in the latter, the CF_3 group withdraws electron density.[21]

A similar relationship is found between hydrogen-bond strength and proton affinity[20] of the base molecule. Both ionization energy and proton affinity reflect the stability of the product ion in its lowest-energy configuration. The alkene-hydrogen fluoride complex is a model species for the intermediate proton addition complex, similar to that formed by proton attachment *before* rearrangement, as has been the subject of theoretical calculations on the ethyl ion with open and bridged configurations.[25]

Conclusions

Cocondensation of substituted alkenes and hydrogen fluoride at high dilution in argon on a 12 K substrate has produced hydrogen-bonded complexes for characterization by FT IR matrix spectroscopy. In the case of methyl-substituted alkenes, the ν_s (H-F stretch) and ν_l (H-F libration) modes show that stronger hydrogen bonds are formed than with ethylene, and the observation of only perturbed out-of-plane C-H_2 base submolecule modes shows that H-F is perpendicular to the alkene plane in these π complexes. The split ν_l modes provide a measure of the anisotropy of the hydrogen-bonding interaction, which shows a dependence on the position and number of methyl substituents. In the case of vinyl fluoride, the ν_s and ν_l modes show that a weaker hydrogen bond is formed compared to ethylene, the observation of a substantially red-shifted C-F stretching mode indicates that H-F attaches to the electron-rich fluorine rather than the π bond, and the observation of four perturbed in-plane modes, two perturbed out-of-plane modes, and two separate ν_l modes for the complex suggests that H-F forms an acute angle with the molecular plane. The observation of acid and base submolecule vibrations in matrix FT IR studies of hydrogen-bonded complexes provides a characterization of the hydrogen-bond strength and the geometry of the complex.

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Registry No. $C_2H_3CF_3$, 677-21-4; C_2H_3F, 75-02-5; C_2H_3Cl, 75-01-4; C_2H_3Br, 593-60-2; 1,1-$C_2H_2F_2$, 75-38-7; *cis*-$C_2H_2F_2$, 1630-77-9; *trans*-$C_2H_2F_2$, 1630-78-0; HF, 7664-39-3; ethylene, 74-85-1; propylene, 115-07-1; *trans*-2-butene, 624-64-6; 2,3-dimethyl-2-butene, 563-79-1; isobutylene, 115-11-7.

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(24) Libit, L.; Hoffman, R. *J. Am. Chem. Soc.* **1974**, *96*, 1370.

(25) Dixon, D. A.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1973**, *95*, 2953.

Structure of Perfluoromethanimine by Microwave, Infrared, and Raman Spectroscopy, Electron Diffraction, and ab Initio Methods

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Abstract: A normal coordinate analysis for CF_2=NF based on infrared, Raman, and microwave data has been performed. The geometric structure was determined experimentally by a joint analysis of electron diffraction and microwave data. The structures of CH_2=NH and CF_2=NF were optimized by ab initio calculations using 4-21G basis sets. For CF_2=NF very short C-F bonds (1.300 (3) Å) and a very long N-F bond (1.389 (2) Å) are determined. These results are in agreement with the corresponding force constants. The N=C bond lengths in CH_2=NH and CF_2=NF are equal within error limits. The bonding properties of CF_2=NF are discussed on the basis of the ab initio calculations.

Introduction

Methanimine, CH_2=NH, is the simplest imine and it has been the subject of considerable chemical and theoretical interest.[1] However, the compound is exceedingly unstable and the gas-phase pyrolysis of amines is the only method for its synthesis. Perfluoromethanimine, CF_2=NF, on the other hand, is a stable compound, much more amenable to experimental study. The latter was first obtained in 1952,[2] but difficult methods of synthesis have limited its structural characterization to ^{19}F NMR and a survey infrared spectrum.[3]

Recently, new preparative methods were found for CF_2=NF,[4] and these allow a detailed investigation of the chemical properties[5] and structure. Here we report the structure of CF_2=NF as determined by infrared, Raman, and microwave spectroscopy, by gas electron diffraction, and by ab initio methods. The results are compared with CH_2=NH and related isoelectronic species O=CF_2, CF_2=NCl, CF_2=CHF, and also CH_2=CF_2.

Experimental Section

Sample. Perfluoromethanimine was prepared from ClCN according to the literature method.[4] The sample for IR and Raman were purified by GLC on a 20 ft × 1/4 in. column packed with 40% perfluorotributylamine on Chromosorb P. The sample for electron diffraction and microwave spectroscoy was purified by distillation and the purity was checked by IR spectra.

Vibrational Spectra. The IR spectra were recorded at ambient temperature in the gas phase (10-cm cell with CsI windows and ca. 10 torr pressure) with a Perkin-Elmer Model 180 spectrophotometer (resolution of 0.8 cm^{-1}). The Raman spectra were taken with a Spex 14018 double monochromator with photon-counting detection. Excitation was via the 514.5-nm line of an Ar^+ ion laser using 150-350 mW of power. Depolarization ratios were determined by method IV as described by Claassen et al.[6] A low-temperature glass cell similar to that described by Brown

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(1) R. Pearson and F. J. Lovas, *J. Chem. Phys.*, **66**, 4149 (1977).

(2) J. A. Cuculo and L. A. Bigelow, *J. Am. Chem. Soc.*, **74**, 710 (1952).

(3) A. Sekiya and D. D. DesMarteau, *J. Am. Chem. Soc.*, **101**, 7640 (1979).

(4) A. Sekiya and D. D. DesMarteau, *J. Org. Chem.*, **46**, 1277 (1981).

(5) S. C. Chang and D. D. DesMarteau, *Polyhedron*, in press.

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Table I. Recorded Vibrational Frequencies (cm^{-1}) of $CF_2{=}NF^a$

IR (gas)			Raman (liq)	
3475	Q	vw	$2\nu_1$	
3460	P			
3129	R			
3120	MIN	vw	$\nu_1 + \nu_2$	
3108	P			
2757	R			
2750.1	Q	w	$2\nu_2$	
2740	P			
2672	R			
2660	MIN	vw	$\nu_1 + \nu_4$	
2652	P			
2405	Q	vw	$\nu_2 + \nu_3$	
2370	Q	vw	$\nu_1 + \nu_5$	
2318	Q	vw	$\nu_2 + \nu_4$	
2025	Q	vw	$2\nu_3$	
1897	Q	w	$\nu_2 + \nu_6$	
1865	R			
1859	MIN	vw	$2\nu_4$	
1850	P			
1748	R			
1740.3	Q	s	ν_1	1733 m, p
1738.5	Q			
1736	Q			
1731	P			
1664	R			
1659	MIN	vw	$\nu_3 + \nu_5$	
1650	P			
1541	Q	w	$\nu_3 + \nu_6$	
1525	P			
1393	R			
1385.5	Q	s	ν_2	1388 vw, p
1384	Q			
1375	P			
1309	Q	vw	$\nu_3 + \nu_7$	
1292	R			
1281	Q	w	$2\nu_8$	
1252	Q	w	$2\nu_5$	
1220	R			
1210	Q	w	$\nu_4 + \nu_7$	
1199	P			
1105	R			
1098	Q	w	$\nu_5 + \nu_6$	
1029	R			
1021.2	Q	s	ν_3	1013 w, p
1019.5	Q			
1018	Q			
1011.5	P			
939.8	R			
932.9	Q	m	ν_4	932 vvs, p
931	Q			
923.5	P			
800	Q	vw	$\nu_6 + \nu_7$	
668	Q	w	$\nu_7 + \nu_8 - \nu_7$	
651.5	R			
643.2	Q	m	ν_8	649 m, dp
636.5	P			
			ν_5	644 vs, p
526	R			
520.0	MIN	w	ν_6	522 s, p
511	P			
302.5	Q	w	ν_9	306 m, dp
290.2	R			
285.7	MIN	w	ν_7	291 w, p
278.5	P			

[a] v, very; w, weak; m, medium; s, strong; MIN, minimum; p, polarized; dp, depolarized.

Table II. Microwave Spectroscopy Data for Structure Determination and Normal Coordinate Analysis

1. Rotational Constants (MHz)

	B_0^i	$B_z^{i\,a}$	B_z^i (calcd)	B^i ($v_7 = 1$)	B^i ($v_9 = 1$)
A	11 235.412 (8)	11 214.78 (207)	11 215.18	10 873.976 (75)	11 568.100 (115)
B	4 316.781 (3)	4 311.27 (55)	4 311.07	4 284.086 (51)	4 342.733 (58)
C	3 115.288 (2)	3 114.04 (13)	3 114.04	3 109.598 (50)	3 120.121 (52)

2. Inertial Defects (u.Å^2)

	$v = 0$	$v = 1$	$v = 1$	zero point^b
exptl	0.1714	−1.920	1.915	0.0041
calcd^c	0.1747	−1.90	2.29	

3. Centrifugal Distortion Constants (kHz)

	$v = 0$ (exptl)	$v = 0$ (calcd)^c	$v_7 = 1^d$	$v_9 = 1^d$
Δ_J	0.857 (13)	0.859	−0.85	0.49
Δ_{JK}	7.195 (79)	7.784	−52.88	67.40
Δ_K	5.457 (15)	4.083	−191.80	134.77
δ_J	0.218 (2)	0.220	−0.36	0.90
δ_K	4.575 (64)	4.906	−85.84	54.91

[a] Error limits are 10% of corrections $B_0^i - B_z^i$. [b] Calcualted from B_z^i rotational constants. [c] Calculated from force field of Table IV. [d] Centrifugal distortion constants used as fitting parameters to partially compensate for Coriolis coupling.

et al.[7] was used to record the low-temperature spectra. Vibrational frequencies are summarized in Table I.

Rotational spectra were recorded using a conventional 100-kHz modulated Stark microwave spectrometer at a pressure of 10^{-2} torr and cell temperature of about −50 °C. The study was facilitated by using the preliminary electron diffraction structure which made it possible to assign some key lines on the very first day of the investigation. The assignment of the ground-state lines was straightforward and more than 200 lines have been accurately measured. A report on the spectrum including an analysis of the hyperfine structure due to ^{14}N quadrupole coupling, as well as that of the ^{13}C-substituted species, has been presented at EUCMOS XV.[8] The data relevant for this investigation are collected in Table II. The inertial defect proves the molecule to be planar as expected from hybridization arguments.

The components of the electric dipole moment have been calculated by measuring the Stark displacements of *M* components of the following transitions: $0_{00} \rightarrow 1_{11}$, $1_{01} \rightarrow 2_{02}$, $2_{12}, \rightarrow 3_{03}$, $3_{03} \rightarrow 4_{04}$, and $3_{22} \rightarrow 4_{23}$, applying a dc field calibrated against OCS and adding enough ac field to modulate the lines. The dipole moment components (Table V) were evaluated at such high fields that the interaction with the nuclear quadrupole coupling at nitrogen could be neglected.

Electron Diffraction. Scattering intensities were recorded on 13 × 18 cm Kodak electron image plates with the Balzers Model KD-G2 gas

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(6) H. H. Claassen, H. Selig, and J. Shamir, *J. Appl. Spectrosc.*, **23**, 8 (1969).

(7) C. W. Brown, A. G. Hopkins, and F. P. Daly, *J. Appl. Spectrosc.*, **28**, 194 (1974).

(8) D. Christen, *J. Mol. Struct.*, **79**, 221 (1982).

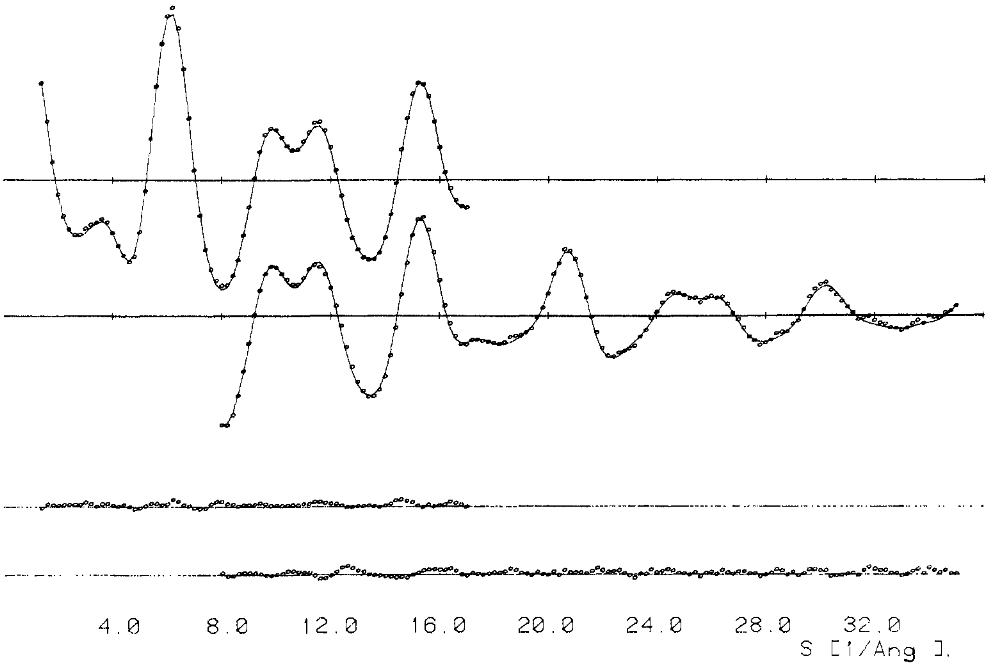

Figure 1. Experimental (o) and calculated (—) molecular intensities and differences.

Table III. Comparison of the Fundamentals of $CH_2{=}CF_2$, $CHF{=}CF_2$, $ClN{=}CF_2$, $O{=}CF_2$, and $FN{=}CF_2$ (cm^{-1})

	${}^{H}_{H}C{=}C^{F}_{F}$ [a] X = C Y = H	${}^{F}_{H}C{=}C^{F}_{F}$ [b] X = C Y = F	${}^{Cl}N{=}C^{F}_{F}$ [c] X = N Y = Cl	$O{=}C^{F}_{F}$ [d] X = O	${}^{F}N{=}C^{F}_{F}$ [e] X = N Y = F	${}^{F}N{=}C^{F}_{F}$ [f] X = N Y = F
CH	3110	3150				
C=X	1729	1788	1728	1929.9	1740.3	1740.2
CF_2(as)	1303	1362	1322	1243.7	1385.5	1385.5
δCFH	1364	1264				
XY	3062	1171	771		1021.2	1021.4
CF_2(s)	926	929	981	965.6	932.9	933.0
δCF_2	550	623	598	582.9	640	641.3
ρCF_2	437	485	465	619.9	520.0	521.0
δXY	954	232	175		285.7	290.1
βCFH	804	750				
βCF_2	561	555	658	767.4	643.2	642.8
tors	611	305	240		302.5	300.6

[a] Reference 13. [b] Reference 12. [c] Reference 14. [d] Reference 15. [e] Experimental frequencies; this study. [f] Calculated from force field in Table IV.

diffractograph,[9] using a 0.25-mm nozzle diameter. The accelerating voltage was about 60 kV and data were collected at nozzle-to-plate distances of 50 and 25 cm. The nozzle temperature was about 10 °C, and the vapor pressure at −90 °C (about 10–15 torr) required exposure times up to 25 and 60 s for the long and short camera distances. The camera pressure never exceeded 2×10^{-5} torr during the experiment. The electron wavelength was determined from ZnO diffraction patterns. For each camera distance two plates were selected and intensity data were evaluated in the usual way.[10] Averaged molecular intensities for both camera distances, interpolated in steps of $\Delta s = 0.2$ Å^{-1}, are presented in Figure 1.[11]

Normal Coordinate Analysis

The planar structure of $CF_2{=}NF$ requires the point group symmetry to be C_s, and the nine normal vibrations are distributed among the irreducible species as 7a′ in-plane vibrations and 2a″ out-of-plane vibrations. The 7a′ vibrations must be A/B-type hybrids (in IR) and polarized (in Raman), whereas the two out-of-plane vibrations are of C type and should exhibit strong, narrow Q branches (in IR) and be depolarized (in Raman). The recorded spectra in gas (IR) and liquid (Raman) seem to adhere to these rules. Four earlier IR investigations of related molecules aided in the decision of an assignment: the isoelectronic trifluoroethylene,[12] 1,1-difluoroethylene,[13] *N*-chlorodifluormethanimine,[14] and carbonyl difluoride.[15] In Table III the frequencies of the assigned fundamentals are compared with those of the four molecules listed above. This comparison results in a rather unambiguous assignment. (1) The highest frequency fundamental (1738 cm^{-1}) must be the C=N stretch ν_1(a′). It appears at somewhat lower frequency than the C=C vibration in trifluoroethylene, which means that the corresponding force constant is somewhat smaller for the C=N vibration (also in $CF_2{=}NCl$) than for the C=C one, contrary to the expected trend, C=C < C=N < C=O. The C=O force constant is larger than the C=C force constant, as expected. (2) The two CF_2 stretches ν_2(a′) and ν_4(a′) are easily assigned. Comparison with $FHC{=}CF_2$, $CH_2{=}CF_2$, and $CF_2{=}NCl$ leaves no doubt about the assignment. The mean values of the asymmetric and symmetric CF_2 stretches are 1146 ($FHC{=}CF_2$), 1115 ($CH_2{=}CF_2$), 1157 ($CF_2{=}NF$), 1152 (CF_2NCl), and 1105 cm^{-1} ($O{=}CF_2$). This comparison indicates a rather strong CF bond in the methanimines and trifluoroethylene, whereas the CF bonds in $O{=}CF_2$ and $CH_2{=}CF_2$ seem

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[9] H. Oberhammer, "Molecular Structure by Diffraction Methods", Vol. 4, The Chemical Society, London, 1976, p 24.

[10] H. Oberhammer, W. Gombler, and H. Willner, *J. Mol. Struct.*, **70**, 273 (1981).

[11] Numerical values for total scattering intensities are available as supplementary data.

[12] D. E. Mann, N. Acquista, and E. K. Plyler, *J. Chem. Phys.*, **22**, 1586 (1954).

[13] A. Oskam and R. Elst, *Recl. Trav. Chim. Pays-Bas*, **94**, 143 (1975).

[14] R. P. Hirschmann, H. L. Simon, and D. E. Young, *Spectrochim. Acta, Part A*, **27** 421 (1971).

[15] P. D. Mallinson, D. C. McKean, J. H. Holloway, and I. A. Oxton, *Spectrochim. Acta, Part A*, **31**, 143 (1975).

Table IV. Force Field of CF_2=NF (mdyn $Å^{-1}$, mdyn rad^{-1}, and mdyn Å rad^{-2}, Respectively)

CN	9.055	CN/NCF_c	0.367
NF	4.388	CN/NCF_t	
CF_c	7.526	NF/δNF	0.705
CF_t	7.492	CF_c/NCF_c	−0.010
δNF	2.054	CF_t/NCF_t	
NCF_c	2.081	CF_c/NCF_t	−0.765
NCF_t	2.539	CF_t/NCF_c	
βCF_2	0.439	$\delta NF/NCF_c$	0.004
tors	0.521	NCF_c/NCF_t	1.374
CF_c/CF_t	0.773	βCF_2/tors	0.007
CN/δNF	0.316		

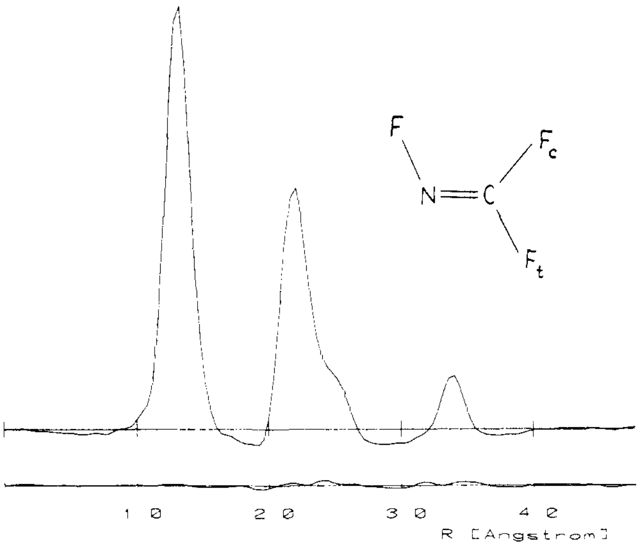

Figure 2. Experimental radial distribution function and difference curve.

to be somewhat weaker. (3) The only remaining fundamental above 700 cm^{-1} is the band at 1018.5 cm^{-1}. This must be the NF stretch, $\nu_3(a')$, although the corresponding CF stretch in trifluoroethylene lies at 1171 cm^{-1}. The NF bond seems to be very much weakened. (4) The assignment of the next two vibrations is rather less straightforward, although the band at 645 cm^{-1} must be a superposition of the CF_2-wagging ν_8 (a″) at 643 cm^{-1} and the CF_2-scissoring $\nu_5(a')$ (hidden) around 640 cm^{-1}. This vibration is often at higher frequency than the CF_2 rocking, which then must be at 520 cm^{-1} ($\nu_6(a')$). The frequencies correspond well with those found in trifluoroethylene, although the assignment there is different. Further comparison with CF_2=NCl ascertains the present assignment and thus requires a new assignment for trifluoroethylene. (5) The band at lowest frequency is again a superposition of two vibrations, the CNF deformation, $\nu_7(a')$ and the torsion $\nu_9(a'')$, also in accord with the assignment for trifluoroethylene.

The normal coordinate analysis was performed with the program NCA,[16] based on mass-weighted Cartesian coordinates. The data used for the calculation of the force field are shown in Tables II and III together with the calculated values from the best fit. That force field is summarized in Table IV. One notes the very small NF force constant. The l vectors (Q = l·q) and the potential energy distribution show two in-plane deformations to be composed of the CNF and the NCF_c bendings, whereas the NCF_t bending appears isolated, contrary to an intuitive guess that the two bendings at the C atom would couple and the CNF bend appear isolated.

Structure Analysis

The procedure for determining molecular structures from a joint analysis of electron diffraction and spectroscopic data has been described in the literature.[17,18] Harmonic vibrational corrections for the rotational constants, $\Delta B^i = B_0^i - B_z^i$[17] (Table II), and for the interatomic distances, $\Delta r = r_a - r_\alpha^0$[19] (Table VI), were calculated from the force field of Table IV. Theoretical molecular intensities were calculated with scattering amplitudes and phases of Haase.[20] A diagonal weight matrix[10] was applied to the electron diffraction data, and the relative weight between electron diffraction and microwave data was adjusted until the rotational constants were reproduced within their estimated error limits. In the first step a preliminary structural model derived from the radial distribution curve (Figure 2) was refined in a least-squares analysis based on the electron diffraction data only. Hereby, the refinement of vibrational amplitudes for bonded distances was not possible, because of high correlations with the bond lengths. The results for the geometric parameters are listed in the first column of Table V. The addition of rotational constants allows the refinement of all vibrational amplitudes, some of which are grouped together on the basis of the spectroscopic calculations (see Table VI). Standard deviations for geometric parameters, especially for bond angles, are reduced in the joint analysis. Attempts to refine the C–F bond lengths separately failed owing to very high correlations. If the difference between the C–F distances is constrained to the ab initio value (0.004 Å; see below), the sum of the errors squared in the least-squares analysis changes insignificantly (0.2%), and variations for the other geometric parameters are considerably smaller than the respective standard deviations. The calculated rotational constants are compared with the experimental values in Table II.

Table V. Experimental and ab Initio Values for Geometric Parameters (Å and deg) and Dipole Moments (D) for $XN=CX_2$, X = F or H[a]

	FN=CF_2			HN=CH_2	
	ed (r_α^0)	ed + mw (r_α^0)	ab initio (r_e)	mw[b] (r_s/r_0)	ab initio (r_e)
C=N	1.273 (7)	1.274 (6)	1.238	1.273	1.252
C–X_c	1.299 (4)	1.300 (3)	1.323	1.090	1.082
C–X_t			1.327		1.079
N–X	1.389 (4)	1.389 (2)	1.401	1.021	1.017
N=C–X_c	127.3 (6)	127.2 (2)	128.1	125.1	125.5
N=C–X_t	120.3 (6)	119.8 (2)	120.4	117.9	119.4
X_c–C–X_t[c]	112.4 (5)	112.5 (2)	111.5	117.0	115.1
C=N–X	108.0 (4)	107.9 (2)	106.9 (9)	110.4	110.3
μ_a		1.24 (4)	0.94	1.3[d]	1.30
μ_b		0.66 (4)	0.28	1.5[d]	1.57
$\lvert\mu\rvert$		1.41 (6)	0.98	2.0	2.04

[a] Uncertainties are 2σ values. ed, electron diffraction, mw, microwave. [b] Mixed r_s/r_0 structure from ref 1. [c] Dependent parameter. [d] Reference 21.

Table VI. Vibrational Amplitudes from Electron Diffraction and Spectroscopic Data and Harmonic Vibrational Corrections $\Delta r = r_a - r_\alpha^0$[a]

	ed + mw[b]	spectr	Δr
C=N	0.043 (3)	0.041	0.0011
C–F_c		0.042	0.0012
C–F_t		0.042	0.0024
N–F	0.051 (6)	0.047	0.0026
$F_c \cdots F_t$	0.052 (4)	0.053	0.0000
C···F		0.055	0.0009
N···F_c		0.053	−0.0002
N···F_t		0.054	0.0007
F···F_c	0.085 (6)	0.088	−0.0022
F···F_t	0.058 (5)	0.057	−0.0007

[a] Error limits are 3σ values. [b] Electron diffraction + microwave.

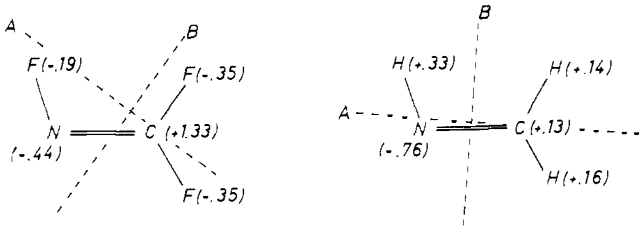

Figure 3. Atomic net charges for CF_2=NF and CH_2=NH. A, B indicate rotational axes.

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(16) D. Christen, *J. Mol. Struct.*, **48**, 101 (1978).

(17) K. Kuchitsu, T. Fukuyama, and Y. Morino, *J. Mol. Struct.*, **1**, 463 (1968).

(18) V. Typke, M. Dakkouri, and H. Oberhammer, *J. Mol. Struct.*, **44**, 85 (1978).

(19) R. L. Hilderbrandt and J. D. Wieser, *J. Chem. Phys.*, **56**, 1143 (1972).

(20) J. Haase, *Z. Naturforsch., A*, **25**, 936 (1970).

(21) D. R. Johnson and F. J. Lovas, *Chem. Phys. Lett.*, **15**, 65 (1972).

Table VII. Mulliken Overlap Populations (au) for XN for $XN=CX_2$, X = F or H

		$FN=CF_2$	$HN=CH_2$
C=N	σ	0.046	0.253
	π	0.216	0.241
$C-X_c$		0.249	0.381
$C-X_t$		0.249	0.388
N–X		0.115	0.314

Table VIII. C–F Bond Lengths, Force Constants (mdyn Å^{-1}), and FCF Angles for Some $Y=CF_2$-Type Molecules

	C–F	f_{CF}	FCF
$O=CF_2$[a]	1.316 (1)	6.734[h]	107.7 (1)
$S=CF_2$[b]	1.316 (2)	6.541[i]	107.1 (2)
$Se=CF_2$[c]	1.314 (2)	6.536[i]	107.5 (4)
$H_2C=CF_2$[d]	1.314 (3)	6.762[j]	110.4 (3)
$FHC=CF_2$[e]	1.312 (18)	7.058[k] 7.375	113.0 (13)
$F_2C=CF_2$[f]	1.319 (2)	7.313[l]	112.5 (2)
$FN=CF_2$[g]	1.300 (3)	7.645[m] 7.561	112.5 (2)

[a] r_{av} values from ref 28. [b] r_{av} values from ref 29. [c] $r_\alpha{}^0$ values from ref 29. [d] r_{av} values from ref 30. [e] r_{av} values from ref 31. [f] r_g values from ref 32. [g] r_{av} values, this study. [h] Reference 14. [i] Reference 33. [j] Reference 13. [k] D. Christen, Thesis, Tübingen, 1981; calculated from data of ref 12. The smaller value corresponds to the $C-F_c$ bond, the larger value to the $C-F_t$ bond. [l] Christen (footnote *k*), calculated from data of ref 34. [m] This study.

Ab Initio Calculations

The geometries of $CH_2=NH$ and $CF_2=NF$ were fully optimized with the ab initio gradient program TEXAS,[22] using 21 and 4-21 basis sets for hydrogen and second-row elements.[23] For nitrogen polarization functions were added.[22] The geometries were optimized until variations for bond lengths and angles were smaller than 0.002 Å and 0.2°, respectively. The results are included in Table VI. Atomic net charges and overlap populations were derived from a Mulliken population analysis[24] (Figure 3 and Table VII). For $HN=CH_2$ the agreement between experimental and ab initio values is satisfactory, except for the C=N bond length. The predicted r_e value is about 0.02 Å shorter than the experimental r_s value. The excellent agreement for the dipole moment components indicates good description of the electronic structure. The results of earlier ab initio calculations for $HN=CH_2$[25–27] are essentially in agreement with the r_e parameters derived here. In ref 25, however, the direction of the tilt of the CH_2 group is reversed (i.e., $N=C-H_c < N=C-H_t$) and $C-H_c$ is shorter than $C-H_t$. For $FN=CF_2$ the ab initio calculations reproduce the bond angles very well, while calculated values for C=N and C—F bond lengths are too short (by 0.036 Å) or too long (by about 0.025 Å). The present calculations predict shortening of the N=C bond upon fluorination (by 0.014 Å), while earlier calculations with STO-3G basis sets[27] predict lengthening of the double bond by 0.022 Å.

Discussion

A comparison with related molecules allows a discussion of the individual structural parameters of $CF_2=NF$. (1) C—F bond lengths and the corresponding force constants of $Y=CF_2$-type molecules are summarized in Table VIII together with FCF bond angles. The C–F bond lengths for all known examples seem to be unaffected by the substituent Y, except for $CF_2=NF$ where these bonds are exceptionally short. (The large error limits for the C—F bonds in trifluoroethylene forces us to exempt this molecule from the discussion.) The C—F force constants follow the general trend of the bond lengths, except for C_2F_4. The bond shortening between $O=CF_2$ and $CF_2=NF$ is partially reproduced by the ab initio calculations (1.330 Å for $O=CF_2$[35] vs. 1.327 and 1.323 Å for $CF_2=NF$). The absolute r_e values are too long in both cases. The small difference between the ab initio values for the cis and trans C—F bonds in $CF_2=NF$ (0.004 Å) is reproduced very well by the force constants. The ^{19}F NMR shows a very pronounced difference between the cis and trans fluorine atoms with a chemical shift difference of 36.2 ppm.[3] (2) According to the FCF angles the molecules in Table VIII can be divided into two groups, one with Y being a group 6 element and FCF angles of 107–108°, and the other with Y being a carbon or nitrogen group and bond angles of 110–113°. In all cases these angles are far from the ideal value for sp^2 hybridization. In $CH_2=NH$ and $CF_2=NF$ the CH_2 and CF_2 moieties are tilted with respect to the N=C bond (tilt = 3.6 and 3.7° (0.2), respectively), away from the NH or NF bond. This indicates stronger repulsion by the NH and NF single bonds than by the nitrogen lone pair, an intuitively unexpected result. (3) The C=N bond lengths in $CH_2=NH$ and CF_2NF are equal within experimental error limits. This is surprising, considering the very different electronic structures of these bonds. Because the ab initio calculations produce different C=N bond lengths (by 0.014 Å shorter in the fluoro compound) which are too short in both cases, the electronic structure from these calculations may only be used as a qualitative guide to the understanding of the nature of these bonds. The π contribution to the double bonds is not drastically different (Table VIII). The σ contribution, however, is much smaller in $CF_2=NF$. On the other hand, the polarity of the bond (attractive in both cases) is much higher in $CF_2=NF$ (Figure 3), thus seemingly compensating for the weak σ bonding. (4) The N–F bond is very long (1.389 (2) Å) compared to the sp^3-hybridized N–F bond in NF_3 (1.3648 Å).[36] This large value is supported by the small force constant (4.413 mdyn Å^{-1}) and is well reproduced by the ab initio calculation which indicates an overlap population only half that of the C–F bonds with additional repulsive polar contributions. In contrast, the overlap populations for the N–H and C–H bonds are roughly equal and the polar contributions are reversed (Figure 3).

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Registry No. $CH_2=NH$, 2053-29-4; $CF_2=NF$, 338-66-9.

Supplementary Material Available: Total electron diffraction scattering intensities for $CF_2=NF$ (2 pages). Ordering information is given on any current masthead page.

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(22) P. Pulay, *Theor. Chim. Acta*, **50**, 299 (1979).

(23) P. Pulay, G. Fogarasi, F. Pang, and J. E. Boggs, *J. Am. Chem. Soc.*, **101**, 2550 (1979).

(24) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

(25) M. Macaulay, L. A. Burnelle, and C. Sandorfy, *Theor. Chim. Acta*, **29**, 1 (1973).

(26) P. Botswina, *Chem. Phys. Lett.*, **29**, 580 (1974).

(27) J. H. Howell, *J. Am. Chem. Soc.*, **98**, 886 (1976).

(28) M. Nakata, K. Kohata, T. Fukuyama, and K. Kuchitsu, *J. Mol. Struct.*, **68**, 271 (1980).

(29) D. Christen, H. Oberhammer, and W. Zeil, *J. Mol. Struct.*, **66**, 203 (1980).

(30) F. C. Mijlhoff, G. H. Renes, K. Oyanagi, and K. Kuchitsu, *J. Mol. Struct.*, **39**, 241 (1977).

(31) P. A. G. Huisman, F. C. Mijlhoff, and G. Renes, *J. Mol. Struct.*, **62**, 95 (1980).

(32) J. L. Carlos, R. R. Karl, and S. H. Bauer, *J. Chem. Soc., Faraday Trans. 2*, **70**, 177 (1974).

(33) A. Haas, H. Willner, H. Bürger, and G. Pawelke, *Spectrochim. Acta, Part A*, **33**, 937 (1977).

(34) J. R. Nielsen, H. H. Claassen, and D. C. Smith, *J. Chem. Phys.*, **18**, 812 (1950).

(35) H. Oberhammer and J. E. Boggs, *J. Mol. Struct.*, **55**, 283 (1979).

(36) J. Sheridan and W. Gordy, *Phys. Rev.*, **79**, 513 (1950).