

EFFECTS OF FLUORINE SUBSTITUTION ON METHYL AMINES [1 - 3]

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SUMMARY

The He(I) photoelectron spectra of the fluorinated methyl amines $(F_3C)_nNF_{3-n}$, $(F_3C)_{3-n}N(CF_2H)_n$ with $n = 1, 2, 3$ and F_2HC-NF_2 have been recorded. Their assignment is based on comparison of equivalent radical cation states in the individual series, assisted by MNDO calculations. The isolated first band results from the nitrogen lone pair ionization, and the substituent effects can be parametrized to form a multilinear regression with only small standard deviation. Trisubstituted derivatives of the series $(F_3C)_{3-n}N(CF_2H)_n$ ($n = 0, 1, 2, 3$) exhibit deviations, presumably due to sterically enforced planarization of the NC_3 trigonal pyramid.

INTRODUCTION

The effects of fluorine substitution on π systems have been extensively investigated by means of photoelectron (PE) spectroscopy [1,4,5], whereas saturated σ -type compounds have received

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less attention [1]. As far as π ionizations are concerned, fluorine substitution gives rise to hardly any shifts, whereas σ ionizations increase considerably in energy, leading to a separation of π and σ states. Therefore, the so-called 'perfluoro effect' i. e. the comparison of H- and F-substituted π compounds has often been used to facilitate PE spectroscopic assignments in the π ionization region [6]. In contrast, the σ ionizations subsequently overlap with the fluorine lone pair ionizations n_F , thus making assignments in this region tedious at best. Undoubtedly, the lack of a suitable 'telltale' indicator for the σ effects of fluorine substitution is one of the reasons for the inadequate knowledge gathered so far [1]. In the following, the nitrogen lone pair ionization n_N of fluorine-substituted methyl amines will be used as such a molecular probe.

As long as no significant structural changes are involved, substituent effects on the n_N ionization should be amenable to first and second order perturbation treatments. An illustrative example deals with a series of methyl-, ethyl-, and trimethylsilylmethyl-substituted amines, and includes a multilinear regression for the n_N ionization energies in dependence of the degree of substitution [7]. In close analogy, a similar regression for the title compounds will be derived here.

EXPERIMENTAL

All compounds investigated, i. e. F_3C-NF_2 [8-10], $(F_3C)_2NF$ [8-10], $(F_3C)_3N$ [9] $F_2CH-N(CF_3)_2$ [10], $(F_2CH)_3NCF_3$ [10] and $(F_2CH)_3$ [10] were synthesized at the University of Wuppertal by electrofluorination of $N(CH_3)$ and purified by repeated low temperature fractional distillation through a slit tube column.

Photoelectron spectra were obtained at the University of Frankfurt using a modified Perkin-Elmer PS 16, and have been calibrated with Xe ($^3P_{3/2}$:12.13 eV) and Ar ($^3P_{3/2}$:15.76). Resolution was of the order of 30meV throughout the experiments.

MNDO calculations [11] were performed on the DEC10 computer of the University of Frankfurt using geometries from electron diffraction experiments [8].

PHOTOELECTRON SPECTRA

The photoelectron spectra of the series $(F_3C)_n N F_{3-n}$, $(F_3C)_{3-n} N (CF_2H)_n$ ($n=1,2,3$) and of F_2CH-NF_2 are presented in Figures 1 to 3, and their ionization energies are given in Table 1. As a first step in PE spectroscopic assignment, a useful rule-of-thumb allows an estimate of the number of ionizations to be expected in the He(I) PE spectrum of a closed shell molecule, which should equal half the number of all element np- and hydrogen 1s-electrons formally present in the molecule [12]. Thus for NF_3 [13] one would expect $1/2 [3 \times 5(2p_F) + 1 \times 3(2p_N)] = 9$ ionizations, and for $(F_3C)_3 N$ altogether $1/2 [9 \times 5(2p_F) + 3 \times 2(2p_C) + 1 \times 3(2p_N)] = 27$ ionizations. The considerable overlap between the PE bands especially in the region between 15 eV and 18 eV renders the ascertaining of this expectation by inspection of the PE spectra alone quite difficult, but it is fully borne out by the MNDO calculations which predict the same number of ionizations as the above formula.

The PE spectra in Figures 1 to 3 can be roughly divided into 4 regions: the first one from 11.5 to 13 eV contains one ionization of predominantly nitrogen lone pair character, the one between 13 eV and 15.3 eV contains ionizations from CHF_2 -combinations and one antibonding N-F radical cation state, the one between 15.3 and contains ionizations from σ_{CH} combinations and one antibonding N-F radical cation state, the one between 15.3 and 18 eV the fluorine lone pair n_F , the σ_{NF} and σ_{CF} bond ionizations, and the last one above 18 eV the NF and CF bonding M^{\oplus} states.

The PE spectra of the series $(F_3C)_n NF_{3-n}$ (Figure 1) exhibit no other bands than the second band of $(F_3C)_2 NF$ in the second ionization region between 13 eV and 15.3 eV (Table 1): while in F_3C-NF_2 the NF-antibonding states range at ionization energies above 15.5 eV, further trifluormethyl substitution stabilizes the corresponding orbital in $(F_3C)_2 NF$ to such an extent that the PE band is shifted to considerably lower energy. The trisubstituted derivative $(F_3C)_3 N$ possesses no NF bond, and therefore displays again an empty second ionization region (Figure 1).

Within the series $(F_3C)_{3-n} N (CF_2H)_n$ with $n=1,2,3$ (Figure 2), all bands in the second region are attributed to M^{\oplus} states with predominant F_2HC group contributions in accordance with the results of the MNDO calculations.

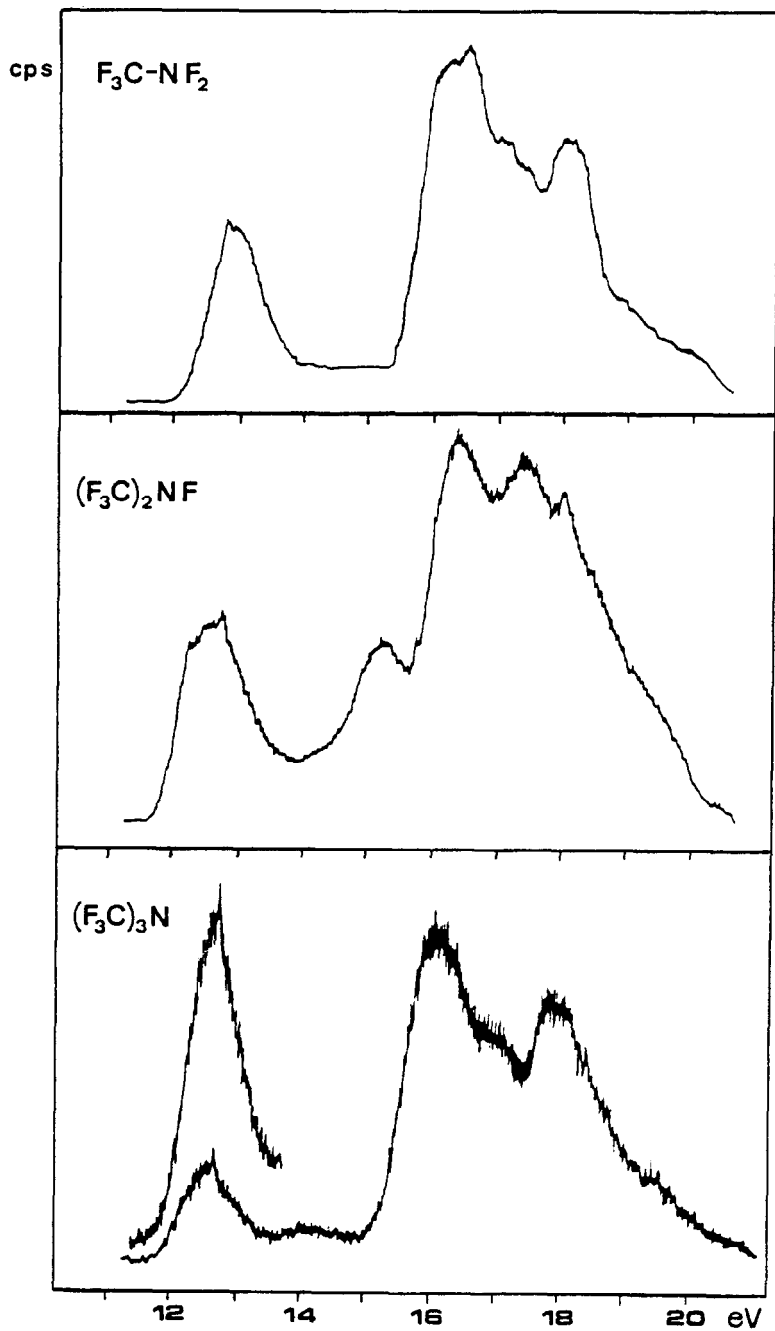


Fig. 1. He(I) PE spectra of the series $(F_3C)_nNF_{3-n}$, where $n=1, 2, 3$

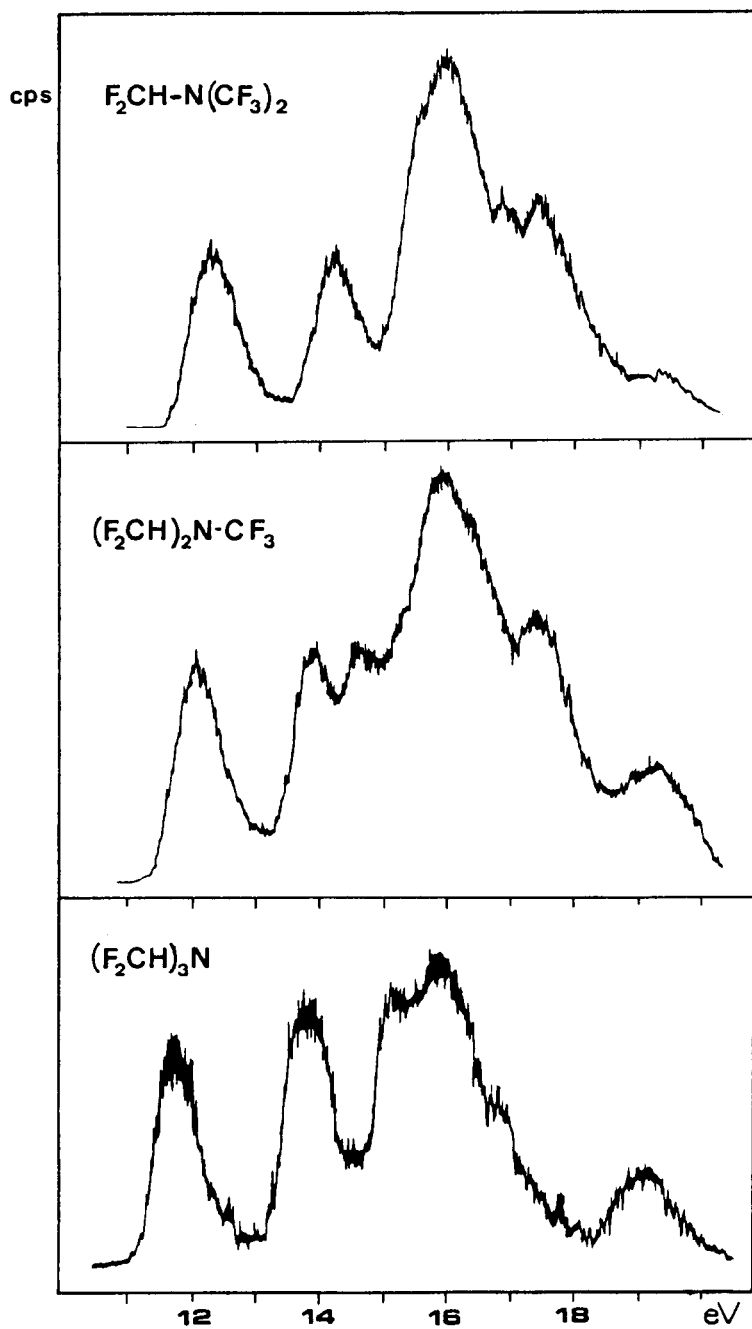


Fig. 2. He(I) PE spectra of the series $(\text{F}_3\text{C})_{3-n}\text{N}(\text{CF}_2\text{H})_n$, where $n=1,2,3$

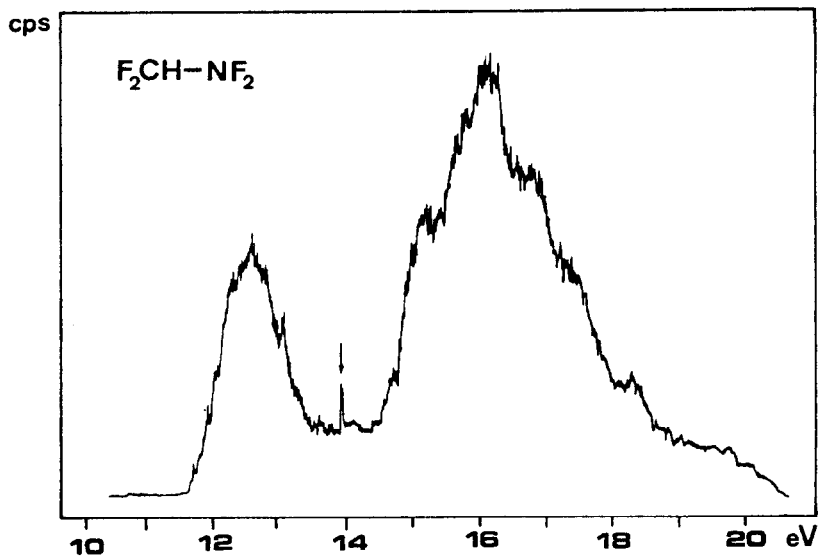


Fig. 3. He(I) PE spectrum of difluoromethyl difluoro amine (the arrow denotes an impurity)

TABLE 1

Vertical and adiabatic nitrogen lone pair ionizations, $IE_1^V(n_N)$ and $IE_1^a(n_N)$, as well as the band maxima IE_n (eV) of the second ionization region between 13 and 15.3 eV (see text).

Compound	IE_1^V	IE_1^a	IE_n (eV)
NF_3 [13]	13.73	13.0	15.49
F_3C-NF_2	12.62	~11.9	-
$(F_3C)_2NF$	12.45	~11.6	15.0
$(F_3C)_3N$	12.52	~11.7	-
$(F_3C)_2NCHF_2$	12.35	~11.7	14.30
$F_3CN(CHF_2)_2$	12.08	~11.4	13.93, 14.66
$(F_2CH)_3N$	11.65	~11.2	13.82
F_2CH-NF_2	12.33	~11.5	14.9

DISCUSSION OF THE FLUORINE SUBSTITUENT EFFECTS

As already outlined in the introduction, the nitrogen lone pair ionization is a sensitive indicator of the electron donating and withdrawing power of substituents [7]. Therefore, if no significant structural changes occur, the substituent effects can be interpreted by first and second order perturbation arguments: 1st order perturbations result in additive changes in the ionization energies, whereas 2nd order effects give rise to additional increments for each substituent [1]. For methyl-, ethyl- and (trimethylsilyl)methyl-substituted amines, the substituent effects on the n_N -ionization are reproduced numerically by the parameters ΔIE_j of the multilinear perturbation regression [7]:

$$\begin{aligned} IE_1^{\text{calc}} \text{ (eV)} &= IE_1^{\circ} - \sum_j \Delta IE_j \cdot n_j \\ &= 9.71 - 0.68 n_{\text{CH}_2\text{SiR}_3} - 0.5 n_{\text{C}_2\text{H}_5} - 0.43 n_{\text{CH}_3} \end{aligned} \quad (1)$$

The dependence of the n_N ionization energy on the degree of substitution is shown graphically in the lower part of Figure 4. Starting from the first ionization energy of the unsubstituted parent compound, the constant of the linear regression is formally obtained by subtracting an energy ΔR from IE_1 . Beginning at this fictitious ionization energy all ionization energies, with the exception of methylamine, are predicted and found in the shaded area (Figure 4). The rate of decrease in ionization energies increases in the substituent series $\text{CH}_2\text{Si}(\text{CH}_3)_3 > \text{CH}_2\text{CH}_3 > \text{CH}_3 > \text{H}$. This order has also been observed for acetylenes [14], ethylenes [15], dialkylsulfides [16], 1,2,4,5-tetrasubstituted benzenes [17], and 1,5-disubstituted pyridines [18], and it is what one would expect from a second order perturbation effect, the size of which should increase with hyperconjugation [19], and thus with donor strength (D). Nonetheless separating first and second order effects proves to be quite difficult, for instance ΔR cannot readily be explained in terms of either [20].

One would expect that an analogous treatment can be carried out for the F-, CF_3 -, and CF_2H -substituted amines. Inspection of the ionization energies in the series $(\text{F}_3\text{C})_n\text{NF}_{3-n}$ ($n=1,2,3$; Table 1) shows, however, that matters are slightly more complicated here: from 12.62 eV in $\text{F}_3\text{C}-\text{NF}_2$, the first ionization energy drops to

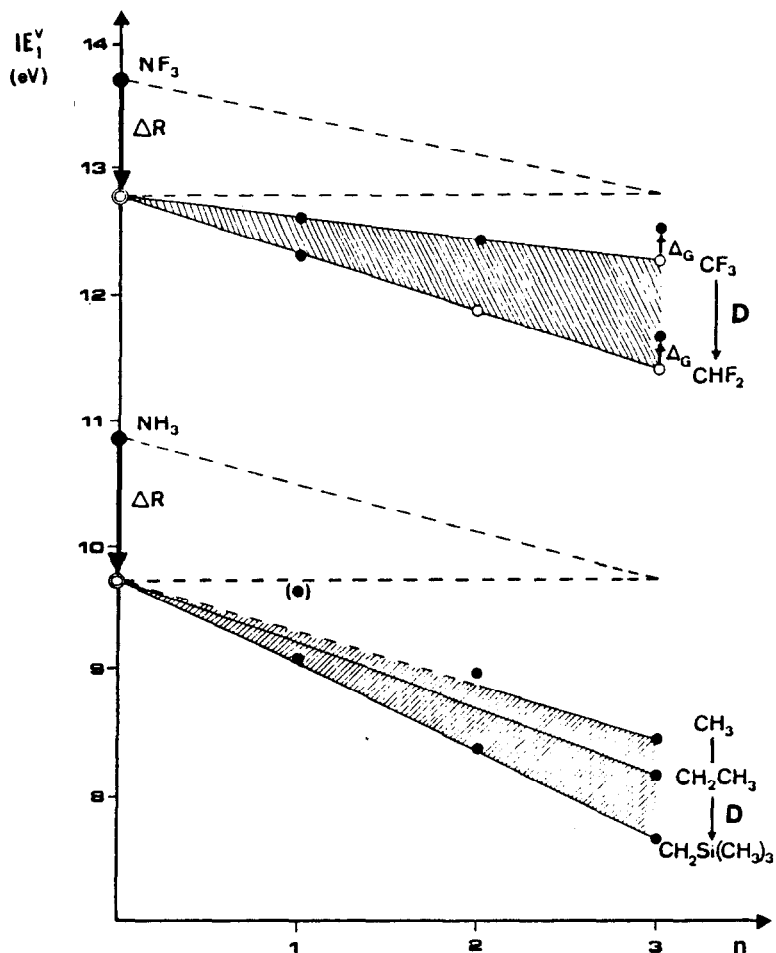


Fig. 4. Nitrogen lone pair ionization energies IE_1^V (eV) of substituted amines R_nNH_{3-n} and fluoroamines R_nNF_{3-n}

12.45 eV in $(F_3C)_2NF$, and rises again to 12.52 eV in $(F_3C)_3N$ (Figure 4, upper part). The electron diffraction structure shows $(F_3C)_3N$ to be nearly planar [21], and the other trisubstituted compounds $(F_3C)_{3-n}N(CF_2H)_n$ can be expected to possess an at least considerably flattened out nitrogen pyramid. These changes in molecular structure can be accounted for by introducing an additional structural increment Δ_G into eq. (1):

$$IE_1^{calc} \text{ (eV)} = IE_1^0 - \sum_j \Delta IE_j \cdot n_j + \Delta_G \cdot \delta_G \quad (2)$$

where $\delta_G=1$ for trisubstituted derivatives and $\delta_G=0$ otherwise. With this modification, one obtains the regression

$$IE_1^{\text{calc}} \text{ (eV)} = 12.79 - 0.17 n_{\text{CF}_3} - 0.46 n_{\text{CHF}_2} + 0.30 \delta_G \quad (3)$$

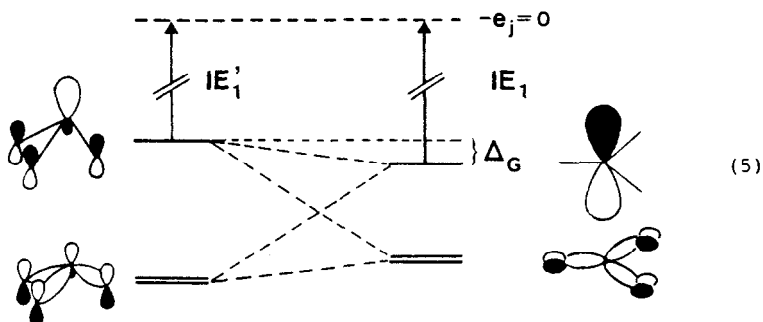
with a standard deviation of $\sigma=0.09$ eV only. Agreement between observed and calculated ionization energies is good enough to allow reliable predictions:

Compound Series	$(\text{F}_3\text{C})_n \text{NF}_{3-n}$			$(\text{F}_3\text{C})_n \text{N}(\text{CF}_2\text{H})_{3-n}$			$(\text{F}_2\text{CH})_n \text{NF}_{3-n}$	
	1	2	3	1	2	3	1	2
IE_1^{obs} (eV)	12.62	12.45	12.52	12.35	12.08	11.65	12.33	-
IE_1^{calc} (eV)	12.62	12.45	12.58	12.29	12.01	11.72	12.33	11.87
ΔIE_1 (eV)	0.00	0.00	0.06	0.06	0.07	0.07	0.00	-

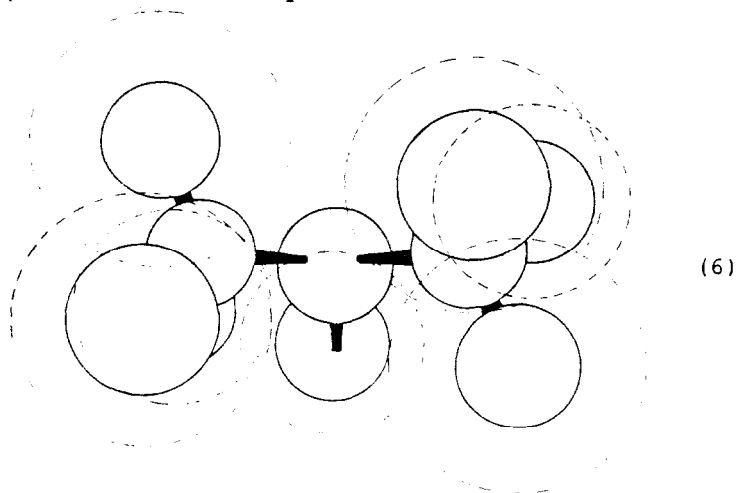
As in the series of CH_2R - substituted amines discussed above, the CF_2R substituents can be classed according to their donor strength. As expected, $\text{R}=\text{H}$ is far better a donor than $\text{R}=\text{F}$, as evidenced by the higher rate of decrease in ionization energies, or, in other words, that the hyperconjugation $n_{\text{N}}/\sigma_{\text{CF}} \ll n_{\text{N}}/\sigma_{\text{CH}}$.

The structural increment Δ_G has been introduced more or less ad hoc in eq. (2). Technically it has been included into regression (4) by performing a four-parameter-regression, with one variable being the Kronecker delta $\delta_G=0,1$. From a practical point of view, its introduction is fully vindicated by the excellent reproduction of both the trends and numerical values of the ionization energies.

In addition, there exists a rather straightforward justification for the introduction of a sterical increment: in MO models for mono- and disubstituted compounds, admixture of ligand orbitals into the nitrogen lone pair orbital results in a second order repulsion [20,22], thus raising the upper orbital; this corresponds to a lowering of the first ionization energy IE_1' . As the maximum possible symmetry of the system changes from C_{2v} to C_{3h} , such admixture is no longer possible, and IE_1 is consequently increased (5).



One question still remains to be elucidated: why is tris(trifluoromethyl)amine planar? Planarization for electronic reasons is often encountered in donor substituted compounds EX_n , in which the higher electron density around the central atom leads to strong electron pair repulsion [23] between the polarized E-X - bonds. Examples are the iso steric pairs $H_3C-O-CH_3/H_3Si-O-SiH_3$ ($\Delta SiOSi=144.1^\circ$) versus $H_3C-S-CH_3/H_3Si-S-SiH_3$ ($\Delta SiSSi=97.4^\circ$), or the planarization of the NX_3 skeleton upon going from $N(CH_3)_3$ to $N(SiH_3)_3$ [25]. However, the trifluoro- and difluoromethyl-groups are strong acceptors - almost comparable to F -, and therefore the flattening of the trigonal pyramid in the trisubstituted compounds $(F_3C)_{3-n}N(CF_2H)_n$ ($n=0,1,2,3$) must entirely be due to steric reasons. On the other hand, the differences in the van der Waal radii (H: 120 pm, F: 130 pm) and in the bond lengths (C-H: 109 pm, C-F: 133 pm) are relatively small [26]. Nonetheless, the cumulative effects of 9 fluorine atoms in $N(CF_3)_3$ relative to $N(CH_3)_3$ would make the space in a pyramidal molecule intolerably crowded, as a comparison with $(F_3C)_2NF$ suggests (scale in van der Waals radii: — 60% and --- 100%, fluorine atoms only):



Planar structures for the trisubstituted compounds are also supported by MNDO calculations with geometry optimization. The MNDO charge distributions for a number of fluorine substituted amines are given in Table 2.

TABLE 2

MNDO charge distributions in fluorine substituted amines

Compound	q(N)	q(C)	q(F _N)	q(F _C)	q(H)
NH ₃	-0.13				+0.05
NH ₂ F	-0.02		-0.16		+0.09
NHF ₂	+0.19		-0.15		+0.12
NF ₃	+0.45		-0.15		
F ₃ C-NF ₂	+0.17	+0.67	-0.12	-0.19	
(F ₃ C) ₂ NF	-0.30	+0.77	-0.09	-0.19	
(F ₃ C) ₃ N	-0.66	+0.79		-0.19	
(F ₂ CH) ₃ N	-0.64	+0.59		-0.21	+0.06
(F ₂ CH) ₂ NF	-0.28	+0.52	-0.11	-0.19	+0.07
F ₂ CH-NF ₂	+0.17	+0.44	-0.14	-0.20	-0.07

In all series $\text{NF}_3 \rightarrow \text{NH}_3$, $\text{NF}_3 \rightarrow (\text{F}_3\text{C})_3\text{N}$, and $\text{NF}_3 \rightarrow (\text{F}_2\text{CH})_3\text{N}$ the charge on the central nitrogen changes sign on replacing the second fluorine substituent. This is in accordance with an argument advanced to explain the change in N-C - bond lengths in the trifluoromethyl-substituted fluoroamines[8]: on going from $\text{F}_3\text{C-NF}_2$ ($d_{\text{NC}}=147.6$ pm) to $(\text{F}_3\text{C})_2\text{NF}$ ($d_{\text{NC}}=144.6$ pm) to $(\text{F}_3\text{C})_3\text{N}$ ($d_{\text{NC}}=142.6$ pm), the bond length is significantly shortened, which is attributed to polar contributions to the N-C - bond.

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