Fluorination and Conjugation. The Structure of Perfluoro-*N*,*N*-dimethylformamide

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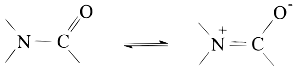
Abstract: The geometric structure of perfluoro-*N*,*N*-dimethylformamide, $(CF_3)_2NC(O)F$, has been determined by gas electron diffraction (GED) and quantum chemical calculations (HF, MP2, and B3LYP with 6-311G* basis sets). The bonds around nitrogen possess a nearly planar configuration with the sum of the nitrogen bond angles $\sum\alpha_N = 359.5(3)°$. The $(CF_3)_2N$ group is rotated around the N−C(sp^2) bond by 33(4)°, away from the configuration in which the nitrogen lone pair is perpendicular to the C(O)F plane. The calculated (B3LYP) barriers to internal rotation around the N−C(sp^2) bond are 7.92 kcal mol^{-1} for perpendicular orientation of the $(CF_3)_2N$ group (nitrogen lone pair parallel to the C(O)F plane) and 0.32 kcal mol^{-1} for planar orientation (nitrogen lone pair perpendicular to the C(O)F plane). The barrier for perpendicular orientation is much lower than the experimental gas-phase value for the parent compound $Me_2NC(O)H$ ($\Delta H^{\neq} = 19.7(3)$ kcal mol^{-1}). This theoretical result is in agreement with ^{19}F NMR spectra which show one doublet for the two CF_3 groups in the temperature range 0 to −70 °C. Thus, fluorination causes a strong decrease of conjugation between the nitrogen electron lone pair and the π(C═O) bond. The following skeletal parameters (r_a distances with 3σ uncertainties) were derived in the GED experiment: C═O 1.182(6) Å, N−C(sp^2) 1.394(15) Å, N−C(sp^3) 1.451(4) Å, and N−C═O 129.4(15)°.

Introduction

The amide functional group is a basic building block of proteins, polymers, and enzymes and its structural and bonding properties have attracted continuing interest. Its structural properties are characterized by planarity or near-planarity of the groups bonded to nitrogen, by short N−C(sp^2) bond lengths, and by a high barrier to internal rotation around this bond. These properties are readily rationalized by delocalization of the nitrogen electron lone pair over the (N−C═O) π-system which can be represented primarily by two resonance structures (Scheme 1). These properties have been confirmed by experimental and theoretical studies of several simple amides. For the parent compound formamide, $H_2NC(O)H$, X-ray crystallography[1] and neutron diffraction[2] studies on the solid compound resulted in a planar or slightly nonplanar structure, respectively. Microwave and infrared spectra of gaseous formamide were reproduced with a planar structure that possesses a large-amplitude out-of-plane vibration.[3] Theoretical calculations lead to planar or slightly nonplanar structures, depending on the approximations used. High-level calculations, however, result in an exactly planar configuration (see ref 4 for a review). Since the positions of hydrogen atoms are not well determined in gas electron diffraction (GED) experiments, planarity of the molecular skeletons was assumed in GED investigations of acetamide, $H_2NC(O)Me$,[5] of *trans*-*N*-methylformamide, HMeNC(O)H,[6] and of *trans*-*N*-methylacetamide, HMeNC(O)Me.[7] The GED intensities for *N*,*N*-dimethylacetamide, $Me_2NC(O)Me$, are reproduced equally well with a planar equilibrium structure or with a pseudoplanar skeleton.[8] Slightly pyramidal configurations around nitrogen were determined in GED studies of *N*,*N*-dimethylformamide, $Me_2NC(O)H$,[9] and of *N*,*N*-dimethylcarbamyl chloride, $Me_2NC(O)Cl$.[10] In both compounds the sum of the nitrogen bond angles is 357.0°. This slight deviation from planarity is most likely due to large-amplitude out-of-plane vibrations of an exactly planar equilibrium structure. Planarity of the skeleton of $Me_2NC(O)H$ is predicted by theoretical calculations with the MP2/6-311G* approximation (see below).

Scheme 1



The N−C(sp^2) bond lengths reported for these compounds (1.36−1.39 Å) are considerably shorter than N−C(sp^3) bond lengths (1.45−1.47 Å). Rotational barriers around the N−C(sp^2) bond depend strongly on the phase and on the solvent. Gas-phase values have been determined for dimethylformamide ($\Delta H^{\neq} = 19.7(3)$ kcal mol^{-1})[11] and for dimethylacetamide ($\Delta H^{\neq} = 15.8(11)$ kcal mol^{-1}).[12] These barriers are reproduced reasonably well by high-level ab initio calculations.[13]

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Recent gas-phase structural studies of fluorinated methyl vinyl ethers and methyl vinyl sulfides have shown that fluorination has a strong effect on the conjugation between the oxygen or sulfur electron lone pair, lp(X), and the π(C=C) bond. The parent compounds, $MeOC(H){=}CH_2$ and $MeSC(H){=}CH_2$, possess planar syn structures (methyl group synperiplanar with respect to the C=C double bond) and this is rationalized by strong lp(X)$\rightarrow\pi^*$(C=C) conjugation (X = O or S). On the other hand, fluorinated derivatives, such as $MeOC(F){=}CF_2$,[14] $CF_3OC(F){=}CF_2$,[14] $CF_3SC(H){=}CH_2$,[15] and $CF_3SC(F){=}CF_2$[16] possess structures with perpendicular or nearly perpendicular orientation of the X$-$C(sp^3) bond. These structures demonstrate that fluorination leads to a strong decrease of conjugation and the X$-$C(sp^3) bond adopts a sterically more favorable perpendicular orientation. In the present study we report a gas-phase structure investigation of perfluorinated *N*,*N*-dimethylformamide, $(CF_3)_2NC(O)F$, using GED and quantum chemical calculations. The primary interest is in the effect of fluorination on conjugation lp(N)$\rightarrow\pi^*$(C=O) and in a possible deviation of the molecular skeleton from planarity.

Experimental Section

$(CF_3)_2NC(O)F$ was synthesized by the reaction of CF_3NCF_2 and CF_3OF. Five millimoles of CF_3NCF_2 and 2.5 mmol of CF_3OF were condensed at −196 °C into a 30 mL Kel-F reactor containing 1 mmol of CsF. The temperature was raised from −78 to 25 °C within 24 h and the reaction mixture was fractionally condensed. $(CF_3)_2NF$, which was also formed in this reaction, was pumped off at −120 °C. According to ^{13}C and ^{19}F NMR spectra the remaining $(CF_3)_2NC(O)F$ was 98% pure in the liquid phase. The yield was 95% $(CF_3)_2NC(O)F$ relative to CF_3OF.

The GED intensities were recorded with a Gasdiffraktopraph KD-G2[17] at 25 and 50 cm nozzle-to-plate distances and with an accelerating voltage of about 60 kV. The sample was kept at −65 °C. To remove small amounts of the more volatile $(CF_3)_2NF$ (ca. 2% in the NMR spectra), the sample was pumped off for about 2 min before recording the intensities. The inlet system and nozzle were at room temperature. The photographic plates (KODAK Electron Image Plates, 13 × 18 cm) were analyzed with the usual methods.[18] Averaged molecular intensities in the s ranges 2−8 and 8−35 Å^{-1}, in intervalls of $\Delta s = 0.2$ Å^{-1} ($s = (4\pi/\lambda)\sin(\theta/2)$, λ = electron wavelength, θ = scattering angle), are presented in Figure 1.

Theoretical Calculations. The geometric structure of $(CF_3)_2NC(O)F$ was fully optimized with HF, MP2, and B3LYP methods, using 6-311G* basis sets.[19] The geometric parameters are included in Table 1. Furthermore, structures with exactly planar and with perpendicular orientation of the $(CF_3)_2N$ group were optimized with the B3LYP method. The structure of $Me_2NC(O)H$ was optimized with the three methods to obtain information about the effect of fluorination on geometric parameters of this compound. According to these calculations the parent compound possesses an exactly planar skeleton. Natural bond orbital (NBO) analyses[20] were performed for the parent and for the fluorinated compound at the B3LYP level. Vibrational amplitudes for the fluorinated derivative were derived from a Cartesian force field obtained with the HF approximation, using the program ASYM40.[21] The calculated force constants were scaled with a uniform factor of 0.90 and the amplitudes are listed in Table 2.

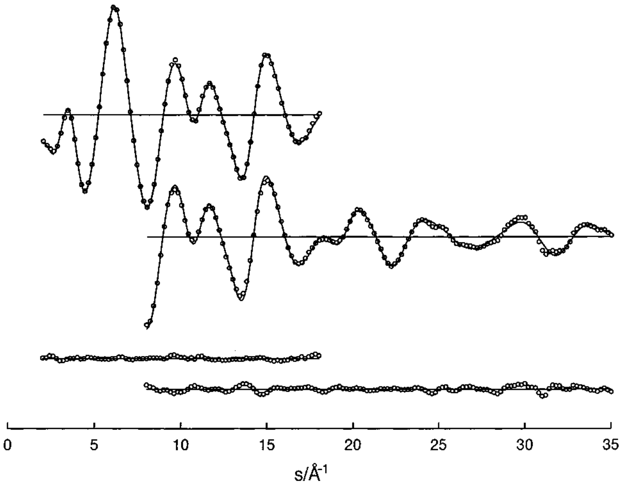

Figure 1. Experimental (dots) and calculated (full line) molecular intensities for long (above) and short (below) nozzle-to-plate distances and residuals.

Table 1. Experimental and Calculated Geometric Parameters for $(CF_3)_2NC(O)F$

	GED[a]		MP2[a,b]	B3LYP[a,b]	HF[a,b]
C=O	1.182 (6)	p_1	1.184	1.180	1.156
N−C1	1.394 (15)	p_2	1.402	1.398	1.393
N−C2	1.451 (4)	p_3	1.444	1.456	1.437
N−C3			1.443	1.446	1.438
$(C-F)_{mean}$	1.328 (2)	p_4	1.338	1.333	1.303
$\Delta CF = (C1-F4) - (C-F)_{Me}$	0.008 [5][c]		0.008	0.007	−0.004
$(C-F)_{Mel}$	1.327 (3)		1.329	1.332	1.304
C1−F4	1.335 (5)		1.337	1.339	1.300
N−C1=O	129.4 (15)	p_5	127.5	127.4	126.8
N−C1−F4	105.7 (24)	p_6	109.0	109.1	110.1
C1−N−C2	121.4 (7)	p_7	119.2	119.3	119.1
C1−N−C3	122.6 (7)[d]		120.4	120.7	120.6
C2−N−C3	115.5 (11)		119.8	119.7	119.9
$\sum\alpha(N)$[e]	359.5 (3)		359.4	359.7	359.6
F−C−F	108.5 (2)	p_8	108.5	108.2	108.4
tilt (CF_3)[f]	1.2 (12)	p_9	1.4	1.3	1.4
ϕ(F4−C1−N−C2)	37.2 (27)	p_{10}	28.5	24.2	28.0
ϕ(O=C1−N−C3)	28.6 (36)	p_{11}	18.5	17.0	19.7
τ(N−C(sp^2))[g]	32.9 (39)		23.5	20.6	23.9
ϕ(C3−N−C2−F1)	97.9 (27)	p_{12}	102.1	102.7	98.6
ϕ(C2−N−C3−F1′)	−166.5 (32)	p_{13}	−160.0	−161.1	−156.4

[a] r_a values in Å and deg. Error limits are 3σ values and include possible systematic errrors (see text). For atom numbering see Figure 3. [b] 6-311G* basis sets. Mean values are given for parameters which are not unique. [c] Not refined but varied within the range given in brackets for estimation of the possible systematic error. [d] Difference (C1−N−C3) − (C1−N−C2) constrained to 1.2° (MP2 value). [e] Sum of bond angles around nitrogen. [f] Tilt angle of CF_3 groups in the CNC plane and away from the opposite CF_3 group. [g] Torsional angle around the N−C(sp^2) bond away from the configuration in which the nitrogen lone pair is perpendicular to the C(O)F plane (see Newman projection in Figure 3).

Structure Analysis. The radial distribution function (RDF) was calculated by Fourier transformation of the molecular intensities which

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Table 2. Interatomic Distances and Vibrational Amplitudes for $(CF_3)_2NC(O)F$

	distance	GED[a]		HF[b]		distance	GED[a]		HF[b]
C=O	1.18	0.036[c]		0.036	C3···F1	3.26	0.136[c]		0.136
C−F	1.33	0.044(2)	l_1	0.043	C1···F3′	3.28	0.162[c]		0.162
N−C1	1.39	0.044(2)	l_1	0.046	C3···F3	3.45	0.090[c]		0.090
N−C2	1.45	0.044(2)	l_1	0.047	C1···F2′	3.46	0.079[c]		0.079
F···F	2.15	0.057(3)	l_2	0.057	C3···F4	3.51	0.070[c]		0.070
N···F	2.17−2.30	0.057(3)	l_2	0.057	O···C2	3.55	0.067[c]		0.067
O···F4	2.23	0.057(3)	l_2	0.059	C1···F2	3.56	0.068[c]		0.068
N···O	2.33	0.057(3)	l_2	0.051	F3···F3′	3.59	0.255[c]		0.255
C2···C3	2.45	0.064[c]		0.064	O···F3′	3.60	0.313[c]		0.313
F2···F3′	2.49	0.268[c]		0.268	C2···F1′	3.61	0.073[c]		0.073
C1···C2	2.49	0.065[c]		0.065	O···F3	3.69	0.145[c]		0.145
C3···F2	2.54	0.111[c]		0.111	F4···F1′	3.85	0.142[c]		0.142
F2···F2′	2.57	0.124[c]		0.124	F2···F1′	3.86	0.076(20)	l_3	0.096
C2···F4	2.65	0.118[c]		0.118	F4···F2	3.95	0.076(20)	l_3	0.101
C1···F1′	2.70	0.086[c]		0.086	F1···F3′	3.97	0.122(40)	l_4	0.141
F4···F3	2.71	0.126[c]		0.126	F3···F2′	4.03	0.076(20)	l_3	0.096
O···F1′	2.72	0.128[c]		0.128	O···F2′	4.12	0.076(20)	l_3	0.090
C1···F3	2.76	0.108[c]		0.108	F4···F2′	4.18	0.122(40)	l_4	0.122
C2···F2′	2.77	0.120[c]		0.120	O···F1	4.29	0.122(40)	l_4	0.147
F4···F1	2.77	0.273[c]		0.273	F1···F1′	4.31	0.208[c]		0.208
C2···F3′	2.87	0.163[c]		0.163	F4···F3′	4.38	0.122(40)	l_4	0.106
O···C3	2.98	0.106[c]		0.106	O···F2	4.48	0.122(40)	l_4	0.111
C1···F1	3.12	0.153[c]		0.153	F3···F1′	4.49	0.076(20)	l_3	0.081
F1···F2′	3.16	0.262[c]		0.262					

[a] Amplitudes in Å; uncertainties are 3σ values. For atom numbering see Figure 3. Amplitudes with the same number have been refined as a group. [b] From the HF/6-311G* force field. [c] Not refined.

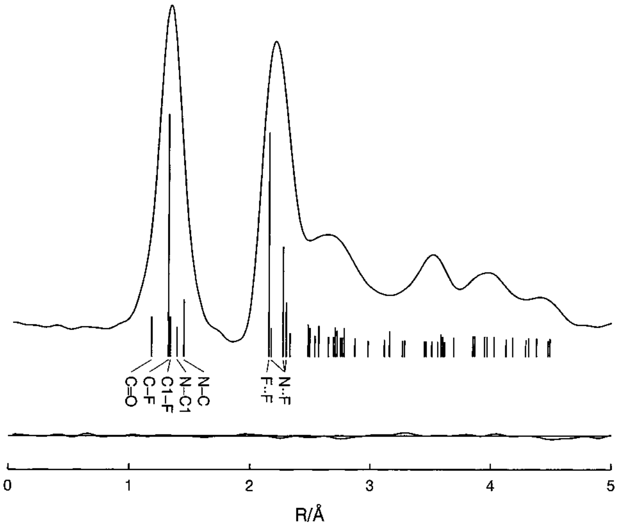

Figure 2. Experimental radial distribution function and difference curve. Important interatomic distances are shown by vertical bars. The identity of unlabeled distances may be deduced from Table 2.

were multiplied with an artificial damping function exp($-0.0019s^2$). The experimental curve (Figure 2) is reproduced best with a molecular model in which the $(CF_3)_2N$ group is rotated by about 30° relative to the C(O)F group. This preliminary model was refined by least-squares fitting of the experimental intensities. The intensities were modified with a diagonal weight matrix. Since all single bond distances and the first nonbonded distances overlap strongly, several geometric constraints had to be applied and the MP2 results were used for quantitative values. (1) C_{3v} symmetry was assumed for the CF_3 groups with a tilt angle between the N−C(sp^3) bonds and the C_3 symmetry axes. The tilt occurs in the C−N−C plane and away from the opposite CF_3 group. (2) The two N−C(sp^3) bond lengths were set equal. This assumption is justified according to the HF and MP2 calculations which result in a difference of 0.001 Å. The B3LYP method predicts a difference of 0.010 Å between these two bonds (see Table 1). (3) The difference between the C(sp^3)−F bonds and the C(sp^2)−F bond was constrained to the calculated value (0.008 Å with an estimated uncertainty of ±0.005 Å). (4) The difference between the two C(sp^2)−N−C(sp^3) angles, (C1−N−C3) − (C1−N−C2), was set to 1.2°. (5) The NC(O)F moiety was constrained to planarity. Vibrational amplitudes which either caused large correlations or were poorly determined in the GED experiment were fixed to calculated values. With these assumptions 13 geometric parameters p_i and four vibrational amplitudes l_k were refined simultaneously. The following correlation coefficients had values larger than |0.6|: $p_2/p_4 = -0.68$, $p_5/p_9 = 0.63$, $p_8/p_{10} = -0.68$, $p_2/l_1 = -0.75$, and $p_{12}/l_4 = -0.70$. The final results of the GED analysis are listed in Tables 1 (geometric parameters) and 2 (vibrational amplitudes). The molecular structure is shown in Figure 3.

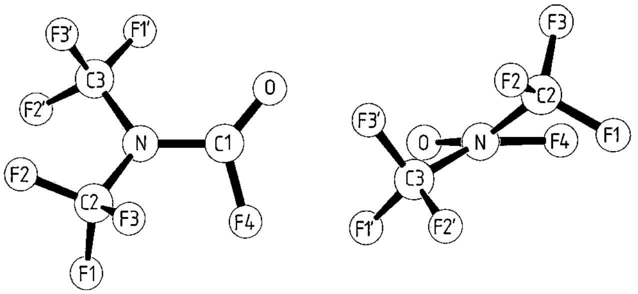

Figure 3. Molecular model with atom numbering (left) and Newman projection along the N−C(sp^2) bond (right).

Discussion

In perfluorinated dimethylformamide, $(CF_3)_2NC(O)F$, the bonds around nitrogen are almost planar with the sum of the nitrogen bond angles $\sum\alpha_N = 359.5(3)°$. This slight deviation from planarity may be due to out-of-plane vibrations. On the other hand, all three computational methods predict a very similar nonplanarity for the equilibrium structure. From the two dihedral angles which describe the orientation of the N−C(sp^3) bonds, ϕ(F4−C1−N−C2) = 37.2(27)° and ϕ(O=C1−N−C3) = 28.6(36)°, we can derive a torsional angle for the $(CF_3)_2N$ group around the N−C(sp^2) bond of τ(N−C(sp^2)) = 33(4)° (see Newman projection along the N−C(sp^2) bond in Figure 3). This torsional angle is the mean value of the two dihedral angles ϕ(F4−C1−N−C2) and ϕ(O=C1−N−C3). The rotation around the N−C(sp^2) bond away from the configuration in which the nitrogen lone pair is exactly perpendicular to the C(O)F plane can be rationalized by two effects: (1) steric repulsions between fluorine atoms of the two CF_3 groups and the fluorine and oxygen atom of the C(O)F group and (2) reduced conjugation between the nitrogen lone pair and the π(C═O) bond. The shortest F···F and F···O contacts (F1···F4 = 2.77 Å and F1′···O = 2.72 Å) are similar to the respective van der Waals radii (2.70 and 2.75 Å, respectively). This indicates that steric repulsions are not very strong.

The GED experiment does not provide any information about the barriers to internal rotation around the N−C(sp^2) bond. Theoretical calculations (B3LYP) predict the planar orientation of the $(CF_3)_2N$ group (nitrogen lone pair perpendicular to the C(O)F plane) to be 0.32 kcal mol^{-1} and the perpendicular orientation (nitrogen lone pair parallel to the C(O)F plane) to be 7.92 kcal mol^{-1} higher in energy than the equilibrium structure. The calculated barrier for the perpendicular orientation is much lower than the experimental $\Delta H^{\neq}$ value for the nonfluorinated dimethylformamide of 19.7(3) kcal mol^{-1}.[11] A low barrier to internal rotation in the fluorinated derivative is also indicated by the ^{19}F NMR spectra. In the temperature range 0 to −70 °C only one doublett at −56.33 ppm is observed for the two CF_3 groups. Thus, fluorination leads to a strong decrease of conjugation lp(N)→π*(C═O) which, however, is still strong enough to keep the $(CF_3)_2N$ group in a sterically unfavorable near-planar orientation. A decrease of conjugation upon fluorination is reflected also in lengthening of the N−C(sp^2) bond and in shortening of the C═O bond. Because of large uncertainties the lengthening of the N−C(sp^2) bond is not obvious from the experimental values (1.391(7) Å in $Me_2NC(O)H$[9] and 1.394(15) Å in $(CF_3)_2NC(O)F$), but the calculated (MP2) bond distances clearly demonstrate such an expected lengthening (1.365 vs 1.402 Å). Shortening of the C═O bond is obvious from experimental (1.224(3) vs 1.182(6) Å) and calculated values (1.220 vs 1.184 Å).

The decrease of conjugation upon fluorination can be rationalized qualitatively by two effects: (1) partial involvement of the nitrogen lone pair in anomeric interactions with the CF_3 groups, lp(N)→σ*(C−F) and (2) partial occupation of the π*(C═O) bond by lp(F)→π*(C═O) interaction. Both effects lead to a decrease of the lp(N)→π*(C═O) conjugation in the fluorinated compound. A clear quantitative explanation of this decrease on the basis of a natural bond orbital (NBO) analysis is not possible, because a large number of orbital interactions is involved. The lp(N)→π*(C═O) interaction energy is predicted to decrease from 63.8 kcal mol^{-1} in $Me_2NC(O)H$ to 22.6 kcal mol^{-1} in the fluorinated species. This difference seems to be unrealistically large, but it is compensated partially by many other less important orbital interactions.

Considering systematic differences between experimental geometric parameters (vibrationally averaged r_a values) and calculated equilibrium values, the MP2 and B3LYP method reproduces the experimental bond lengths very well (better than ±0.01 Å). As expected, most HF bond lengths are too short. Experimental and calculated bond angles differ by up to 4°. The experimental N−C1−F4 angle which has a large uncertainy is about 3° smaller than the calculated value. The C(sp^2)−N−C(sp^3) angles are by about 2° larger and the C(sp^3)−N−C(sp^3) angle is by about 4° smaller than the calculated values. The experimental and calculated sums of the nitrogen bond angles, however, agree exactly with each other. The largest difference occurs for the torsional angle around the N−C(sp^2) bond. The GED analysis results in a larger "effective" torsional angle of 33(4)° than the calculations which predict 23.5° (MP2), 20.6° (B3LYP), and 23.9° (HF). This difference of about 10° between the vibrationally averaged experimental angle and the calculated equilibrium values is at least to some extent due to large-amplitude vibrational effects. The HF method predicts a very low frequency (34 cm^{-1}) for the torsional vibration around the N−C(sp^2) bond.

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