N≡SF_2—N=SF_2: Calculated potential curves for internal rotation around the S—N bond for *anti* orientation of the terminal SF_2 group.

sets possess additional minima about 0.7–0.8 kcal/mole higher in energy for *trans* (B3LYP, ϕ(N≡S—N=S) = 180°) or near-*trans* (MP2, ϕ(N≡S—N=S) ≈ 160°) conformation of the N≡S—N=S skeleton. The potential curve derived with the MP2 method possesses very flat minima in the *trans* region. On the other hand, no additional minimum in the *trans* region is predicted by both methods (B3LYP and MP2) using large basis sets.

The shape of the potential curve derived for *anti* orientation of the SF_2 group depends also on the computational method (Fig. 3). All curves possess minima for the *cis–anti* conformation with C_S symmetry. The B3LYP method predicts additional minima in the *trans* region (6-31G(d) basis sets) or *gauche* region (6-311+G(2df) basis sets). The MP2/6-31G(d) approximation results in an additional minimum for a *trans–anti* conformer, whereas no additional minimum exists according to the MP2/6-311+G(2df) calculation.

In the final step full structure optimizations with frequency calculations were performed for all stable conformers using B3LYP and MP2 methods with small and large basis sets. The dihedral angles, relative energies, free energies and contributions of these fully optimized conformers are listed in Table 1. It is evident from the potential functions that both methods with small basis sets (6-31G(d)) predict the presence of four stable conformers (see Chart 3), three of which possess C_S symmetry. According to the B3LYP method the *trans–anti* conformer and according to the MP2 approximation the *trans–syn* conformer is distorted to C_1 symmetry. Structure optimizations with large basis sets (6-311+G(2df)) yield somewhat different results. The B3LYP method predicts the presence of three stable conformers, *cis–syn* and *cis–anti* with C_S symmetry and *gauche–anti* (ϕ(N≡S—N=S) = 126.9°) with C_1 symmetry. The latter conformer is listed in the *trans–anti* column. On the other hand, the MP2 approximation with large basis sets predicts the presence of only two stable conformers, both with *cis* orientation of the N≡S—N=S skeleton and C_S symmetry.

Table 1
Torsional angles, relative energies, Gibbs free energies and contributions of conformers of N≡SF_2—N=SF_2.[a]

	cis–syn	*cis–anti*	*trans–syn*	*trans–anti*
*B3LYP/6-31G**				
ϕ(N≡S—N=S)	0.0	0.0	180.0	164.9
ϕ(S—N=S—X)[b]	0.0	180.0	0.0	179.2
ΔE (kcal/mol)[c]	0.00	5.16	0.82	6.05
ΔG^0 (kcal/mol)	0.00	5.38	0.92	5.38
%	82	0	18	0
*MP2/6-31G**				
ϕ(N≡S—N=S)	0.0	0.0	161.1	164.9
ϕ(S—N=S—X)	0.0	180.0	−4.2	179.2
ΔE (kcal/mol)[d]	0.00	5.96	0.74	6.68
ΔG^0 (kcal/mol)	0.00	6.72	1.22	5.74
%	88	0	12	0
B3LYP/6-311+G(2df)				
ϕ(N≡S—N=S)	0.0	0.0	Not stable	126.9
ϕ(S—N=S—X)	0.0	180.0	Optimizes to	178.9
ΔE (kcal/mol)[e]	0.00	3.14	*cis–syn*	4.79
ΔG^0 (kcal/mol)	0.00	3.46		4.26
%	100	0		0
MP2/6-311+G(2df)				
ϕ(N≡S—N=S)	0.0	0.0	Not stable	Not stable
ϕ(S—N=S—X)	0.0	180.0	optimizes to	optimizes to
ΔE (kcal/mol)[f]	0.00	2.54		
ΔG^0 (kcal/mol)	0.00	3.20	*cis–syn*	*cis–anti*
%	100	0		

[a] *cis/trans* of N≡S—N=S chain and *syn/anti* of terminal SF_2 group relative to S—N single bond.
[b] X is a dummy atom on the bisector of the terminal SF_2 group.
[c] Total energy of *cis–syn* conformer E = −1305.015127 a.u.
[d] Total energy of *cis–syn* conformer E = −1302.716835 a.u.
[e] Total energy of *cis–syn* conformer E = −1305.331026 a.u.
[f] Total energy of *cis–syn* conformer E = −1303.471210 a.u.

This compound demonstrates that predictions of conformational properties by quantum chemical methods have to be taken with great care, since they may depend strongly on computational methods and basis sets. Results obtained with methods which include electron correlation and use large basis sets are conventionally considered to be more reliable in conformational studies. Although MP2 and B3LYP methods with large basis sets predict different numbers of stable conformers, i.e. two or three, respectively, only the *cis–syn* form (see Fig. 4 for molecular model) should be observed in experiments according to both methods. The other conformers, *cis–anti* in the case of MP2 and *cis–anti* and *gauche–anti* in the case of B3LYP are more than 3 kcal/mol higher in free energy and their contributions (see Table 1) are negligible. The geometric parameters of the *cis–syn* conformer derived with large basis sets are summarized in Table 2 and the vibrational frequencies are listed together with the experimental values.

N≡SF_2—N=S(O)F_2: Analogous calculations have been performed for the sulfuryl difluoride derivative. All four methods result in equal shape of the potential functions for internal rotation around the N=S bond and only the results derived with large basis sets are

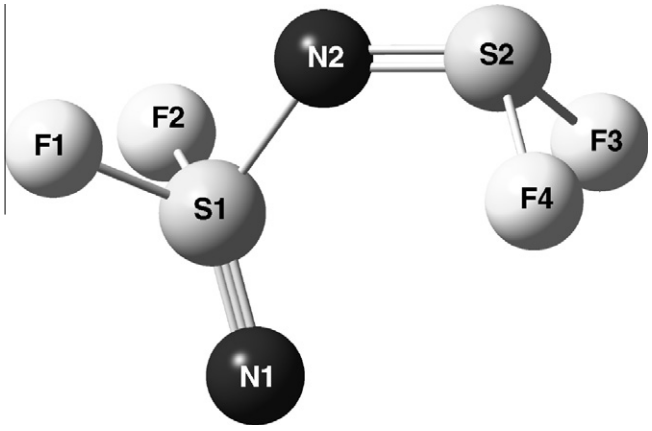

Fig. 4. *cis–syn* structure of N≡SF_2—N=SF_2 with atom numbering.

Table 2
Calculated geometric parameters for *cis–syn* conformer of N≡SF_2—N=SF_2.[a]

	B3LYP/6-311+G(2df)	MP2/6-311+G(2df)
Bond Lengths		
N1≡S1	1.424	1.438
N2=S2	1.506	1.507
N2—S1	1.683	1.678
[b]S1—F (1 and 2)	1.615	1.599
[b]S2—F (3 and 4)	1.600	1.586
Angles		
N1≡S1—N2	125.9	126.1
S1—N2=S2	127.9	124.6
[b]N1≡S1—F (1 and 2)	121.0	121.1
[b]N2—S1—F (1 and 2)	94.3	93.9
[b]N2=S2—F (3 and 4)	109.7	109.7
F3—S2—F4	92.1	91.9
N1≡S1—N2=S2	0.0	0.0

[a] Bond lengths in Å, angles in degrees. For atom numbering see Fig. 4.
[b] For parameters that are not unique, average values are given.

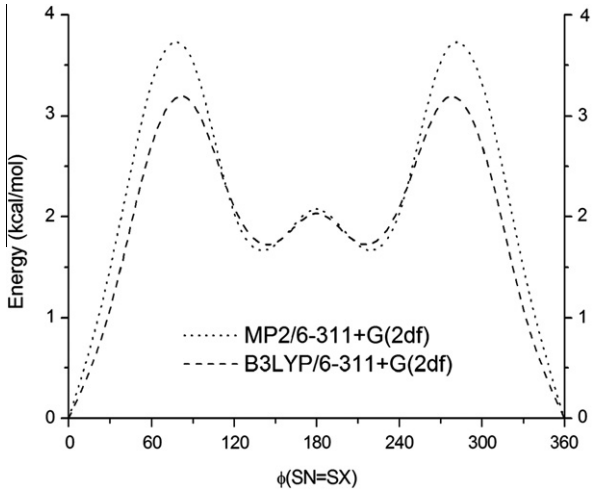

Fig. 5. N≡SF_2—N=S(O)F_2: Calculated potential curves for internal rotation around N=S bond for *cis* orientation of the N≡S—N=S skeleton.

shown in Fig. 5. This shape differs from that for the sulfur difluoride. The global minimum occurs again for *syn* orientation of the bisector of the SF_2 group (ϕ(S—N=S—X) = 0°), but the second minimum occurs for *anticlinal* orientation of the SF_2 bisector (ϕ(S—N=S—X) ≈ 145°) and the energy difference between both orientations is considerably smaller (1.6–2.0 kcal/mol) than in the case of N≡SF_2—N=SF_2. This result is in agreement with previous studies for R—N=S(O)F_2 compounds (see Section 1).

The calculated potential functions derived with the four methods for rotation around the S—N bond are rather similar as well (Fig. 6). All functions possess the global minimum for *cis–syn* conformation and additional minima in the *trans–syn* region (ϕ (N≡S—N=S) ≈ 160°), except for the B3LYP/6-31G(d) curve, where the additional minimum occurs for exact *trans* orientation (ϕ (N≡S—N=S) = 180°). Thus, these potential functions demonstrate that all applied computational methods predict four stable conformers for this compound. The structures of these conformers were fully optimized and their frequencies were calculated with all four methods. Dihedral angles and relative energies, free energies and their contributions are summarized in Table 3. All computational methods predict the *cis–syn* (see Fig. 7 for molecular model) conformer to be predominant with contributions between 77% and 94%. The geometric parameters of the most stable *cis–syn* conformer derived with large basis sets are listed in Table 4.

2.2. Assignment of vibrational spectra

The vibrational spectra of N≡SF_2—N=SF_2 and N≡SF_2—N=S(O)F_2 were assigned assuming the presence of only the most stable *cis–syn* form. As mentioned in the Experimental section both compounds are rather unstable in the liquid phase and therefore it was not possible to record the corresponding Raman spectra for the complete frequency range in one step. Figs. 8 and 9 show the gas phase infrared spectra of N≡SF_2—N=SF_2 and N≡SF_2—N=S(O)F_2, respectively.

In the case of N≡SF_2—N=S(O)F_2, where the calculations predict the presence of small amounts of other conformers, vibrational spectra do not provide information about their contributions. Calculated shifts of wavenumbers between conformers are small and not observable in the experimental spectra. The calculated vibrational frequencies for these most stable conformers are listed in Tables 5 and 6, together with the experimental values and tentative assignments of the fundamental modes. Only few vibrational spectra of molecules containing the N≡S group were reported in the literature and the experimental values agree very closely with the calculated wavenumbers.

It is reasonable to assign the strong signals centered at the highest frequencies in the vibrational spectra to the corresponding N≡S stretching modes (1470 cm^{-1} IR, 1473 cm^{-1} Raman for

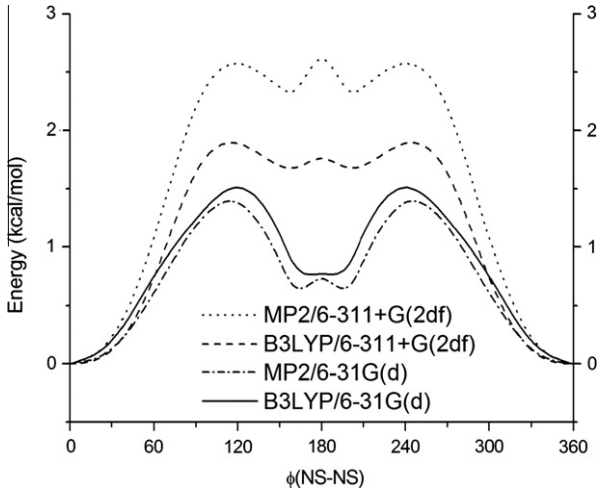

Fig. 6. N≡SF_2—N=S(O)F_2: Calculated potential curves for internal rotation around S—N bond for *syn* orientation of the S(O)F_2 group.

Table 3
Torsional angles, relative energies, Gibbs free energies and contributions of conformers of N≡SF_2—N=S(O)F_2.[a]

	cis–syn	*cis–anti*	*trans–syn*	*trans–anti*
*B3LYP/6-31G**				
ϕ(N≡S—N=S)	0.0	−31.3	180.0	188.5
ϕ(S—N=S—X)[b]	0.0	148.2	0.0	154.7
ΔE (kcal/mol)[c]	0.00	2.02	0.77	2.09
ΔG^0 (kcal/mol)	0.00	1.58	1.04	1.80
%	77	5	14	4
*MP2/6-31G**				
ϕ(N≡S—N=S)	0.0	−27.0	165.9	188.7
ϕ(S—N=S—X)	0.0	148.9	−8.3	147.6
ΔE (kcal/mol)[d]	0.00	1.77	0.67	1.70
ΔG^0 (kcal/mol)	0.00	1.50	1.25	2.10
%	81	7	10	2
B3LYP/6-311+G(2df)				
ϕ(N≡S—N=S)	0.0	−27.9	159.7	186.2
ϕ(S—N=S—X)	0.0	142.5	−6.7	153.1
ΔE (kcal/mol)[e]	0.00	1.71	1.68	2.62
ΔG^0 (kcal/mol)	0.00	2.04	2.33	2.97
%	94	4	2	0
MP2/6-311+G(2df)				
ϕ(N≡S—N=S)	0.0	−23.9	156.9	189.1
ϕ(S—N=S–X)	0.0	138.7	−9.1	147.2
ΔE (kcal/mol)[f]	0.00	1.63	2.34	3.08
ΔG^0 (kcal/mol)	0.00	1.21	2.59	2.99
ν_{min} (cm^{-1})	87	12	1	0

[a] *cis/trans* of N≡S—N=S chain and *syn/anti* of the fluorine atoms of the S(O)F_2 group relative to S—N single bond.
[b] X is a dummy atom on the F—S—F bisector of the S(O)F_2 group.
[c] Total energy of *cis–syn* conformer E = −1380.198157 a.u.
[d] Total energy of *cis–syn* conformer E = −1377.726273 a.u.
[e] Total energy of *cis–syn* conformer E = −1380.557560 a.u.
[f] Total energy of *cis–syn* conformer E = −1378.581888 a.u.

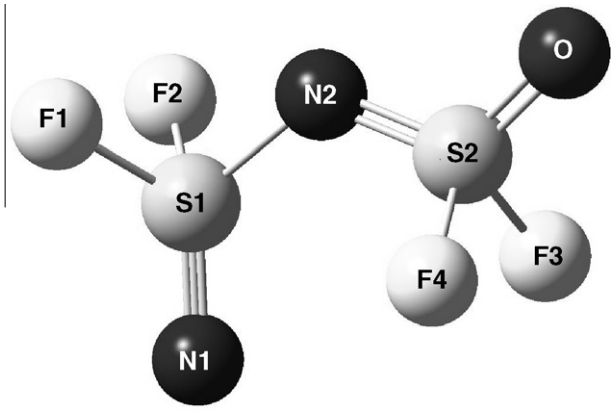

Fig. 7. *cis–syn* structure of N≡SF_2—N=S(O)F_2 with atom numbering.

N≡SF_2—N=SF_2, 1481 cm^{-1} IR and Raman for N≡SF_2—N=S(O)F_2). Comparison between calculated (B3LYP/6-311+G(2df)) wavenumbers and N≡S distances in the series N≡SF_3 (1538 cm^{-1}, 1.418 Å), N≡SF_2—N=S(O)F_2 (1500 cm^{-1}, 1.424 Å), N≡SF_2—N=SF_2 (1498 cm^{-1}, 1.424 Å) and N≡SF (1410 cm^{-1}, 1.442 Å) supports the assumption that substitution of a sulfur bonded fluorine atom in N≡SF_3 weakens the NS triple bond. Experimental data reported for N≡SF_3 (1515 cm^{-1} IR; 1.416(3) Å) [17] and N≡SF (1372 cm^{-1} IR; 1.448(2) Å) [17,18] are in perfect agreement with the proposed assignment.

According to MP2 calculations ν(N=S) shifts by 85 cm^{-1} between *cis–syn* and *cis–anti* conformers for N≡SF_2—N=SF_2. No such splitting of the N=S vibration was observed in the IR or in the Raman spectra. The experimental infrared spectrum of

Table 4
Calculated geometric parameters for *cis–syn* conformer of N≡SF_2—N=S(O)F_2.[a]

	B3LYP/6-311+G(2df)	MP2/6-311+G(2df)
Bond Lengths		
N1≡S1	1.424	1.438
N2=S2	1.502	1.501
N2—S1	1.677	1.667
[a]S1—F (1 and 2)	1.596	1.581
[a]S2—F (3 and 4)	1.559	1.545
S2=O	1.411	1.409
Angles		
N1≡S1—N2	125.7	125.7
S1—N2=S2	123.1	120.1
[b]N1≡S1—F (1 and 2)	121.1	121.1
[b]N2—S1—F (1 and 2)	94.3	94.2
[b]N2=S2—F (3 and 4)	111.4	111.2
N2=S2=O	118.2	118.2
F3—S2—F4	94.9	94.9
N1≡S1—N2=S2	0.0	0.0

[a] Bond lengths in Å, angles in degrees. For atom numbering see Fig. 7.
[b] For parameters that are not unique, average values are given.

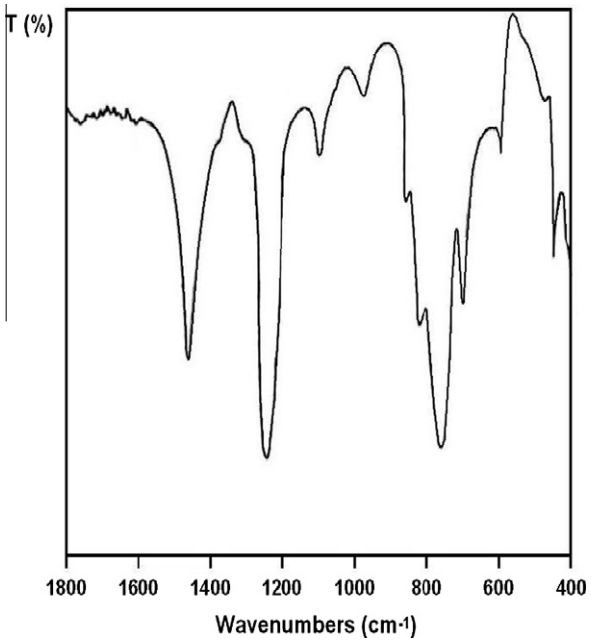

Fig. 8. Gas phase infrared spectra of N≡SF_2—N=SF_2 (P = 5 mbar).

N≡SF_2—N=SF_2 show a strong and somewhat broad signal which could be assigned to this fundamental mode (1220 cm^{-1} IR and Raman spectra) in agreement with calculated frequencies for this vibrational mode (1249 cm^{-1}, B3LYP; 1285 cm^{-1}, MP2). Data reported for FSO_2N=SF_2 (1278 cm^{-1}, IR) [3] and $ClSO_2N$=SF_2 (1277 cm^{-1}, IR) [19] confirm this proposal.

On the other hand, two intense and narrow peaks are shown in the same region of the infrared spectra of N≡SF_2—N=S(O)F_2. As in the case of FC(O)N=S(O)F_2 and SF_5N=S(O)F_2, the N=S and the S=O stretching modes are strongly coupled [10,12]. The antisymmetric stretching of these bonds (ν_2, see Table 6) could be assigned to the signal centered at 1430 cm^{-1} of the infrared spectrum (1432 cm^{-1} Raman) while the feature located at 1210 cm^{-1} of the infrared spectrum stands for the N=S=O symmetric stretching (ν_3). The corresponding observed bands were found at 1442 cm^{-1} and 1282 cm^{-1}, respectively for FC(O)N=S(O)F_2 (IR) and at 1446 cm^{-1} and 1277 cm^{-1} for SF_5N=S(O)F_2 [10,12].

To conclude with the N—S stretching vibrations, the single bond stretching was assigned to signals of similar characteristics in the

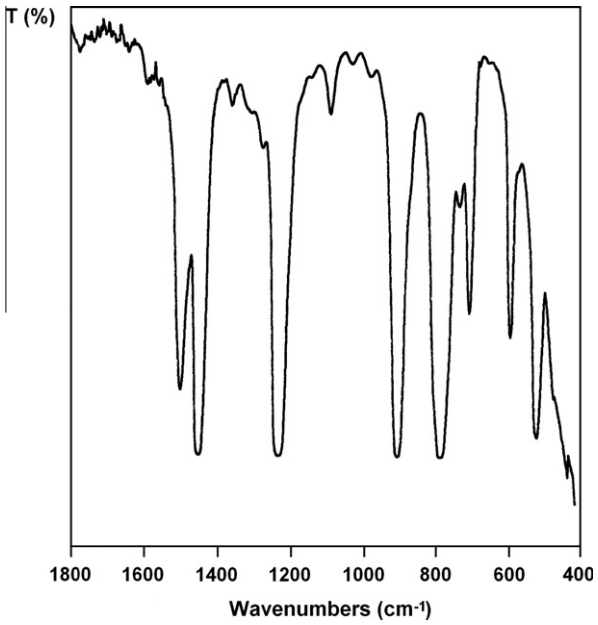

Fig. 9. Gas phase infrared spectra of $N{\equiv}SF_2{-}N{=}S(O)F_2$ (P = 3 mbar).

vibrational spectra of both compounds. For $N{\equiv}SF_2{-}N{=}SF_2$ the band was observed at 660 cm^{-1} in the infrared and in the Raman spectra ($FSO_2N{=}SF_2$: 685 cm^{-1} IR, 693 cm^{-1} Raman) [3]. For $N{\equiv}SF_2{-}N{=}S(O)F_2$ the band was observed at higher frequencies (690 cm^{-1} IR and 692 cm^{-1} Raman). Experimental values reported in the literature for $FSO_2N{=}S(O)F_2$ (714 cm^{-1} IR, 717 cm^{-1} Raman) [9] confirm this assignment.

The experimental features involving the S—F stretching modes were compared with theoretical calculations for these molecules. In agreement with data reported for molecules of the type R–N=S(O)F_2, for example FC(O)N=S(O)F_2 (876 and 815 cm^{-1}) [10] $FSO_2N{=}S(O)F_2$ (885 and 819 cm^{-1}) [9] and $SF_5N{=}S(O)F_2$ (857 and 808 cm^{-1}) [12], the SF_2 symmetric stretching mode in the S(O)F_2 group was easily assigned to the band observed at 886 cm^{-1} in the infrared spectra (896 cm^{-1} Raman) while the antisymmetric vibration could not be observed either in the infrared nor in the Raman spectra (see Table 6 for theoretical values). The SF_2 symmetric stretching mode in the $N{\equiv}SF_2$ moiety was assigned to the feature centered at 769 cm^{-1} in the IR spectrum (764 cm^{-1} Raman) while the antisymmetric stretching was observed in the IR spectrum at 712 cm^{-1} (713 cm^{-1} Raman). These values are in good agreement with theoretical wavenumbers (723 and 722 cm^{-1} B3LYP; 755 and 745 cm^{-1} MP2).

On the other hand, the assignment of the signals corresponding to the expected vibrational modes for both SF_2 groups in $N{\equiv}SF_2{-}N{=}SF_2$ it is not straightforward, since both groups are quite similar. Furthermore, their features and intensities have shown to be different from one compound to the other according to reported data. However, in the present case their environments are different enough to allow an unambiguous distinction between them. Taking into account values reported for the symmetric and antisymmetric SF_2 stretching modes of compounds of type $R{-}N{=}SF_2$, the vibrational modes observed at 892 and 715 cm^{-1} in the Raman spectrum (879 cm^{-1}, IR) could be assigned to the corresponding vibrations of the terminal group (see Table 5 for theoretical values). The vibrational modes observed at 815 and 740 cm^{-1} in the IR spectrum (813 and 726 cm^{-1}, Raman) could be assigned to the SF_2 symmetric and antisymmetric stretching modes of the $N{\equiv}SF_2$ moiety. These assignments are in agreement with theoretical wavenumbers (717 and 712 cm^{-1}, B3LYP; 750 and 729 cm^{-1}, MP2).

The deformation modes involving the $N{\equiv}SF_2$, S(O)F_2 and S—N=S groups were assigned by comparison with related molecules and on the basis of the predicted wavenumbers by DFT and *ab initio* calculations.

3. Discussion

The most stable conformer of $N{\equiv}SF_2{-}N{=}SF_2$ possesses a *cis–syn* structure. A natural bond orbital (NBO) analysis [20] with the MP2/6-31G(d) wave function demonstrates that the sterically unfavorable *syn* orientation of the terminal SF_2 group is stabilized by a strong anomeric effect between the electron lone pair of the N2 atom and the antibonding S2—F orbitals ($lp(N2) \rightarrow \sigma^*(S2{-}F)$) which amounts to 16.6 kcal/mol in the *syn* form compared to 9.3 kcal/mol for *anti* orientation (for atom numbering see Fig. 4). It is more difficult to rationalize the preference for *cis* conformation of the N≡S—N=S skeleton, compared to the *trans* structure. Both computational methods with small basis sets predict the *trans–*

Table 5
Assignments of fundamental modes and experimental and calculated wavenumbers (cm^{-1}) for the *cis–syn* conformer of $N{\equiv}SF_2{-}N{=}SF_2$.

Mode	Approximate description[a]	Experimental[b]		Calculated	
		IR (gas)	Raman (liquid)	B3LYP/6-311+G(2df)	MP2/6-311+G(2df)
ν_1	N1≡S1 stretch.	1470 s	1473 s	1498 (18)	1467 (12)
ν_2	N2=S2 stretch.	1220 vs	1220 vw	1249 (100)	1285 (100)
ν_3	S2—F_2 sym. stretch.	879 m	892 m	768 (14)	803 (20)
ν_4	S1—F_2 asym. stretch.	815 s	813 w	717 (68)	750 (64)
ν_5	S1—F_2 sym. stretch.	740 vs	726 m	712 (83)	729 (78)
ν_6	S2—F_2 asym. stretch.	–	715 w	692 (12)	723 (14)
ν_7	N2—S1 stretch.	660 m	660 vs	604 (38)	632 (40)
ν_8	N1≡S1—N2 def. i.p.	579 w	590 s	566 (<1)	571 (<1)
ν_9	N1≡S1—N2 def. o.o.p	500 vw	–	464 (<1)	477 (1)
ν_{10}	F1—S1—F2 sym.def.	434 w	–	424 (<1)	441 (<1)
ν_{11}	F1—S1—F2 sym.def.	413 m	414 vs	389 (6)	396 (6)
ν_{12}	F3—S2—F4 sym.def.	–	381 m	370 (<1)	390 (2)
ν_{13}	F1—S1—F2 asym. def.	–	–	351 (<1)	359 (<1)
ν_{14}	F3—S2—F_4 asym. def.	–	273 s	263 (<1)	273 (<1)
ν_{15}	F3—S2—F4 sym.def.	–	255 m	255 (<1)	261 (<1)
ν_{16}	S1—N2=S2 def. i.p.	–	–	118 (<1)	121 (<1)
ν_{17}	N2=S2 torsion	–	–	91 (<1)	99 (<1)
ν_{18}	S1—N2 torsion	–	–	9 (<1)	9 (<1)

[a] stretch., stretching; def., deformation; sym., symmetric; asym., antisymmetric; i.p., in plane; o.o.p, out of plane. For atom numbering, see Fig. 4.
[b] vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

Table 6
Assignments of fundamental modes and experimental and calculated wavenumbers (cm^{-1}) for the *cis–syn* conformer of N≡SF_2—N=S(O)F_2.

Mode	Approximate description[a]	Experimental[b]		Calculated	
		IR (gas)	Raman[c] (liquid)	B3LYP/6-311+G(2df)	MP2/6-311+G(2df)
ν_1	N1≡S1 stretch.	1484 s	1481 s	1500 (25)	1472 (55)
ν_2	N2=S2=O asym. stretch.	1432 vs	1432 m	1411 (100)	1454 (72)
ν_3	N2=S2=O sym. stretch.	1213 vs	1203 vvw	1199 (93)	1236 (100)
ν_4	S2—F_2 sym. stretch.	886 vs	896 vw	846 (26)	886 (33)
ν_5	S2—F_2 asym. stretch.	–	–	833 (55)	869 (58)
ν_6	S1—F_2 sym. stretch.	769 vs	764 w	723 (77)	755 (41)
ν_7	S1—F_2 asym. stretch.	712 vw	713 m	722 (39)	745 (84)
ν_8	N2—S1 stretch.	690 m	692 vs	646 (14)	685 (15)
ν_9	N2=S2(O)F_2 sym.def.	579 s	618 s	558 (12)	570 (16)
ν_{10}	N1≡SF_2 sym.def.	506 s	506 m	490 (25)	503 (4)
ν_{11}	N2=S2(O)F_2 asym.def.	450 m	465 m	483 (4)	494 (23)
ν_{12}	F1—S1—F2 sym.def.	421 s	420 s	429 (3)	445 (4)
ν_{13}	N1≡SF_2 asym.def.	–	–	424 (<1)	437 (<1)
ν_{14}	N2=S2(O)F_2 sym.def.	–	373 m	395 (1)	413 (2)
ν_{15}	N1≡SF_2 asym.def.	–	–	349 (<1)	360 (1)
ν_{16}	N2=S2=O def. o.o.p.	–	327 s	307 (<1)	317 (<1)
ν_{17}	N2=S2(O)F_2 asym.def.	–	291 s	270 (<1)	283 (<1)
ν_{18}	N1≡S1—N2 def.	–	–	266 (<1)	276 (<1)
ν_{19}	S—N=S def.	–	–	120 (<1)	129 (<1)
ν_{20}	N=S torsion	–	–	72 (<1)	80 (<1)
ν_{21}	S—N torsion	–	–	9 (<1)	20 (<1)

[a] stretch., stretching; def., deformation; sym., symmetric; asym., antisymmetric; o.o.p., out of plane. For atom numbering, see Fig. 7.
[b] vs, very strong; s, strong; m, medium; w, weak; vw, very weak.
[c] Ref. [14].

syn structure as stable conformer, only about 1 kcal/mol higher in energy than the *cis–syn* structure. This *trans–syn* structure does not correspond to a stable structure according to the calculations with large basis sets. The orbital interactions within the N≡S—N=S skeleton of the *cis–syn* and *trans–syn* conformers, differ mainly in the interaction between the electron lone pair of the central N2 atom with the N≡S triple bond. In the *cis* conformer this interaction occurs with the σ^*(N≡S) orbital (interaction energy 9.4 kcal/mol) and in the *trans* structure with the π^*(N≡S) orbital (interaction energy 13.9 kcal/mol). All other interaction energies in the N≡S—N=S skeleton (lp(S2) → σ^*(S—N), σ(N=S) → π^*(N≡S) and π(N=S) → π^*(N≡S)) do not depend strongly on the conformation of the skeleton. The overall stabilizing orbital interactions in the *trans* conformer exceed those in the *cis* structure by 3.3 kcal/mol. Thus, the preference of the *cis* conformation must be due to steric effects. In the *trans–syn* conformer close contacts occur between the fluorine atoms of the two SF_2 groups (see Chart 3). These F···F distances (2.76 Å) are shorter than the van der Waals distance (2.94 Å [21] or 2.80 Å [22]). Steric strain in the *trans* conformer is evident also from an increase of the S—N=S angle from 123° to 129° and of the N2—S1—F angles from 93° to 97° compared to the *cis* form.

As pointed out in the Introduction, these compounds are of special interest because of the simultaneous presence of S—N single, double and triple bonds. Experimental values for the S≡N triple bond length in N≡SF_3 have been reported for the gas phase (1.416(3) Å) [17] and for the crystal (1.415(3) Å) [23]. A very similar bond length (1.418(2) Å) occurs in the crystal of the [N≡SF_2NCH_3CH_2−]$_2$ dimer [23]. For comparison of experimental bond lengths with calculated values we need to determine the systematic difference between vibrationally averaged experimental and calculated equilibrium distances. Calculated values depend on the computational method and values between 1.418 and 1.447 Å are predicted by the four applied methods for N≡SF_3. Calculations with the B3LYP/6-311+G(2df) method (S≡N = 1.418 Å) reproduce the experimental value very closely. Thus, from values derived with this method for N≡SF_2—N=SF_2 and N≡SF_2—N=S(O)F_2 (1.424 Å in both compounds) we conclude that the triple bond in the two latter compounds is only slightly longer than that in N≡SF_3.

Gas electron diffraction studies of several sulfurdifluoride derivatives, R—N=SF_2, and sulfuryldifluoride derivatives, R—N=S(O)F_2, resulted in N=S double bond lengths of 1.48 ± 0.01 Å [12]. For FSO_2N=SF_2 and FSO_2N=S(O)F_2, which possess similar S=N and N—S bonds as the two title compounds, experimental N=S distances of 1.487(5) and 1.475(5) Å, and S(VI)—N(sp^2) distances of 1.638(5) and 1.631(6) Å, respectively, were determined [24]. Calculations with the B3LYP/6-311+G(2df) method overestimate double and single bond lengths in these compounds by about 0.02 Å. Thus, from the calculated double bond lengths for N≡SF_2—N=SF_2 (1.506 Å) and N≡SF_2—N=S(O)F_2 (1.502 Å) we estimate the experimental N=S bond lengths to be in the usual range of 1.48 ± 0.01 Å. From the calculated S—N single bond lengths in N≡SF_2—N=SF_2 (1.683 Å) and N≡SF_2—N=S(O)F_2 (1.677 Å) the experimental bond lengths in these compounds are estimated to lie between 1.65 and 1.66 Å when the systematic difference between experimental and calculated S—N distances is taken into account. This is definitely much longer than the S(VI)—N(sp^3) distance of 1.587(1) Å determined for the crystalline [N≡SF_2NCH_3CH_2−]$_2$ dimer [23].

Acknowledgments

Financial support by the Volkswagen Stiftung (I/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.

References

[1] R. Mews, T. Bormann, R. Hoppenheit, E. Lork, S. Parsons, J. Petersen, M. Schröter, W.-D. Stohrer, A. Waterfeld, P.G. Watson, J. Fluor. Chem. 125 (2004) 1649.
[2] N.L. Robles, E.H. Cutin, C.O. Della Védova, J. Mol. Struct. 784 (2006) 265.
[3] R.M.S. Álvarez, E.H. Cutin, C.O. Della Védova, Spectrochim. Acta A 58 (2002) 149.
[4] R.M.S. Álvarez, E.H. Cutin, R.M. Romano, C.O. Della Védova, Spectrochim. Acta A 52 (1996) 667.

[5] R.M.S. Álvarez, E.H. Cutin, C.O. Della Védova, R. Mews, H. Oberhammer, Inorg. Chem. 40 (2001) 5188.
[6] M.I. Mora Valdez, E.H. Cutin, C.O. Della Védova, R. Mews, H. Oberhammer, J. Mol. Struct. 607 (2002) 207.
[7] H. Oberhammer, O. Glemser, H. Klüber, Z. Naturforsch. 29a (1974) 901.
[8] E.H. Cutin, C.O. Della Védova, H.-G. Mack, H. Oberhammer, J. Mol. Struct. 354 (1995) 165.
[9] R.M.S. Álvarez, M.I. Mora Valdez, E.H. Cutin, C.O. Della Védova, J. Mol. Struct. 657 (2003) 291.
[10] N.L. Robles, E.H. Cutin, H. Oberhammer, J. Mol. Struct. 789 (2006) 152.
[11] F. Trautner, E.H. Cutin, C.O. Della Védova, H. Oberhammer, J. Mol. Struct. 510 (1999) 53.
[12] R.M.S. Álvarez, E.H. Cutin, R. Mews, H. Oberhammer, J. Phys. Chem. A 111 (2007) 2243.
[13] O. Glemser, R. Höfer, Angew. Chem. Int. Ed. Engl. 10 (1971) 815.
[14] O. Glemser, R. Höfer, Z. Naturforsch. 29b (1974) 121.
[15] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian, Inc., Wallingford CT, 2004
[16] Synperiplanar corresponds to dihedral angles 0 ± 30°, synclinal 60 ± 30°, anticlinal 120 ± 30° and antiperiplanar 180 ± 30°.
[17] O. Glemser, R. Mews, Angew. Chem. Int. Ed. 19 (1980) 883.
[18] W.H. Kirchoff, E.B. Wilson Jr., J. Am. Chem. Soc. 85 (1963) 1726.
[19] R.M.S. Álvarez, E.H. Cutin, R.M. Romano, H.-G. Mack, C.O. Della Védova, J. Mol. Struct. 443 (1998) 155.
[20] A.E. Reed, L.A. Curtis, F. Weinhold, Chem. Rev. 88 (1988) 899.
[21] A. Bondi, J. Phys. Chem. 68 (1964) 441.
[22] Yu.V. Zefirof, M.A. Porai-Koshits, J. Struct. Chem. 21 (1981) 526.
[23] T. Bormann, E. Lork, R. Mews, S. Parsons, J. Petersen, W.-D. Stohrer, Inorg. Chim. Acta 361 (2008) 479.
[24] R. Haist, R.M.S. Álvarez, E.H. Cutin, C.O. Della Vedova, H. Oberhammer, J. Mol. Struct. 484 (1999) 249.