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The effect of fluorination in trimethylamine: gas-phase structures of $CF_3N(CH_3)_2$ and $(CF_3)_2NCH_3$

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Abstract

The molecular structures of $CF_3N(CH_3)_2$ and $(CF_3)_2NCH_3$ have been determined by gas electron diffraction. The following skeletal parameters (r_a distances and $\angle_\alpha$ angles) have been obtained for $CF_3N(CH_3)_2$: C–F = 135.1(4) pm, N–C_H = 148.1(10) pm, N–C_F = 138.3(16) pm, C_HNC_H = 113.0(27)°, C_HNC_F = 111.9(9)°; $(CF_3)_2NCH_3$: C–F = 133.3(3) pm, N–C_H = 147.8(13) pm, N–C_F = 142.0(8) pm, C_HNC_F = 116.8(13)°, C_FNC_F = 117.8(11)°. C_H and C_F are the methyl and trifluoromethyl carbon atoms, respectively. Experimental uncertainties are 3σ values and include possible systematic errors. The most surprising result is the large difference between the N–C_H and N–C_F bond lengths of about 10 and 6 pm in these compounds. All nitrogen bond angles increase concomitantly with increasing number of CF_3 groups. An attempt is made to rationalize the observed structural trends.

1. Introduction

It has been shown that fluorination has a strong effect on skeletal parameters in trimethyl- and triethylamine. Perfluorination of trimethylamine leads to shortening of the N–C bonds from 145.9(2) pm in $N(CH_3)_3$ [1] to 142.7(6) pm in $(CF_3)_3N$ [2] and to an increase of the CNC angles from 110.9(3)° to 117.9(4)°. In triethylamine the N–C bonds lengthen from 146.6(1) pm [3] to 148.2(7) pm [4] and the CNC angles increase from 112.6(26)° to 119.3(4)° upon perfluorination. The opposite trends for the N–C bond lengths in these two amines suggest that several effects have to be considered to rationalize the observed structural effects: (1) electrostatic interactions between the high positive net charge at the fluorinated methyl or ethyl carbon atoms and the nitrogen net charge (positive or negative?); (2) different hybridization of nitrogen in the protonated and fluorinated compounds; (3) steric repulsions between fluorine atoms; (4) partial delocalization of the nitrogen lone pair in fluorinated species and the generalized anomeric effect of negative hyperconjugation [5]. The last effect has been discussed extensively by theoreticians for the model compound fluoromethylamine, CFH_2NH_2 [6]. The classic explanation for this effect involves a double bond–no bond resonance, and the localized orbital picture corresponds to interaction between the nitrogen lone

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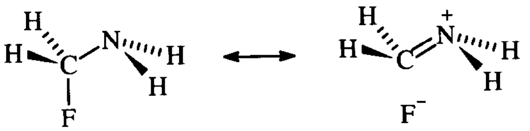
pair n_N and the anti-bonding C–F orbital σ^*_{CF} ($n_N \rightarrow \sigma^*$). This overlap is favored in the anti-periplanar orientation of C–F relative to the lone pair.



In this paper we present experimental structure determinations for (trifluoromethyl)dimethylamine, $CF_3N(CH_3)_2$ and bis(trifluoromethyl)methylamine, $(CF_3)_2NCH_3$, using gas electron diffraction (GED). The experimental studies are supplemented by ab initio calculations at the HF/3-21G$^{(*)}$ level. G$^{(*)}$ implies polarization functions for the central nitrogen atom only. The calculations are done with the GAUSSIAN 90 program package [7].

2. Experimental

2.1. Synthesis of $CF_3N(CH_3)_2$

A 10 mmol (0.73 g) portion of *N*,*N*-dimethylformamide and 20 mmol (1.2 g) of potassium fluoride are placed in a 75 ml stainless steel reactor fitted with a stainless steel Whitey valve. The reactor is cooled to −196°C, and is evacuated. After 25 mmol of sulfur tetrafluoride is condensed into the reactor, the mixture is allowed to warm slowly to room temperature and is then heated to 150°C for 48 h. The crude product mixture is fractionated by trap-to-trap distillation, with the product isolated in a trap held at −95°C having passed through a trap held at −50°C. Spectral data obtained for the product (b.p. = 20°C) agree with the data reported in the literature [8].

2.2. Synthesis of $(CF_3)_2NCH_3$

To a 100 ml Pyrex flask equipped with a Kontes Teflon stopcock are added silver fluoride (1.5 mg, 12 mmol) and 5 ml of benzonitrile. The flask is evacuated at −196°C, and 10 mmol of perfluoroazapropene and 10 mmol of methyl iodide are condensed in. The reaction mixture is allowed to warm to room temperature, and is stirred at room temperature for 3 days. The resulting product is fractionated by trap-to-trap distillation with the desired amine found in a trap held at −110°C having passed through a trap at −78°C. Spectral data of the product (b.p. = 15°C) agree with the data reported in the literature [9].

The electron diffraction intensities were recorded with a Gas Diffraktograph KD-G2 at 25 and 50 cm camera distances and with an accelerating voltage of about 60 kV. The electron wavelength was calibrated for each experiment with ZnO powder diffraction. The sample reservoirs were cooled to −50°C and −62°C for $CF_3N(CH_3)_2$ and $(CF_3)_2NCH_3$, respectively. Exposure times of 5–8 s and 18–25 s were used for the long and short camera distances. The photographic plates were analyzed by the usual methods [10] and averaged molecular intensities in the *s*-ranges 20–180 and 80–350 nm^{-1} in steps of $\Delta s = 2\,\text{nm}^{-1}$ are presented in Figs. 1 and 2.

3. Structure analyses

The radial distribution curves for both compounds are shown in Figs. 3 and 4. In the least squares refinements the molecular intensities were modified with a diagonal weight matrix and known

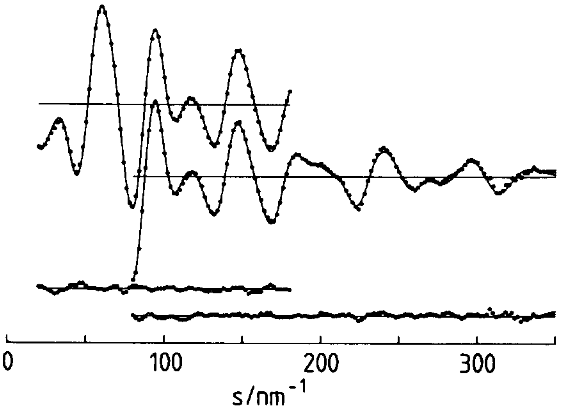


Fig. 1. Experimental (o) and calculated (—) molecular intensities and differences for $CF_3N(CH_3)_2$.

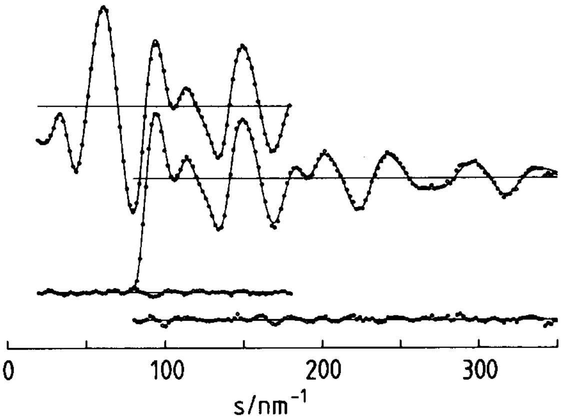


Fig. 2. Experimental (○) and calculated (—) molecular intensities and differences for $(CF_3)_2NCH_3$.

scattering amplitudes and phases were used [11]. The mean values of the N–C bonds, $(N–C)_m$, and the bond length differences $\Delta NC = (N–C_H) - (N–C_F)$ were chosen as independent parameters. C_H and C_F are the methyl and trifluoromethyl carbon atoms, respectively. C_{3v} symmetry was assumed for the CH_3 and CF_3 groups, with a tilt angle between the C_3 axis and the $N–C_F$ bond direction. The ab initio calculations for $CF_3N(CH_3)_2$ predicted different C–F bond lengths with the bond anti to the nitrogen lone pair being longer by 1.8 pm than the two gauche bonds. This difference could not be determined by the GED experiment and a mean value $(C–F)_m$ was refined. For $(CF_3)_2NCH_3$ the calculated C–F bond lengths varied only by 0.3 pm. Overall C_s symmetry was assumed for $CF_3N(CH_3)_2$ with the two methyl groups exactly staggered to the opposite $N–C_H$ bond. In the case of $(CF_3)_2NCH_3$ various models with local C_s, C_2 and C_1 symmetry for the $(CF_3)_2N$ group were tested. In the C_s model both CF_3 groups were rotated in opposite directions ($\tau_1(CF_3) = -\tau_2(CF_3)$; $\tau = 0$ corresponded to the exact staggered orientation). In the C_2 model the groups were rotated in the same directions ($\tau_1(CF_3) = \tau_2(CF_3)$) and in the C_1 structure both torsional angles had the same sign but different values. The C_2 and C_1 models fitted the experimental intensities almost equally well and the uncertainties for the torsional angles were very large (±8°). In the final refinement the torsional angles were constrained to the ab initio values which corresponded to C_1 symmetry. The HCH angles were set to the ab initio results in both molecules. Because of high correlations, the vibrational amplitudes for the N–C bonds could not be refined in the least squares analyses. The possible systematic errors caused by this constraint were estimated by varying this amplitude by ±0.5 pm and these errors were included in the experimental uncertainties of the refined parameters.

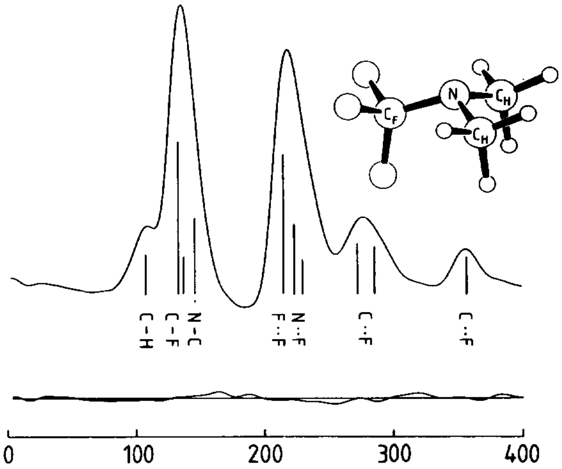


Fig. 3. Experimental radial distribution function and difference curve for $CF_3N(CH_3)_2$.

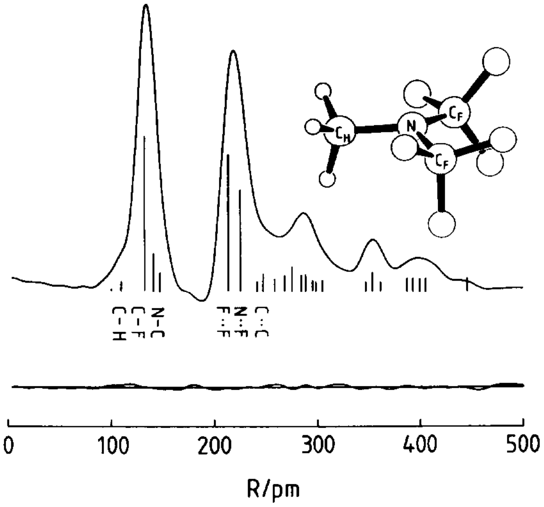


Fig. 4. Experimental radial distribution function and difference curve for $(CF_3)_2NCH_3$.

With these assumptions eight and seven geometric parameters p_i and five and eight vibrational amplitudes a_k were refined simultaneously for $CF_3N(CH_3)_2$ and $(CF_3)_2NCH_3$, respectively. The following correlation coefficients had values larger than $|0.6|$. $CF_3N(CH_3)_2$: $p_1/p_2 = -0.67$, $p_1/p_3 = -0.91$, $p_1/p_7 = 0.91, p_2/p_3 = 0.77, p_2/p_6 = -0.71$, $p_2/p_7 = -0.69$, $p_2/p_8 = 0.70$, $p_3/p_7 = -0.88$, $p_1/a_1 = 0.74$, $p_2/a_1 = -0.82, p_3/a_1 = -0.84, p_7/a_1 = 0.73$, $p_2/a_3 = 0.77$, $p_5/a_3 = 0.88$. $(CF_3)_2NCH_3$: $p_1/p_3 = 0.66$, $p_5/p_6 = -0.72$, $p_5/a_5 = -0.65$, $p_6/a_5 = 0.69$, $p_7/a_3 = -0.70$, $a_3/a_4 = 0.68$. The final results of the electron diffraction analyses are listed in Tables 1 and 2 together with the calculated geometric parameters.

4. Discussion of results

The skeletal parameters, N–C bond lengths and CNC bond angles, of the series $(CF_3)_nN(CH_3)_{3-n}$ with $n = 0$ to 3 are listed in Table 3. The mean N–C bond length, $(N\text{–}C)_m$, decreases smoothly with increasing number of CF_3 groups from 145.9(2) pm to 142.7(6) pm. Concomitantly, the sum of the nitrogen bond angles, $\Sigma\alpha_N$, increases from about 333° to 354° and this increase occurs predominantly between $CF_3N(CH_3)_2$ and $(CF_3)_2NCH_3$. The opening of the nitrogen bond angles can be rationalized by steric repulsions between CF_3 groups and/or by partial delocalization of the nitrogen lone pair into the electron withdrawing CF_3 groups. Since all bond angles (C_HNC_H, C_HNC_F, and C_FNC_F) increase with an increasing number of CF_3 groups, this last effect appears to be predominant. Furthermore, the shortest $F\cdots F$ contacts between neighboring CF_3 groups (271 pm in $(CF_3)_2NCH_3$ and 260 pm in $(CF_3)_3N$) are equal or only slightly shorter than the respective van der Waals distance (270 pm).

The most surprising result is the large difference between the N–C bond distances to CH_3 groups ($N\text{–}C_H$) and to CF_3 groups ($N\text{–}C_F$) in the two

Table 1
Results of GED analysis and ab initio calculations for $CF_3N(CH_3)_2$

	GED[a]		HF/3-21G(*)
Geometric parameters			
$(C\text{–}F)_m$	135.1(4)	(p_1)	135.2
$(N\text{–}C)_m$	144.9(6)	(p_2)	144.1
$\Delta NC = (N\text{–}C_H) - (N\text{–}C_F)$	9.8(22)	(p_3)	8.6
$N\text{–}C_H$	148.1(10)		146.9
$N\text{–}C_F$	138.3(16)		138.3
C–H	109.1(8)	(p_4)	108.2
$C_H\text{–}N\text{–}C_H$	113.0(27)	(p_5)	112.7
$C_H\text{–}N\text{–}C_F$	111.9(9)	(p_6)	112.5
F–C–F	106.1(5)	(p_7)	106.8
H–C–H	109.0[b]		108.9
Tilt(CF_3)[c]	3.6(13)	(p_8)	1.9

Interatomic distances and vibrational amplitudes[d]

C–F	135	4.8(4) (a_1)	$C\cdots C$	237–247	6.8(14) (a_3)
N–C	138–148	5.0[5][e]	$C\cdots F$	273–288	10.1(19) (a_4)
$F\cdots F$	216	5.8(6) (a_2)	$C\cdots F$	358	7.8(10) (a_5)
$N\cdots F$	225–232				

[a] r_a distances and $\angle_\alpha$ angles in pm and degrees. Error limits are 3σ values and include possible systematic errors (see text).
[b] Not refined.
[c] Tilt angle between C_3 axis of CF_3 group and N–C bond direction towards nitrogen lone pair.
[d] Without distances involving hydrogens.
[e] Not refined but varied within the given range (see text).

Table 2
Results of GED analysis and ab initio calculations for $(CF_3)_2NCH_3$

	GED[a]		HF/3-21G$^{(*)}$
Geometric parameters			
$(C\text{–}F)_m$	133.3(3)	(p_1)	134.3
$(N\text{–}C)_m$	143.9(4)	(p_2)	142.8
$\Delta NC = (N\text{–}C_H) - (N\text{–}C_F)$	5.8(18)	(p_3)	8.0
$N\text{–}C_H$	147.8(13)		148.1
$N\text{–}C_F$	142.0(8)		140.1
C–H	111.4(25)	(p_4)	107.8
$C_H\text{–}N\text{–}C_F$	116.8(13)	(p_5)	115.3
$C_F\text{–}N\text{–}C_F$	117.8(11)	(p_6)	115.6
F–C–F	107.6(3)	(p_7)	107.5
H–C–H	110.0[b]		109.7
$Tilt(CF_3)$[c]	1.8[b]		1.8
$\tau_1(CF_3)$[f]	25[b]		25.8
$\tau_2(CF_3)$[f]	13[b]		13.3

Interatomic distances and vibrational amplitudes[d]

C–F	133	4.5(3)	(a_1)	C···F	259–306	18(6)	(a_5)
N–C	142–148	5.0[5][e]		C···F	349–365	8(1)	(a_6)
F···F	215	6.5(5)	(a_2)	F···F	271–290	10(2)	(a_7)
N···F	225–229	7.5(8)	(a_3)	F···F	388–409	16(2)	(a_8)
C···C	243–250	7.2(19)	(a_4)	F···F	449	10[b]	

[a–e] See footnotes to Table 1.

[f] Torsional angles of the two CF_3 groups. For $\tau = 0°$ the CF_3 group staggers exactly the opposite $N\text{–}C_F$ bond.

mixed methyl/trifluoromethyl substituted amines. The $N\text{–}C_F$ bonds are about 10 pm and 6 pm shorter than the $N\text{–}C_H$ bonds. These large differences are reproduced within the experimental uncertainties by ab initio calculations at the HF/3-21G$^{(*)}$ level. It is difficult to rationalize these trends for the individual bond lengths. The anomeric effect accounts at least to some extent for the short $N\text{–}C_F$ bond in $CF_3N(CH_3)_2$. Ab initio calculations for CH_3NH_2 and CF_3NH_2 predict shortening of the N–C bond by 6 pm upon fluorination [6]. In $CF_3N(CH_3)_2$ the anomeric

Table 3
Skeletal geometric parameters for the series $(CF_3)_nN(CH_3)_{3-n}$, $n = 0$ to 3

	$N(CH_3)_3$[a]	$CF_3N(CH_3)_2$[b]	$(CF_3)_2NCH_3$[b]	$N(CF_3)_3$[c]
C–F	–	135.2(4)	133.3(3)	132.4(4)
$(N\text{–}C)_m$	145.9(2)	144.9(6)	143.9(4)	142.7(6)
$N\text{–}C_H$	145.9(2)	148.1(10)	147.8(13)	–
$N\text{–}C_F$	–	138.3(16)	142.0(8)	142.7(6)
$C_H\text{–}N\text{–}C_H$	110.9(3)	113.0(27)	–	–
$C_H\text{–}N\text{–}C_F$	–	111.9(9)	116.8(13)	–
$C_F\text{–}N\text{–}C_F$	–	–	117.8(11)	117.9(4)
$\Sigma\alpha_N$[d]	332.7(6)	336.8(30)	351.6(21)	353.7(7)

[a] Ref. 1.

[b] This work.

[c] Ref. 2.

[d] Sum of the nitrogen bond angles.

effect is expected to be enhanced relative to that in $(CF_3)NH_2$ by the electron donating methyl groups. The presence of the anomeric effect is demonstrated also by the small FCF angles (106.1(5)°) and by the theoretical results for the C–F bond distances. The bond anti to the lone pair is predicted to be 1.8 pm longer than the gauche bonds. In addition to this effect, electrostatic interactions between the positively polarized CF_3 carbon atom and the negative nitrogen atom shorten the $N-C_F$ bond. Besides the strong shortening of the $N-C_F$ bond, the $N-C_H$ bonds in $CF_3N(CH_3)_2$ (148.1(10) pm) lengthen by about 2 pm relative to the bonds in $N(CH_3)_3$ (145.9(2) pm). This trend can again be rationalized by the anomeric effect. This effect also involves the methyl groups, although $n_N \rightarrow \sigma^*_{CH}$ interactions are generally weaker than $n_N \rightarrow \sigma^*_{CF}$ interactions [6]. Substitution of a methyl group in $N(CH_3)_3$ by a CF_3 group leads to a reduction of the $n_N \rightarrow \sigma^*_{CH}$ interaction and thus to lengthening of the $N-C_H$ bonds in $CF_3N(CH_3)_2$, relative to those in $N(CH_3)_3$.

In $(CF_3)_2NCH_3$ the anomeric effect is expected to be less important, since the two electron withdrawing CF_3 groups lower the energy of the nitrogen lone pair. This is also indicated by the calculated values for the C–F bond lengths, which vary only by 0.3 pm in this compound. Furthermore, the negative net charge at the nitrogen atom and thus the electrostatic interactions will be reduced in $(CF_3)_2NCH_3$. This makes the $N-C_F$ bonds in this compound about 4 pm longer than that in $CF_3N(CH_3)_2$. The $N-C_H$ bonds are equal in both compounds and the $N-C_H$ and $N-C_F$ bond lengths still differ by about 6 pm.

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