Vibrational Spectra and Gas Phase Structure of *N*-Cyanoimidosulfurous Difluoride, NCN═SF$_2$

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Received April 30, 2001

The vibrational spectra, IR (gas) and Raman (liquid) of *N*-cyanoimidosulfurous difluoride, NCN═SF$_2$, were recorded, and the molecular structure was determined by gas electron diffraction. The spectra were assigned by comparing the vibrational frequencies with those in related molecules and with calculated (HF, MP2, B3LYP with 6-31G(d) basis sets) values, and a normal coordinate analysis was performed. The molecule possesses a syn conformation (C≡N syn with respect to the bisector of the SF$_2$ angle). This has been rationalized by orbital interactions of the electron lone pairs of sulfur and nitrogen with the N−C and S−F bonds, respectively, which are antiperiplanar or anticlinal to these lone pairs (anomeric effects). Quantum chemical calculations with the B3LYP and MP2 methods reproduce the experimental structure reasonably well if large basis sets (6-311G(2d,f)) are used.

Introduction

Vibrational spectra and gas phase structures of several imidosulfurous difluorides of the type RN═SF$_2$ have been reported in the literature. The substituent R includes CF$_3$[1] with an sp^3-hybridized carbon atom and FC(O)[2] or CF$_3$C(O)[3] with sp^2-hybridized carbon atoms. All imidosulfurous difluorides whose gas phase structures have been studied possess the syn conformation with the substituent R syn relative to the bisector of the SF$_2$ angle. This implies also syn orientation of the two electron lone pairs of sulfur and nitrogen. In the present study we report the vibrational spectra and geometric structure as determined by gas electron diffraction (GED) for *N*-cyanoimidosulfurous difluoride, NCN═SF$_2$, in which the substituent possesses an sp-hybridized carbon atom. The experimental investigations are supplemented by quantum chemical calculations. NCN═SF$_2$ was prepared for the first time in 1967 by Sundermeyer,[4] and an alternative synthetic route was reported in the same year by Glemser et al.[5]

Experimental Section

NCN═SF$_2$ was synthesized by the reaction of cyanamide (H$_2$N−CN) with SF$_4$ in the presence of NaF.[5] The product was purified at reduced pressure by repeated trap-to-trap distillation at −60 °C.

The gas IR spectrum at 4 Torr was recorded between 4000 and 400 cm^{-1} (resolution 2 cm^{-1}) with a FT-IR Perkin-Elmer Paragon 500 spectrometer, using a gas cell equipped with KBr windows. Raman spectra of the liquid between 3500 and 50 cm^{-1} were obtained using a Jobin Yvon U 1000 spectrometer equipped with both argon and krypton ion lasers (Spectra Physics model 165), and radiation of 514.5 nm (Ar$^+$) was used for excitation. The liquid samples were handled in glass capillaries at room temperature. The spectral resolution was 4 cm^{-1}.

The GED intensities were recorded with a Gasdiffraktograph KD-G2[6] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of approximately 60 kV. The sample reservoir was kept at 15 °C, and the inlet system and nozzle were at room temperature. The photographic plates (Kodak electron image plates 18 × 13 cm) were analyzed with the usual methods,[7] and averaged molecular intensities in the s ranges 2−18 and 8−35 Å^{-1} in steps of $\Delta s = 0.2$ Å^{-1} ($s = (4\pi/\lambda) \sin \theta/2$, λ = electron wavelength, θ = scattering angle) were used in the structure analysis.

Quantum Chemical Calculations

The geometry of the syn conformer of NCN═SF$_2$ was optimized with the HF and MP2 approximations and with the hybrid method B3LYP using 6-31G(d) and 6-311G(2d,f) basis sets. The structure of the anti conformer was optimized only with the smaller basis sets, and its energy is predicted to be higher by 5.4 (HF), 6.4 (MP2), or 5.8 kcal/mol (B3LYP). The anti form possesses C_s symmetry and represents a stable structure with no imaginary frequency. The frequencies of the syn form were calculated with the 6-31G(d) basis sets. Cartesian force constants which were obtained with the B3LYP method were scaled in order to fit the experimental frequencies, transformed to symmetry force constants, and used for calculating vibrational amplitudes. All quantum chemical calculations were performed with the GAUSSIAN

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(1) Trautner, F.; Christen, D.; Mews, R.; Oberhammer, H. *J. Mol. Struct.* **2000**, *525,* 135.

(2) Leibold, C.; Cutin, E. H.; Della Vedova, C. O.; Mack, H.-G.; Mews, R.; Oberhammer, H. *J. Mol. Struct.* **1996**, *375*, 207.

(3) Mora Valdez, M. I.; Cutin, E. H.; Della Vedova, C. O.; Oberhammer, H. To be published.

(4) Sundermeyer, W. *Angew. Chem.* **1967**, *79*, 98; *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 90.

(5) Glemser, O.; Biermann, U. *Inorg. Nucl. Chem. Lett.* **1967**, *3*, 223.

(6) Oberhammer, H. *Molecular Structure by Diffraction Methods*; The Chemical Society: London, 1976; Vol. 4, p 24.

(7) Oberhammer, H.; Gombler, W.; Willner, H. *J. Mol. Struct.* **1981**, *70*, 273.

10.1021/ic010458h CCC: \$20.00

Table 1. Experimental and Calculated Wavenumbers (cm^{-1}) for $NCN{=}SF_2$

IR		Raman		HF/	B3LYP/	MP2/
vapor	int[a]	liquid	int[b]	6-31G(d)[c]	6-31G(d)	6-31G(d)
2256	m	2241	100	2351	2339	2207
1337	vs	1312	16	1337	1360	1378
843	m	848	10	856	850	877
766	s	774	35	802	766	781
728	s	718	8	791	732	752
615	w	622	8	633	604	608
529	w	537	6	565	543	528
		449	11	446	415	410
		389	5	387	359	367
		350	6	346	315	315
		141	52	126	117	117
		85	35	102	95	96

[a] Key: vs, very strong; s, strong; m, medium; w, weak. [b] Relative intensities (%). [c] Wavenumbers scaled by factor 0.9.

Table 2. Assignment of Fundamental Modes, Calculated Force Constants, and Potential Energy Distribution (PDE) for $NCN{=}SF_2$

mode	approx description[a]	wavenumbers (cm^{-1})	symmetry force const[b]	PED[c]
A′				
ν_1	C≡N stretch	2256 (IR)	18.65	95.6(1)
ν_2	S═N stretch	1337 (IR)	9.72	92.5(2)
ν_3	N−C stretch	843 (IR)	3.69	37.7(3); 27.2(5)
ν_4	SF_2 sym stretch	766 (IR)	4.62	50.5(4); 17.0(3)
ν_5	NCN in-plane def.	615 (IR)	0.95	60.0(5); 36.8(4)
ν_6	SF_2 def	449 (Ra)	2.37	88.7(6)
ν_7	SF_2 wagging	389 (Ra)	1.45	96.0(7)
ν_8	CNS def	141 (Ra)	0.44	87.4(8)
A″				
ν_9	SF_2 asym stretch	728 (IR)	3.60	96.0(9)
ν_{10}	NCN out-of-plane def	529 (IR)	0.40	96.2(10)
ν_{11}	SF_2 twisting	350 (Ra)	1.13	89.8(11)
ν_{12}	torsion	85 (Ra)	0.04	94.3(12)

[a] Key: stretch, stretching; sym, symmetric; asym, asymmetric; def, deformation. [b] In mdyn $Å^{-1}$ or mdyn Å rad^{-2} for bonding and angular force constants, respectively. [c] $V(k) = F_{dia}L_{ij}^2(100)/F_{ij}L_{ik}$ for $V(k) > 15$.

98 program suite,[8] and the vibrational amplitudes were derived with the program ASYM40.[9]

Vibrational Spectra

The vibrational analysis for $NCN{=}SF_2$ was performed by taking into account the wavenumbers and intensities of the observed signals in the gas phase IR spectrum and liquid Raman spectrum, and by comparing spectral data with those of related molecules. The results obtained with quantum chemical calculations were also considered. Experimental and calculated wavenumbers are listed in Table 1. The HF values (scaled with 0.9) and the unscaled B3LYP and MP2 values agree reasonably well with the experimental frequencies. Some vibrations, however, appear to be strongly coupled, which makes their identification difficult. For this reason, the assignment of the fundamental modes of the $N{=}SF_2$ group in $NCN{=}SF_2$ was established by comparison with the features observed for $FC(O)NSF_2$,[10] $ClSO_2NSF_2$,[11] FSO_2NSF_2,[12] and $CF_3C(O)NSF_2$.[3] The modes belonging to the cyanide group were assigned by comparison with $F_2S(O)NCN$,[13] $(CH_3)_2NCN$,[14] and ONCN.[15] Although some vibrations are strongly coupled (in particular ν_3, ν_4, and ν_5), the assignments of all bands are based solely on the internal coordinates with the major contributions to the potential energy distribution. The observed wavenumbers together with a tentative assignment for $NCN{=}SF_2$ are given in Table 2.

The $3N - 6 = 12$ normal modes of vibrations are classified as 8 A′ and 4 A″ taking into account the C_s symmetry which results from the quantum chemical calculations. A subsequent normal coordinate analysis was performed, and the potential energy distribution (PED) and symmetry force constants derived from this analysis are also presented in Table 2. The N−C≡N moiety shows two different stretching modes which can immediately be assigned by comparison with the characteristic group wavenumbers of similar molecules.[13−15] Thus, the C≡N stretching vibration is observed as the strongest Raman peak at 2241 cm^{-1} and at 2256 cm^{-1} in the IR gas phase spectrum, whereas the N−C single bond stretching gives a signal centered at 843 cm^{-1} in the IR and at 848 cm^{-1} in the Raman. The S═N stretching mode in $NCN{=}SF_2$ is assigned to the strongest IR band at 1337 cm^{-1} (1312 cm^{-1} in Raman), showing good agreement with the values reported for $FC(O)NSF_2$[10] (1330 cm^{-1}) and $CF_3C(O)NSF_2$[3] (1361 cm^{-1}). The SF_2 symmetric and asymmetric stretching modes appear as intense IR signals at 766 and 728 cm^{-1}, respectively, and as a medium (774 cm^{-1}) and a weak (718 cm^{-1}) peak in the Raman spectrum. Other molecules possessing the NSF_2 moiety show these stretching modes at 758/725 cm^{-1} ($FC(O)NSF_2$) and 749/728 cm^{-1} ($CF_3C(O)NSF_2$), whereas for molecules of the type XSO_2NSF_2 (X = Cl,[11] F[12]) the symmetric and asymmetric modes appear at slightly higher wavenumbers, 849/803 and 848/804 cm^{-1}, respectively. In all cases, both fundamentals produce very intense IR signals.

The molecule possesses two skeletal vibrations, and they are defined as CNS deformation (A′) and as torsion around the S═N bond (A″). The former is assigned to the signal centered at 141 cm^{-1} in the Raman of $NCN{=}SF_2$, in accordance with the observed peak for $FC(O)NSF_2$[10] (149 cm^{-1}) as well as for $F_2S(O)NCN$[13] (137 cm^{-1}), and the latter is observed at 85 cm^{-1}.

Structure Analysis

The averaged molecular intensities for the two nozzle-to-plate distances are shown in Figure 1. The radial distribution function (RDF) was derived by Fourier transformation of the molecular intensities, which were modified with an artificial damping function $\exp(-\gamma s^2)$, $\gamma = 0.0019$ $Å^2$. The RDF (Figure 2) is reproduced satisfactorily only with a syn structure. The geometric parameters (r_a values) were derived by least-squares fitting of the molecular intensities. C_s overall symmetry was assumed. Vibrational amplitudes which either caused high correlations between geometric parameters or are badly determined in the experiment were set to the theoretical values. With these assumptions eight geometric parameters (p1 to p8) and eight vibrational amplitudes (*l*1 to *l*8) were refined simulta-

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(8) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN98*, Version A6; Gaussian, Inc.: Pittsburgh, PA, 1998.

(9) Hedberg, L.; Mills. I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117.

(10) Álvarez, R. M. S.; Cutin, E. H.; Romano, R. M.; Della Védova, C. O. *Spectrochim. Acta, Part A* **1996**, *52*, 667.

(11) Álvarez, R. M. S.; Cutin, E. H.; Romano, R. M.; Mack, H.-G.; Della Védova, C. O. *J. Mol. Struct.* **1998**, *443*, 155.

(12) Álvarez, R. M. S.; Cutin, E. H.; Della Vedova, C. O. To be published.

(13) Álvarez, R. M. S.; Cutin, E. H.; Mack, H.-G.; Sala, O.; Della Vedova, C. O. *J. Mol. Struct.* **1994**, *328*, 221.

(14) Brown, F. B.; Fletcher, W. H. *Spectrochim. Acta* **1963**, *19*, 915.

(15) Dorko, E. A.; Buelow, L. *J. Chem. Phys.* **1975**, *62*, 1869.

Table 3. Experimental and Calculated Geometric Parameters for NCN=SF_2[a]

	GED[b]		B3LYP/6-31G(d)	B3LYP/6-311G(2d,f)	MP2/6-31G(d)	MP2/6-311G(2d,f)
C≡N	1.167(3)	p1	1.166	1.154	1.186	1.173
N−C	1.368(4)	p2	1.339	1.331	1.351	1.340
S=N	1.484(3)	p3	1.522	1.504	1.517	1.503
S−F	1.593(2)	p4	1.634	1.614	1.632	1.596
S=N−C	126.2(15)	p5	128.3	129.8	125.3	125.6
N=S−F	108.8(8)	p6	109.4	108.9	109.3	108.9
F−S−F	90.5(3)	p7	90.6	91.2	90.0	91.2
N−C≡N	179.0(28)	p8	175.3	175.9	175.5	176.3

[a] Bond lengths in angstroms, angles in degrees. [b] r_a values with 3σ uncertainties.

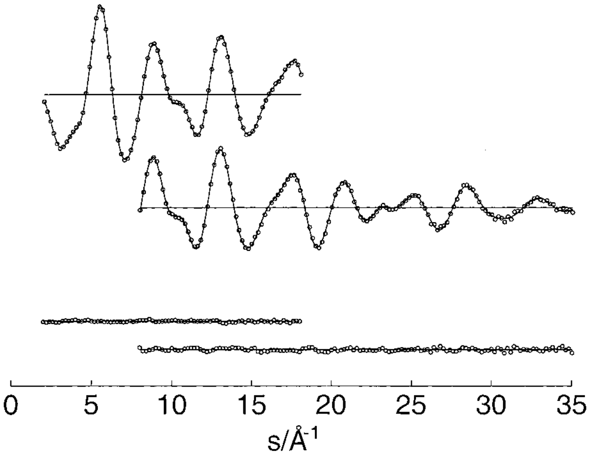


Figure 1. Experimental (dots) and calculated (full line) molecular intensities for long (above) and short (below) nozzle-to-plate distances and residuals.

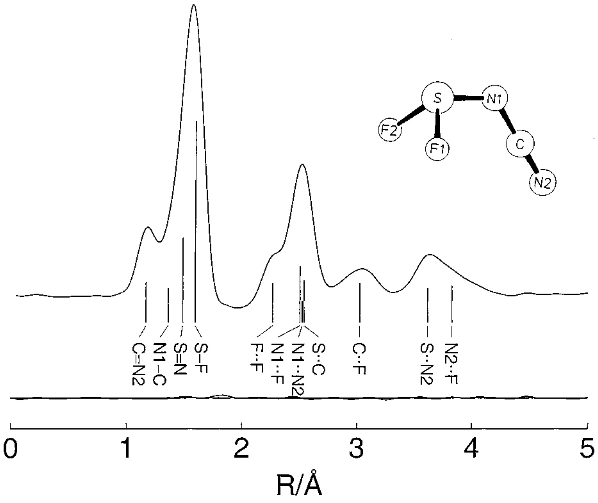


Figure 2. Experimental radial distribution function and difference curve. Vertical bars indicate the positions of interatomic distances.

neously. The following correlation coefficients had values larger than |0.6|: p5/p6 = −0.90, p5/p8 = −0.88, p6/p8 = 0.82, p3/*l*2 = 0.68, p4/*l*3 = −0.67, p5/*l*5 = −0.80, p6/*l*5 = 0.85, p8/*l*5 = 0.75, *l*2/*l*3 = 0.88. The results are listed together with the theoretical values in Table 3 (geometric parameters) and Table 4 (vibrational amplitudes). It was not attempted to derive an r_α structure, since the concept of perpendicular vibrations in the presence of a low frequency torsional vibration (85 cm^{-1}) results in unreasonably large corrections, particularly for N−C and C≡N bond lengths (0.015 and 0.016 Å, respectively).

Discussion

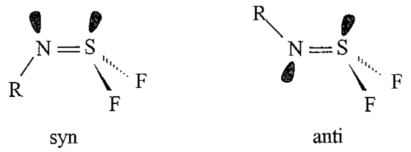
N-Cyanoimidosufurous difluoride possesses a syn conformation in agreement with all other compounds of the type RN=SF_2 whose structures have been determined. Intuitively one would expect that steric repulsion between the substituent R and the fluorine atoms and interaction between the electron lone pairs of nitrogen and sulfur favor the anti structure (see Scheme 1). Quantum chemical calculations predict this anti form to be a stable structure but higher in energy by about 6 kcal/mol. A natural bond orbital analysis (NBO)[16] reveals that the syn conformation is stabilized by orbital interactions between the two lone pairs of sulfur and nitrogen with the N−C and S−F bonds, respectively, which are antiperiplanar or anticlinal to these lone pairs. The stabilization energies of these two interactions are calculated (MP2/6-31G(d)) to be 10.7 and 9.8 kcal/mol for $n_S \rightarrow \sigma^*(N-C)$ and $n_N \rightarrow \sigma^*(S-F)$, respectively. The total stabilization energy due to these anomeric effects amounts to about 30 kcal/mol and thus overcompensates steric repulsion.

Table 4. Interatomic Distances and Experimental and Calculated (B3LYP/6-31G(d)) Vibrational Amplitudes[a]

	distance	exptl amplitude[b]		calcd amplitude[c]
C≡N	1.17	0.035(4)	*l*1	0.034
N−C	1.36	0.042[d]		0.042
S=N	1.48	0.036(5)	*l*2	0.039
S−F	1.59	0.044(2)	*l*3	0.045
F1···F2	2.26	0.067(6)	*l*4	0.074
N1···F	2.50	0.076[d]		0.076
N1···N2	2.52	0.046[d]		0.046
S···C	2.54	0.067 (4)	*l*5	0.066
C···F	3.02	0.134(8)	*l*6	0.159
S···N2	3.61	0.092(9)	*l*7	0.089
F···N2	3.83	0.177(20)	*l*8	0.224

[a] Values in angstroms. For atom numbering see Figure 2. [b] Uncertainties are 3σ values. [c] B3LYP/6-31G*. [d] Not refined.

Scheme 1



Cyanoimidosulfuryl fluoride, NCN=S(O)F_2, does not show such a strong preference for the syn conformation. For this compound a small contribution of the anti form (C≡N anti to the bisector of the SF_2 angle, i.e., eclipsing the S=O bond) was observed and the experimental free energy difference ($\Delta G° =$ 1.3(6) kcal/mol) is reproduced correctly by ab initio methods (ΔE = 1.6 kcal/mol from HF and MP2 with 6-31G* basis sets).[17] Increase of the sulfur oxidation number from S(IV) to S(VI) leads to shortening of the S−F bonds from 1.593(2) Å

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(16) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct. (Theochem.)* **1988**, *169*, 41.

(17) Cutin, E. H.; Della Vedova, C. O.; Mack, H.-G.; Oberhammer, H. *J. Mol. Struct.* **1995**, *354*, 165.

Table 5. Skeletal Geometric Parameters of Imidisulfurous Difluorides $RN{=}SF_2$

compound	N=S	N−R	S−F	R−N=S	F−S−F	N=S−F
$CF_3N{=}SF_2$[a]	1.477(6)	1.409(8)	1.594(2)	127.2(11)	92.8(4)	112.7(10)
$FC(O)N{=}SF_2$[b]	1.479(4)	1.395(6)	1.586(2)	126.1(11	93.4(3)	110.4(8)
$NCN{=}SF_2$[c]	1.484(3)	1.368(4)	1.593(2)	126.2(15)	90.5(3)	108.8(8)
$ClN{=}SF_2$[d]	1.476(4)	1.703(4)	1.596(2)	120.0(2)	89.3(3)	111.2(2)
$SF_5N{=}SF_2$[e]	1.470	1.679	1.603	141.9	87.6	103.4
$FSO_2N{=}SF_2$[f]	1.487(5)	1.638(5)	1.575(3)	129.9(8)	92.2(9)	109.7(8)

[a] Reference 1. [b] Reference 2. [c] This work. [d] Reference 18. [e] Reference 19, no uncertainties are given. [f] Reference 20.

in $NCN{=}SF_2$ to 1.543(6) Å in $NCN{=}S(O)F_2$, whereas the S=N double bond remains unaffected within the experimental uncertainties (1.484(3) vs 1.498(12) Å).

Considering systematic differences between experimental (vibrationally averaged r_a values) and calculated (equilibrium values) geometric parameters, the quantum chemical methods (B3LYP and MP2) reproduce the experimental results reasonably well. The S=N and S−F bond lengths are predicted too long by about 0.04 Å with small basis sets (6-31G(d)). This discrepancy is reduced somewhat with larger basis sets (6-311G-(2d,f)), but the calculated S=N bond distance is still too long, even more so if the correction between r_e and r_a values is taken into account.

Table 5 summarizes skeletal geometric parameters for some imidosulfurous difluorides whose structures have been determined by GED or microwave spectroscopy ($SF_5N{=}SF_2$). The S=N and S−F bond lengths are remarkably constant in these compounds, with $S{=}N = 1.48 \pm 0.01$ Å and $S{-}F = 1.59 \pm 0.01$ Å. Only the S−F bonds in $FSO_2N{=}SF_2$ are slightly shorter (1.575(3) Å), and this is in agreement with the observed S−F stretching vibrations which are almost 100 cm^{-1} higher than those in the other $RN{=}SF_2$ compounds (see above). In the series $R = CF_3$, FC(O), and CN the N−C bond shortens steadily from 1.409(8) Å in $CF_3N{=}SF_2$ to 1.368(4) Å in $NCN{=}SF_2$ when hybridization of the carbon atom changes from sp^3 to sp. The decrease of the N=S−F angles in this series from 112.7(10)° to 108.8(8)° reflects decreasing steric repulsion between the substituent R and the fluorine atoms. A very small N=S−F angle (103.4°) has been derived from the rotational constants of $SF_5N{=}SF_2$. On the other hand, quantum chemical calculations (B3LYP/6-31G(d)) predict a value of 111.7° for this angle, which is in much better agreement with the values for all the other compounds. The R−N=S angle is constant within its experimental uncertainties (ca. 127°) in the series $R = CF_3$, FC(O), and CN, and it is smaller (120.0(2)°) for R = Cl and much larger for $R = SF_5$ (141.9°).

Acknowledgment. R.M.S.A. and E.H.C. thank the CONICET and Universidad Nacional de Tucuman, República Argentina, for financial support. We thank the Fundación Antorchas (República Argentina), Alexander von Humboldt Stiftung, 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. C.O.D.V. also thanks the Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET), ANPCYT (PICT 122) (Argentina), and the Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC), República 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 the National Award to the Argentinean cooperation.

IC010458H

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(18) Haase, J.; Oberhammer, H.; Zeil, W.; Glemser, O.; Mews, R. *Z. Naturforsch.* **1970**, *25a*, 153.

(19) White, R. M.; Bailey, S. R.; Graybeal, J. D.; Thrasher, J. S.; Palmer, M. H. *J. Mol. Spectrosc.* **1988**, *129*, 243.

(20) Haist, R.; Alvárez, R. S. M.; Cutin, E. H.; Della Vedova, C. O. Oberhammer, H. *J. Mol. Struct.* **1999**, *484*, 249.