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Effect of Fluorination: Gas-Phase Structures of *N*,*N*-Dimethylvinylamine and Perfluoro-*N*,*N*-dimethylvinylamine

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Abstract: The gas-phase structures of *N*,*N*-dimethylvinylamine, $(CH_3)_2NC(H){=}CH_2$ (**1**), and perfluoro-*N*,*N*-dimethylvinylamine, $(CF_3)_2NC(F){=}CF_2$ (**2**), were determined by gas electron diffraction and quantum chemical methods (B3LYP and MP2 with 6-31G* basis sets). The configuration around nitrogen is slightly pyramidal in both compounds, with the sum of the nitrogen bond angles 351.2(12)° and 354.8(6)° in **1** and **2**, respectively. In the parent compound **1**, the $(CH_3)_2N$ group lies nearly in the plane of the vinyl group, and the nitrogen lone pair (lp) is almost perpendicular to this plane ($\Phi(C{=}C{-}N{-}lp) = 98(6)°$). In the perfluorinated species **2**, however, the $(CF_3)_2N$ group is oriented perpendicular to the vinyl plane, and the lone pair is parallel to the C═C bond ($\Phi(C{=}C{-}N{-}lp) = 2(5)°$). A natural bond orbital analysis provides a qualitative explanation for this conformational change upon fluorination. The sterically unfavorable in-plane orientation of the dimethylamino group in **1** is stabilized by conjugation between the nitrogen lone pair and the C═C π-bond. The anomeric effect between the lone pair and the $C_\alpha{-}F$ σ-bond in addition to steric effects favors the perpendicular orientation of the $(CF_3)_2N$ group in **2**. Both quantum chemical methods reproduce the experimental structures satisfactorily.

Introduction

Conjugation between electron lone pairs (lp's) and π-bonds plays an important role in structural chemistry. Typical examples of conjugation between the p-shaped oxygen lone pair and a C═O or C═C π-bond are methylformate, $CH_3OC(O)H$,[1] and methylvinyl ether, $CH_3OC(H){=}CH_2$.[2] In both compounds, such orbital interactions ($lp(O) \rightarrow \pi^*(C{=}O)$ or $lp(O) \rightarrow \pi^*(C{=}C)$) lead to sterically unfavorable synperiplanar structures with the $C(sp^3){-}O$ bond syn to the double bond. Similarly, conjugation between the nitrogen lone pair and the C═O π-bond ($lp(N) \rightarrow \pi^*(C{=}O)$) leads to sterically unfavorable planar or nearly planar structures of amides, such as formamide,[3] *N*,*N*-dimethylformamide,[4] and *N*,*N*-dimethylacetamide.[5] In these compounds, the nitrogen atom possesses a planar configuration, and the lone pair is perpendicular to the C═O double bond ($\phi(O{=}C{-}N{-}lp) = 90°$). This orientation allows maximum orbital interaction with the C═O π-bond. The barrier to internal rotation ($\Delta H^\ddagger$) around the $N{-}C(sp^2)$ bond, which can be considered a measure of the strength of conjugation, is 19.7(3) kcal/mol in *N*,*N*-dimethylformamide.[6]

Perfluorination of these compounds has different effects on their conformational properties. Whereas no change is observed for perfluoromethylformate, $CF_3OC(O)F$, which also possesses a synperiplanar structure,[7] the conformation of methylvinyl ether is strongly affected upon fluorination. In perfluoromethylvinyl ether, $CF_3OC(F){=}CF_2$, the $C(sp^3){-}O$ bond is no longer in the plane but is nearly perpendicular to the plane of the vinyl group.[8] The effect of fluorination in *N*,*N*-dimethylformamide is intermediate. In perfluoro-*N*,*N*-dimethylformamide, $(CF_3)_2NC(O)F$, the $(CF_3)_2N$ group is rotated around the $N{-}C(sp^2)$ bond away from the planar conformation ($\phi(O{=}C{-}N{-}lp) = 57(4)°$).[9] Quantum chemical calculations (B3LYP/6-31G*) reproduce this effect of fluorination correctly and predict a barrier to internal rotation of 8 kcal/mol, which is much lower than the experimental value for the parent compound (see above).

Only very little is known about gas-phase structures and conformational properties of enamines, in which conjugation between the nitrogen lone pair and the C═C π-bond ($lp(N) \rightarrow \pi^*(C{=}C)$) can occur. From microwave spectroscopic measurements it was concluded that in vinylamine, $H_2NC(H){=}CH_2$, the simplest enamine, the nitrogen lone pair is nearly perpendicular to the double bond and nitrogen possesses a pyramidal configuration.[10] In the present study we report structure determinations for *N*,*N*-dimethylvinylamine, $(CH_3)_2NC(H){=}CH_2$ (**1**), and for the perfluorinated derivative $(CF_3)_2NC(F){=}CF_2$ (**2**), using gas electron diffraction (GED). The experimental studies are supplemented by quantum chemical calculations. No experimental structural studies have been performed so far for **1**, which is the simplest tertiary enamine. The geometric struc-

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(1) Curl, R. F. *J. Chem. Phys.* **1959**, *30*, 1529. Shen Q. *Acta Chem. Scand. A* **1977**, *31*, 795. Cradock, S.; Rankin, D. W. H. *J. Mol. Struct.* **1980**, *69*, 145.

(2) Cahill, P.; Gold, P.; Owen, N. L. *J. Chem. Phys.* **1968**, *48*, 1620. Fujitake, M.; Hayashi, M. *J. Mol. Struct.* **1985**, *127*, 21. Samdal, S.; Seip, H. M. *J. Mol. Struct.* **1975**, *28*, 193. van den Enden, L.; Geise, H. J. *J. Mol. Struct.* **1983**, *97*, 139. Pykhout, W.; van Nuffel, P.; van Alsenoy, C.; van den Enden, L.; Geise, H. J. *J. Mol. Struct.* **1983**, *102*, 333.

(3) Brown, R. D.; Godfrey, P. D.; Kleibömer, B. *J. Mol. Spectrosc.* **1987**, *124*, 34.

(4) Schultz, G.; Hargittai, I. *J. Phys. Chem.* **1993**, *97*, 4966.

(5) Mack, H.-G.; Oberhammer, H. *J. Am. Chem. Soc.* **1997**, *119*, 3567.

(6) Ross, B. D.; Tru, N. S. *J. Am. Chem. Soc.* **1984**, *106*, 2451.

(7) Trautner, F.; Varetti, E. L.; Willner, H.; Oberhammer, H. Unpublished.

(8) Leibold, C.; Reinemann, S.; Minkwitz, R.; Resnik, P. R.; Oberhammer, H. *J. Org. Chem.* **1997**, *62*, 6160.

(9) Trautner, F.; Reinemann, S.; Minkwitz, R.; Oberhammer, H. *J. Am. Chem. Soc.* **2000**, *122*, 4193.

(10) Lovas, F. J.; Clark, F. O.; Tiemann, E. *J. Chem. Phys.* **1975**, *62*, 1925. Brown, R. D.; Godfrey, P. D.; Kleibömer, B. *J. Mol. Spectrosc.* **1987**, *124*, 21. Brown, R. D.; Godfrey, P. D.; Kleibömer, B.; Pierlot, A. P.; McNaugthon, D. *J. Mol. Spectrosc.* **1990**, *142*, 195.

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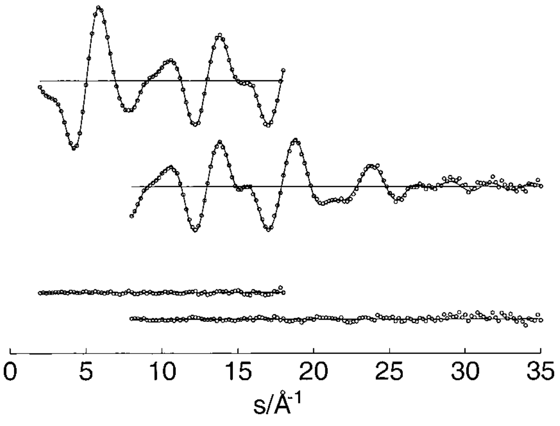

Figure 1. $(CH_3)_2NC(H){=}CH_2$: Experimental (dots) and calculated (full line) averaged molecular intensities for long (above) and short (below) nozzle-to-plate distances and residuals.

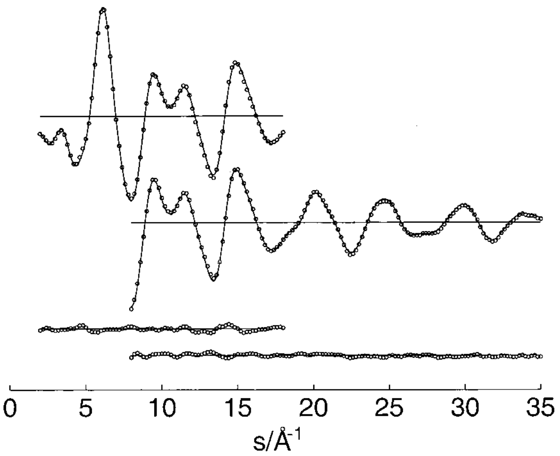

Figure 2. $(CF_3)_2NC(F){=}CF_2$: Experimental (dots) and calculated (full line) averaged molecular intensities for long (above) and short (below) nozzle-to-plate distances and residuals.

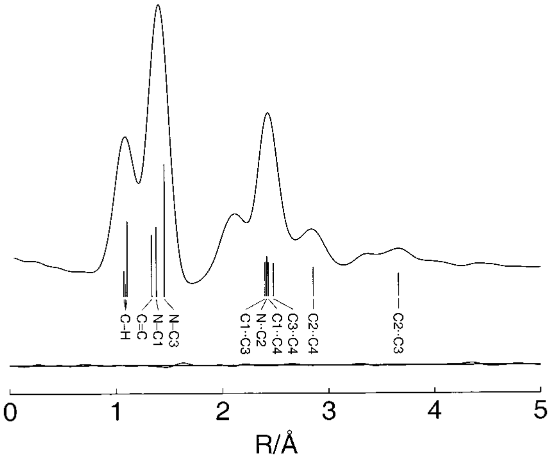

Figure 3. $(CH_3)_2NC(H){=}CH_2$: Experimental radial distribution function and difference curve. Vertical bars indicate skeletal interatomic distances.

ture and the potential for internal rotation around the N—C(sp^2) bond have been calculated in the HF/6-31G** approximation.[11]

Experimental Section

1 and **2** were synthesized according to literature methods,[12,13] and their purity was checked by NMR spectroscopy. **1** was stored at liquid nitrogen temperature to prevent polymerization. The GED intensities were recorded with a Gasdiffraktograph KD-G2[14] at 50- and 25-cm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. The sample reservoirs were kept at −30 °C (**1**) and −56 °C (**2**), respectively. The inlet system and nozzle were at room temperature. The photographic plates (Kodak electron image plates, 13 cm × 18 cm) were analyzed by the usual methods.[15] Averaged molecular intensities in the s-ranges 2−18 and 8−35 Å^{-1} ($s = (4\pi/\lambda)\sin\theta/2$, where λ is the electron wavelength and θ is the scattering angle) are shown in Figures 1 and 2.

Theoretical Calculations. The geometries of **1** and **2** were fully optimized by the B3LYP/6-31G* and MP2/6-31G* methods. The potential curves for internal rotation around the N—C(sp^2) bond were derived by optimizing the geometries for fixed dihedral angles Φ(C═C—N—lp),[16] using the B3LYP method. Natural bond orbital (NBO) analyses[17] were performed for $\Phi = 0°$ and $\Phi = 90°$ for both compounds at the B3LYP level. All quantum chemical calculations were done with the GAUSSIAN98 program set.[18] The vibrational amplitudes were calculated from theoretical Cartesian force constants (B3LYP) using the program ASYM40.[19]

Structure Analyses. Radial distribution functions (RDFs) were derived by Fourier transformation of the molecular intensities. The experimental curve for **1** (Figure 3) is reproduced best with a slightly pyramidal configuration at nitrogen and the $(CH_3)_2N$ group lying in the plane of the vinyl group (Φ(C═C—N—lp) ≈ 90°). The experimental RDF for **2** (Figure 4) can be reproduced satisfactorily only with a slightly pyramidal configuration at nitrogen but with perpendicular orientation of the $(CF_3)_2N$ group (Φ(C═C—N—lp) ≈ 0°). These preliminary molecular models were refined by least-squares fitting of the molecular intensities. The following constraints were used in these analyses: (1) C_{3v} symmetry was assigned for CH_3 and CF_3 groups. (2) Planarity of the vinyl groups was assumed. (3) Bond lengths and bond angles which are predicted by the quantum chemical calculations to differ by less than 0.005 Å or 1°, respectively, were set equal. (4) Differences between similar geometric parameters were set to the calculated (B3LYP) values (see Tables 1 and 3). (5) The C═C bond length in **2**, which is not well determined in the GED experiment, was set to 1.320 Å, about 0.01 Å shorter than the B3LYP value. Such a systematic difference between experimental and calculated C═C bond lengths occurs also in **1**. (6) The C═C—H angles in **1** were set to B3LYP values. (7) Vibrational amplitudes which either cause large correlations or are not well determined in the GED experiment were set to the calculated values. Amplitudes with very similar values were refined in groups. With the above constraints, 11 (**1**) or 10 (**2**) geometric parameters and four (**1**) or eight (**2**) vibrational amplitudes were refined simultaneously. The following correlation coefficients had values larger than |0.7|. For **1**: $p1/p2 = -0.71$, $p5/p6 = -0.71$, $p6/p7 = 0.72$, $p7/p11 = 0.90$, $p6/l2 = 0.78$, $p9/l3 = 0.80$, $p11/l2 = -0.82$. For **2**: $p3/$

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[11] Häfelinger G.; Mack, H.-G. In *The Chemistry of Enamines*; Rappoport, Z., Ed.; John Wiley: New York, 1994; Part 1, pp 1−85.

[12] Chang, P. L. F.; Dittmer, D. C. *J. Org. Chem.* **1969**, *34*, 2791.

[13] Abe, T.; Hayashi, E.; Shimuzu, T. *Chem. Lett.* **1989**, 905.

[14] Oberhammer, H. *Molecular Structures by Diffraction Methods*; The Chemical Society: London 1976; Vol. 4, p 24.

[15] Oberhammer, H.; Gombler, W.; Willner, H. *J. Mol. Struct.* **1981**, *70*, 273.

[16] The direction of the nitrogen lone pair is assumed to be the trisector of the three nitrogen angles.

[17] Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F. *NBO*, Version 3.1; Theoretical Chemistry Institute, University of Wisconsin, Madison, Wisconsin 53706, 1990.

[18] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratman, 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.; Menucci, 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.; Cioslovski, 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.; Gonzales, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzales, C.; Head-Gordon M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN98*, Version A6; Gaussian, Inc.: Pittsburgh, PA, 1998.

[19] Hedberg, L.; Mills, I. M. *J. Mol. Spectrosc.* **1993**, *160*, 117.

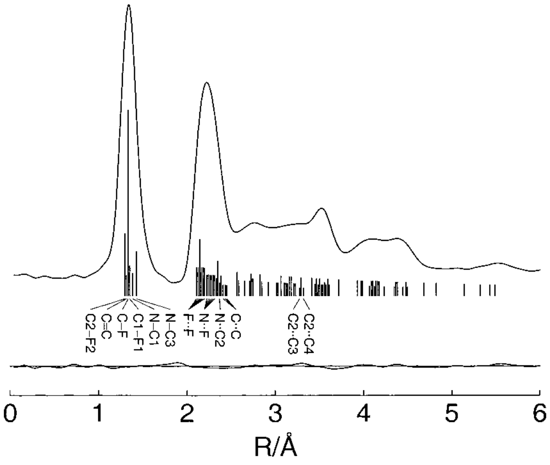


Figure 4. $(CF_3)_2NC(F){=}CF_2$: Experimental radial distribution function and difference curve. Vertical bars indicate bonded distances, skeletal interatomic distances, and some other important distances.

Table 1. Experimental and Calculated Geometric Parameters for *N,N*-Dimethylvinylamine, $(CH_3)_2NC(H){=}CH_2$[a]

parameter	GED[b]		MP2/ 6-31G*[c]	B3LYP/ 6-31G*[c]
r(C1═C2)	1.333(4)	*p*1	1.346	1.343
r(N—C1)	1.383(3)	*p*2	1.394	1.389
r(N—C3) = *r*(N—C4)	1.453(2)	*p*3	1.453	1.454
r(C—H)$_{methyl}$	1.096(2)	*p*4	1.096	1.098
r(C1—H1)	1.087(2)[f]		1.089	1.089
r(C2—H$_2$) = *r*(C2—H3)	1.082(2)[f]		1.083	1.084
α(C2═C1—N)	125.3(14)	*p*5	127.4	127.9
α(C1—N—C3)	117.4(15)	*p*6	115.0	117.1
α(C1—N—C4)	118.0(15)[f]		116.1	117.7
α(C3—N—C4)	115.8(10)	*p*7	113.8	115.4
Σα(N)[d]	351.2(12)		347.5	350.2
α(H—C—H)$_{methyl}$	107.9(6)	*p*8	108.5	108.2
α(C2═C1—H1)	119.4[g]		119.5	119.4
α(C1═C2—H2)	119.5 g		119.3	119.5
α(C1═C2—H3)	123.4 g		123.5	123.4
Φ(C4—N—C3—H4)	177(9)	*p*9	165.1	160.7
Φ(C4—N—C3—H7)	182(6)	*p*10	183.2	186.3
Φ(C═C—N—lp)[e]	98(6)	*p*11	107.5	103.1

[a] Parameters in angstroms (bonds) and degrees (angles). For atom numbering, see Figure 5. [b] r_a parameters from gas electron diffraction with 3σ uncertainties. Parameters *p*1−*p*11 were refined in the least-squares analysis. [c] Mean values are given for parameters which are not unique. [d] Sum of angles around nitrogen. [e] Dihedral angle between the C═C bond and the nitrogen lone pair. [f] The difference from the preceding value is fixed to the B3LYP value. [g] Not refined.

Table 2. Interatomic Distances and Experimental and Calculated Vibrational Amplitudes for **1**[a] (Without Nonbonded Distances Involving Hydrogen)

	distance	ampl, GED		ampl, B3LYP
C—H	1.08−1.01	0.079(2)	*l*1	0.077
C═C	1.33	0.042[b]		0.042
N—C1	1.38	0.042[b]		0.042
N—C3	1.45	0.050[b]		0.050
N···C2	2.42	0.054[b]		0.054
C1···C3	2.42	0.071(15)	*l*2	0.069
C1···C4	2.43	0.071(15)	*l*2	0.071
C3···C4	2.48	0.071(15)	*l*2	0.072
C2···C4	2.86	0.093(24)	*l*3	0.105
C2···C3	3.66	0.089(16)	*l*4	0.084

[a] Values in angstroms. Uncertainties are 3σ values. [b] Not refined.

*p*4 = −0.89, *p*3/*p*6 = 0.75, *p*3/*p*9 = −0.75, *p*5/*p*10 = 0.90, *p*6/*p*7 = −0.88, *l*2/*l*3 = 0.78. The final results are given in Tables 1 and 3 (geometric parameters *p*) and Tables 2 and 4 (vibrational amplitudes *l*). Molecular models are shown in Figure 5.

Table 3. Experimental and Calculated Geometric Parameters for Perfluoro-*N,N*-dimethylvinylamine **2**[a]

parameter	GED[b]		MP2[c]	B3LYP[c]
r(C1═C2)	1.320[g]		1.334	1.331
r(N—C1)	1.386(6)	*p*1	1.393	1.395
r(N—C3) = *r*(N—C4)	1.427(5)[f]		1.434	1.441
r(C—F)$_{methyl}$	1.328(2)	*p*2	1.342	1.340
r(C1—F1)	1.339(2)[f]		1.354	1.351
r(C2—F29 = *r*(C2—F3)	1.304(2)[f]		1.320	1.316
α(C2═C1—N)	119.5(15)	*p*3	122.1	122.8
α(C1—N—C3)	117.6(12)	*p*4	115.7	117.3
α(C1—N—C4)	119.4(12)[f]		117.7	119.1
α(C3—N—C4)	117.8(10)	*p*5	117.0	117.6
Σα(N)[d]	354.8(6)		355.4	353.9
α(F—C—F)$_{mean}$	110.8(6)	*p*6	110.6	110.7
α(C2═C1—F1)	120.7(18)	*p*7	119.7	119.3
α(C1═C2—F2) = α(C1═C2—F3)	125.0(18)[f]		123.5	123.6
Φ(C4—N—C3—F4)	164(9)	*p*8	159.1	158.7
Φ(C4—N—C3—F7)	174(11)	*p*9	166.4	167.2
Φ(C═C—N—lp)[e]	2(5)	*p*10	4.6	1.6

[a] Parameters in angstroms (bonds) and degrees (angles). For atom numbering, see Figure 5. [b] r_a parameters from gas electron diffraction with 3σ uncertainties. Parameters *p*1−*p*10 were refined in the least-squares analysis. [c] 6-31G* basis sets. Mean values are given for parameters which are not unique. [d] Sum of angles around nitrogen. [e] Dihedral angle between the C═C bond and the nitrogen lone pair. [f] The difference from the preceding value is fixed to the B3LYP value. [g] Not refined.

Table 4. Interatomic Distances and Experimental and Calculated Vibrational Amplitudes for **2**[a]

	distance	ampl, GED[b]		ampl, B3LYP[b]
C—F	1.31−1.34	0.045(2)	*l*1	0.045
C═C	1.31	0.041[c]		0.041
N—C1	1.39	0.045(2)	*l*1	0.046
N—C3	1.43	0.050[c]		0.050
F···F	2.13−2.17	0.056(5)	*l*2	0.058
N···F	2.25−2.29	0.058(12)	*l*3	0.061
C···F	2.30−2.58	0.059(15)	*l*4	0.057
N···C2	2.33	0.061(17)	*l*5	0.071
N···F1	2.36	0.061(17)	*l*5	0.068
C···C	2.41−2.45	0.061(17)	*l*5	0.067
F···F	2.56−3.18	0.311[c]		0.311
C1···F2	3.02	0.311[c]		0.311
C···F	2.65−3.46	0.152[c]		0.152
F1···F8	2.73	0.112[c]		0.112
N···F9	2.73	0.110[c]		0.110
C···F	3.03−3.22	0.204[c]		0.204
C···C	3.27−3.32	0.138[c]		0.138
F···F	3.28−3.47	0.400[c]		0.400
C···F	3.51−3.55	0.076(9)	*l*6	0.067
F1···F9	3.53	0.076(9)	*l*6	0.072
N···F8	3.56	0.076(9)	*l*6	0.069
C···F	3.55−4.13	0.255[c]		0.255
F···F	3.57−5.43	0.323(163)	*l*7	0.316
F···F	3.97−5.49	0.152[c]		0.152
C···F	4.23−4.49	0.158[c]		0.158
F4···F5	4.48	0.070(33)	*l*8	0.065

[a] Values in angstroms. Uncertainties are 3σ values. [b] Mean values are given for amplitudes which are not unique. [c] Not refined.

Discussion

In *N,N*-dimethylvinylamine **1**, the configuration at nitrogen is slightly pyramidal, with the sum of the nitrogen bond angles Σα(N) = 351.2(12)°. The $(CH_3)_2N$ group is nearly parallel to the plane of the vinyl group, and the nitrogen lone pair is almost perpendicular to the C═C bond (Φ(C═C—N—lp) = 98(6)°). Such a structure allows maximum overlap between the lone pair and the π-bond. From the pyramidal configuration at nitrogen, we conclude that conjugation of the nitrogen lone pair with the C═C bond is weaker than that with the C═O bond in *N,N*-

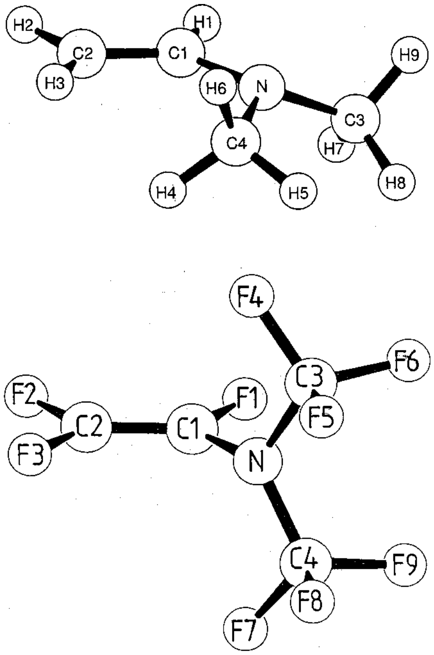


Figure 5. Molecular models for **1** (above) and **2** (below).

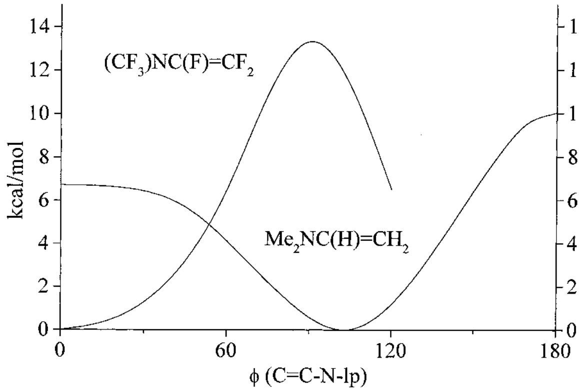


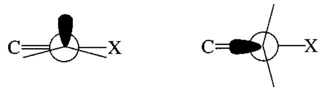
Figure 6. Calculated (B3LYP/6-31G*) potential functions for internal rotation around the N—C(sp^2) bond in $(CH_3)_2NC(H){=}CH_2$ (**1**) and $(CF_3)_2NC(F){=}CF_2$ (**2**).

dimethylformamide, which possesses an exactly planar structure. In the perfluorinated species **2**, the configuration at nitrogen is less pyramidal ($\Sigma\alpha(N) = 354.8(6)°$), and the $(CF_3)_2N$ group is oriented perpendicular to the plane of the vinyl group. Thus, the nitrogen lone pair is parallel to the C=C bond (Φ(C=C—N—lp) = 2(5)°), and no conjugation with the π system is possible. The calculated (B3LYP) potential functions for internal rotation around the N—C(sp^2) bond are shown in Figure 6. The minimum for **1** lies at Φ(C=C—N—lp) = 103°, in good agreement with the GED experiment. Maxima of 6.8 and 10.0 kcal/mol occur for parallel orientation of the lone pair at $\Phi = 0°$ (lone pair toward C=C bond and methyl groups bent away from C=C bond) and $\Phi = 180°$. These calculated barriers are much lower than the experimental value for *N*,*N*-dimethylformamide ($\Delta H^{\ddagger} = 19.7(3)$ kcal/mol), demonstrating that lp(N) → π*(C=C) conjugation is much weaker than lp(N) → π*(C=O) conjugation. In the perfluorinated derivative **2**, the minimum of the potential function lies at $\Phi = 0°$ and the maximum at $\Phi = 90°$. Geometry optimizations for dihedral angles larger than 120° led to inversion at nitrogen, indicating that such geometries do not correspond to stable structures.

Table 5. Stabilization Energies of Orbital Interactions between the Nitrogen Lone Pair and the Vinyl Group and Relative Total Energies (kcal/mol) for Conformation I, (ϕ(C=C—N—lp) = 90°, and Conformation II, (ϕ(C=C—N—lp) = 0°

	$(CH_3)_2NC(H){=}CH_2$		$(CF_3)_2NC(F){=}CF_2$	
	I	II	I	II
lp(N) → π*(C=C)	−18.0		−19.8	
lp(N) → σ*(C=C)	−4.2	−2.6	−1.4	−5.1
lp(N) → σ*(C1-X)		−9.3		−19.4
Σ(stabilization energies)	−22.2	−11.9	−21.2	−24.5
relative total energies	−6.8	0.0	0.0	−13.4

This drastic conformational change of *N*,*N*-dimethylvinylamine upon fluorination can be attributed to two effects: (1) increased steric repulsions between the fluorine atoms of the methyl and vinyl groups and (2) different orbital interactions between the nitrogen lone pair and the vinyl group. Whereas the effect of steric interactions cannot be described quantitatively, the stabilization energies due to the relevant orbital interactions can be derived from NBO analyses. The results of NBO analyses for perpendicular (conformation I) and parallel (conformation II) orientations of the lone pair relative to the vinyl plane are summarized for both compounds **1** and **2** in Table 5. In addition, the relative energies are given in this table.



(I) (II)

In conformation I, the strongest orbital interaction is conjugation between the lone pair and the π orbital (lp(N) → π*(C=C)), and the stabilization energies are −18.0 and −19.8 kcal/mol in **1** and **2**, respectively. This stabilization energy is practically independent of fluorination. In conformation II, the anomeric effect between the lone pair and the (C1—X) σ orbital (lp(N) → σ*(C1—X), X = H or F) with stabilization energies of −9.3 and −19.4 kcal/mol, in **1** and **2**, respectively, is the dominant orbital interaction, and this interaction depends strongly on fluorination. Compared to these stabilization energies, interactions between the lone pair and the (C=C) σ-bond play a minor role. In the parent compound **1**, orbital interactions favor conformation I by 10.3 kcal/mol relative to conformation II. The actual energy difference is smaller (6.8 kcal/mol) because of stronger steric repulsions in conformation I. In the fluorinated derivative **2**, the anomeric effect lp(N) → σ*(C1—F) is much stronger than the lp(N) → σ*(C1—H) interaction in the parent compound **1**. This leads to a preference for conformation II relative to conformation I by 3.3 kcal/mol. The actual energy difference between the two conformations is considerably larger (13.4 kcal/mol), and this difference between orbital stabilization energies and total energies must be attributed to steric repulsions which strongly favor conformation II.

Comparison between the geometric parameters of **1** and **2** reveals that the N—C(sp^2) bond lengths are equal within their experimental uncertainties in both compounds (1.383(3) and 1.386(6) Å). This experimental result is reproduced correctly by the quantum chemical calculations and can be rationalized by the NBO analyses. Both conjugation and the anomeric effect, which are the predominant interactions in **1** and **2**, respectively, cause shortening of this bond. Such shortening is also observed for the N—C(sp^3) bonds in **2** (1.427(5) vs 1.453(2) Å), where anomeric effects occur between the lone pair and the CF_3 fluorine atoms. Additional shortening of all N—C bonds in **2** is expected due to electrostatic effects, since fluorination leads to higher positive net charges at the carbon atoms. A remarkable difference between the geometric parameters of **1** and **2** is observed for the C═C—N angle (125.3(14)° vs 119.5(15)°). The larger angle in **1** reflects the steric repulsion between the methyl and vinyl groups which is absent in **2**.

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