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Nitrogen-14 and Nitrogen-15 NMR Spectroscopy of Fluoronitrogen Cations: π and σ Fluoro Effects

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High-resolution spectra have been obtained for (anhydrous HF) solutions of NOF_2^+, NF_4^+, NH_4^+, NO_2^+, and NO^+ in ^{14}N resonance and for NH_3F^+ (in CF_3SO_3H) in ^{15}N resonance. Broader ^{14}N lines were obtained for N_2F^+ (although the one-bond NF coupling was resolved), $N_2F_3^+$, and NH_3F^+. For $F_2N{=}\mathit{N}F^+$ and NH_3F^+ the reduced electronic symmetry promotes quadrupolar broadening of the ^{14}N line; for N_2F^+ and $F_2\mathit{N}{=}NF^+$ exchange processes may contribute also. The nitrogen lines in the linear or planar species $N{\equiv}NF^+$, NOF_2^+, and $F_2N{=}NF^+$ show *π fluoro effects*, being shifted upfield relative to those in corresponding species with hydrogen, alkyl, or aryl groups instead of fluorine, despite the reduction in electron density on nitrogen. The higher shielding is related to increase in energy of $n_N \rightarrow \pi^*$ and $\sigma \rightarrow \pi^*$ paramagnetic circulations and so corresponds to perfluoro effects which are well-known in electronic and photoelectron spectroscopy. In planar systems, fluorination stabilizes σ relative to π orbitals, since interaction with the filled F_π orbitals counteracts the inductive stabilization of the π orbitals. In the nonplanar species, however, the nitrogen line moves strongly downfield with fluorination, as from NH_4^+ to NH_3F^+ to NF_4^+. These shifts are described as *σ fluoro effects* and are explained, at least in part, by the decrease in electron density on nitrogen. The higher shielding of nitrogen in NH_4^+ in anhydrous HF relative to that in aqueous solutions can be attributed to N-H···F hydrogen bonding.

Introduction

Because of the extreme position of fluorine in the periodic table, effects that occur to a lesser degree with other substituents can be "tested" in fluorine chemistry; indeed some are then so marked as to be called "(per)fluoro effects". An example is the perfluoro effect in planar systems which is used to distinguish σ from π orbitals in photoelectron spectroscopy and to characterize $n \rightarrow \pi^*$ (or $\sigma \rightarrow \pi^*$) excitations in electronic spectroscopy.[1-3] It results from the marked stabilization of the σ-orbital manifold relative to the π when hydrogens or alkyl groups are replaced by fluorine. Although the (-I) inductive effect of fluorine stabilizes the σ and the π orbitals, the effect on the π orbitals is offset by the repulsion of the fluorine nonbonding electrons ($+I_\pi$).

Corresponding effects can be discerned in ^{13}C and ^{15}N NMR shifts.[4] In the azabenzenes,[4c] for example, $n_N \rightarrow \pi^*$ bands are strongly blue shifted and nitrogen resonances shifted upfield, since (planar) nitrogen carrying a lone pair is deshielded by $n_N \rightarrow \pi^*$ electronic circulations in the magnetic field, and an increase in the excitation energy $\Delta E(n_N \rightarrow \pi^*)$ acts to reduce the circulation and the deshielding. Such "perfluoro" effects are usefully (following Liebman[6]) termed π fluoro effects, as they are evident also on partial fluorination, with some additivity. The term "σ fluoro effects" can then be applied to nonplanar systems (in which dramatic *downfield* shifts may be observed for atoms directly bonded to fluorine) and also to contributory influences of fluorine attached to a resonant atom in a π-bonded system. These effects reflect changes in electron density and orbital coefficients as well as in excitation energies, as discussed below.

We now report a nitrogen NMR spectroscopic study of the cations NF_4^+,[7] NH_3F^+,[8] $F_2N{=}NF^+$,[9] NOF_2^+,[10] $FN{\equiv}N^+$,[11,12] NH_4^+, NO^+, and NO_2^+, in anhydrous HF (or CF_3SO_3H) solution, to throw light on the effects of fluorination in these ions.

^{14}N vs. ^{15}N NMR Spectroscopy

Nitrogen NMR spectroscopy in high resolution normally requires the ^{15}N nucleus, but the low abundance (0.365%) has severely restricted its application to fluoronitrogen chemistry. Sharp lines can, however, be obtained for the abundant but quadrupolar ^{14}N nucleus in mobile solutions of NH_4^+, CH_3-$N{\equiv}C$, or NO_3^-, since the high local symmetry (small electric field gradient) allows the nuclear electric quadrupole and therefore the nuclear spin to relax sufficiently slowly.[5] Thus high-resolution ^{14}N NMR spectroscopy should in principle be possible for the NF_4^+, $FN{\equiv}N^+$, and $F_2N{\equiv}X^+$ ions, but greater quadrupolar broadening is expected for the $F_2N{=}\mathit{N}F^+$ nitrogen, which carries a lone pair of electrons, although $^1J_{NF}$ and $^2J_{NF}$ were resolved in $^{19}F\{^{14}N\}$ double resonance studies of *cis*- and *trans*-FN=NF.[13] ($^{14}N^{14}N$ coupling constants are expected to be small, 5 Hz or less, since $^1J_{^{15}N^{15}N}$ is about 6 Hz for the dinitrogen ligand $M{-}N{\equiv}N$[14a] or 10 Hz for the hydrazido(2-) ligand $M{=}N{-}NH_2$.[14b])

The low viscosity of fluoro compounds and liquid HF as solvent is advantageous for ^{14}N work since the quadrupolar relaxation rate is proportional to the molecular reorientation time and therefore to the viscosity. Pure liquid HF has a viscosity of 0.26 cP at 0 °C and 0.45 cP at -45 °C (cf. 1 cP at 20 °C for water). Unfortunately this solvent is (understably) unpopular with operators of widebore spectrometers for

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Table I. π-Bonded Fluoronitrogen and Related Compounds[i]

compd		solvent	T/°C[a]	δ(N)[b]	$^1J_{^{14}\mathrm{NF}}$/Hz[c]	$^2J_{^{14}\mathrm{NF}}$/Hz[c]	$W_{1/2}$/Hz[d]	T_q/ms[e]	ref (^{19}F)[f]	ref (^{14,15}N)[g]
$FN{\equiv}N^+AsF_6^-$	N-1	HF		−191.2	339 (14)	nr	120 (12)			
1 2					[328]				11	
			−50				400			
	N-2			−166.1	nr	nr	205 (14)			
			−50				600			
$PhN{\equiv}N^+BF_4^-$	N-1			−156.4						19 (^{15}N)
1 2	N-2			−63.4						
$NOF_2^+AsF_6^-$		HF		−99.0	254 (3)	. . .	18 (3)	18 (6)		
					[250]				10	
NO_2F		neat liq	−110	−87.6	109 (5)	. . .				24
					[112.5]					
$F_2N{=}NF^+AsF_6^-$	N-1	HF		−75.9	nr	nr	870 (50)			
1 2			−50				2200			
	N-2			26.0	195 (15)	nr	280 (20)			
			−50				950			
cis-FN=NF		CCl_3F		4	±145	∓37				13
trans-FN=NF		CCl_3F		66	±136	∓73				13
NOF		neat liq	−80	104	. . .	nr	245			21
			−78	110						24
$CF_3N(O){=}NF$	N-1		−123							*h*
1 2	N-2		−58							

[a] Other than ambient temperature. [b] ^{14}N shift relative to neat liquid CD_3NO_2, with low field positive. The new measurements were made at 28.9 MHz (400 MHz for protons) except for $NOF_2^+AsF_6^-$, which was measured at 4.33 MHz (60 MHz for protons). The reference for shifts measured at 4.33 MHz is 5 M NH_4NO_3 in 2 M HNO_3, for which NH_4^+(aq) has δ −360.0 relative to neat liquid CH_3NO_2. [c] $J_{^{15}\mathrm{N}}/J_{^{14}\mathrm{N}} = -1.403$. nr means "not resolved". The spin-spin coupling unresolved in ^{14}N resonance has not been resolved in ^{19}F resonance. Coupling constants shown in brackets were measured in ^{19}F resonance. [d] Line width at half-height. [e] Quadrupolar relaxation time, given by $T_q = 1/\pi W_{1/2}$ when the line is not broadened significantly by unresolved coupling or exchange. [f] Reference to ^{19}F measurement of J_{NF}. [g] Reference to nitrogen NMR measurement. [h] Frazer, J. W.; Holder, B. E.; Worden, E. F. *J. Inorg. Nucl. Chem.* **1962,** *24,* 45. [i] Uncertainties are given in parentheses in units of the last digits.

Table II. Nitrogen Oxo Ions

compd	solvent	T/°C[a]	δ(N)[b]	$W_{1/2}$/Hz	T_q/ms	ref
$NO_2^+AsF_6^-$	HF	−70	−136.3	5 (1)	65 (30)	
$NO_2^+BF_4^-$ (FSO_3^-)	SO_2	−60	−131.5			34 (^{15}N)
$NO_2^+HSO_4^-$	4:1 H_2SO_4-HNO_3		−132 (1)	29	11	*c*
$^-O_2N{=}NO^-Na_2^{2+}$	aq		−43.4			16
			−27.9			
$NO^+AsF_6^-$	HF		−7.5	95 (14)	3 (0.3)	
$NO^+HSO_4^-$	H_2SO_4		−5 (10)	broad		21
$NO^+BF_4^-$ (PF_6^-)	SO_2	−60	−3.2			34 (^{15}N)
$NH_4^+NO_3^-$ (5 M)	HNO_3(aq) (2 M)		−4.5			
$Na^+NO_2^-$	(satd, aq)		229			

[a] See footnote *a* of Table I. [b] See footnote *b* of Table I. [c] Chew, K. F. unpublished results. Quoted by: Logan, N. In "Nitrogen NMR"; Witanowski, M., Webb, G. A., Eds.; Plenum Press: London, 1973; Chapter 6.

the study of ^{15}N in natural abundance when the sample volume is 12 cm^3 or more, particularly if the solute is under pressure. Triflic acid (CF_3SO_3H) is more acceptable, and we used this for the ^{15}N spectrum of NH_3F^+.

Results and Discussion

As recorded in Tables I–III, the ^{14}N lines are very sharp for NF_4^+ and NH_4^+, quite sharp for NOF_2^+ and NO_2^+, but rather broad for NO^+, and broader still for $N{\equiv}NF^+$, $FN{=}NF_2^+$, and NH_3F^+. For solutions of similar viscosity, the quadrupolar broadening should perhaps increase as $NF_4^+ < F_2NO^+ < F_2\mathit{N}{=}NF^+ \leq N{\equiv}\mathit{N}F^+ < N{\equiv}NF^+ << F_2N{=}\mathit{N}F^+$, and also $NF_4^+ < NH_3F^+$. Thus some of the lines are broader than might be expected from the electronic asymmetry near nitrogen and the resolution of $^1J_{\mathrm{NF}}$ and $^2J_{\mathrm{NF}}$ in NF_3 and FN=NF.[13]

Another possible mechanism for line broadening is exchange of F^- or H^+ with the solvent, e.g.

$$N_2F_3^+ + F^- \rightleftharpoons N_2F_4$$

$$N_2F^+ + F^- \rightleftharpoons N_2F_2$$

$$NH_3F^+ \rightleftharpoons NH_2F + H^+$$

Such exchange is evident in the ^{19}F spectrum of $N_2F_3^+$ in liquid HF, the line sharpening with decrease in temperature, or addition of a Lewis acid such as AsF_5 to slow down exchange by withdrawing F^- as AsF_6^-.[9] The three FF couplings were resolved but NF coupling was not. In the ^{14}N spectra, unexpectedly, $^1J_{\mathrm{NF}}$ could be observed for the less symmetrical nitrogen (carrying a lone pair) but not for the other (Table I). Both resonances are broad and broaden further with decrease in temperature because of the increase in viscosity.[5] For N_2F^+ the one-bond NF coupling was resolvable in ^{14}N and in ^{19}F resonance, but no two-bond coupling was resolved, and these ^{14}N lines, also, broaden with decrease in temperature (Table I). Clearly there is a conflict between the temperature conditions needed for the reduction of quadrupolar broadening and of exchange broadening.

In ^{19}F resonances of ($^{14}NH_3F$)(CF_3SO_3) in concentrated H_2SO_4 no coupling was resolved at 30 °C. An optimum spectrum was obtained at −40 °C, a quartet with $^2J_{\mathrm{HF}} = 43$ Hz and $W_{1/2} = 5.6$ Hz, but no ^{14}NF coupling was resolved. No NH or NF coupling in NH_3F^+ in HF solution could be resolved in ^{14}N resonance under the various conditions given in Table III. Addition of AsF_5 increased the line width, indicating that any decrease in exchange broadening is outweighed by effects of increased viscosity. [75]As observations of $KAsF_6$ in acetone showed[15a] that doubling the concentration (from 1 to 2 M) increased the viscosity by a factor of about 1.7 and roughly halved the spin–lattice relaxation time, cor-

Table III. Nonplanar Fluoronitrogen and Related Compounds[a]

compd	solvent	T/°C[a]	δ(N)[b]	$^1J_{^{14}NF}$/Hz[c]	$^1J_{^{14}NH}$/Hz	$W_{1/2}$/Hz[d]	T_q/ms[e]	ref (^{19}F)[f]	ref (^{14,15}N)[g]
NH_3	neat liq		−380.0						
$NH_4^+AsF_6^-$	HF		−369.6	. . .	54.3 (1.7)	2 (1)	160		
$NH_4^+NO_3^-$ (5 M)	HNO_3(aq) (2 M)		−360.0	. . .	52				
N_2H_4	neat liq		−335						25 (^{15}N)
$NH_3F^{+-}O_3SCF_3$	CF_3SO_3H	+20	−252.1[b]	33.9 (3.0)[b]	30.8 (3.0)[b]	3			
	HF	+10	−259.6	nr	nr	350[c]	1		
		−40	−257.6			600[c]	0.6		
	HF/AsF_5	+10	−260.0	nr	nr	420			
		−40	−256			730			
NOF_3	neat liq	−120	−147			208			23a
		−110	−137	134					24
				[135.5]				23b	
$NF_4^+BF_4^-$	HF		−92.3	230.5	. . .	2 (1)	160		
				[231]					
$NF_4^+AsF_6^-$	HF		−92.2	230.5	. . .	3 (1)	100		
				[234]				7b	
				[231]				7c	
N_2F_4	neat liq		−49						13
			−41	nr					24
				[160]				*d*	
NF_3	neat liq	−130	−9	nr	. . .	225			23
		−152	−14.3	158					24
				[155]				13	

[a] Terms in the column heads are defined in footnotes *a–g* of Table I. [b] ^{15}N measurements at 18.24 MHz giving $^1J_{^{15}NF} = 47.6$ (3.0) Hz with proton decoupling and $^1J_{^{15}NH} = 43.2$ (3.0) Hz. [c] Broad-band proton decoupling reduced these line widths by about 50 Hz. [d] Ettinger, R.; Colburn, C. B. *Inorg. Chem.* 1963, *2*, 1311.

responding to a doubling of the line width. We obtained a septet for the ^{75}As line for AsF_5 in the $(NH_3F)(CF_3SO_3)$ solution in HF, with $^1J_{AsF} = 933$ Hz as obtained previously,[15] but with a greater line width ($W_{1/2} = 800$ Hz at 25 °C) than those reported for aqueous solutions (94 Hz)[15b] or in organic solvents (150–450 Hz)[15a] despite the lower viscosity of liquid HF. This indicates exchange broadening as well as quadrupolar broadening of the ^{75}As line. (In highly symmetric environments, as in AsF_6^-, quadrupolar relaxation is mediated by transient electric field gradients at the nucleus during Brownian motions.)

Fortunately we could measure the natural-abundance ^{15}N spectrum of NH_3F^+ in solution in triflic acid, CF_3SO_3H. Proton decoupling gave a doublet with negative intensity corresponding to the maximal NOE factor for ^{15}N ($\eta = -4.93$) and an ^{15}NF coupling constant of 48 Hz, equivalent to 34 Hz for ^{14}N. The fully coupled spectrum gave an ^{15}NH coupling constant of 43 Hz, equivalent to 31 Hz for ^{14}N.

π Fluoro Effects. Table I gives the nitrogen NMR parameters for linear or planar fluoronitrogen ions and molecules, with some related compounds for comparison. Some interesting correspondences can be observed in the chemical shifts. The F_2N^+= nitrogen has similar shifts in $F_2N{=}O^+$ and in $F_2N{=}NF^+$, and the mean of the two nitrogen shifts in $F_2N{=}NF^+$ resembles that for the isoelectronic nitrohydroxamate ion $(O_2N{=}NO)^{2-}$.[16] The resonance of the =NF nitrogen in $F_2N{=}NF^+$, which has fluorine cis and trans, lies between the resonances for *cis*- and *trans*-FN=NF.[13]

A π fluoro effect is evident in the upfield shift of up to 100 ppm on replacement of R or Ar by fluorine in diazenes (azo compounds) RN=NR,[17] and similarly for the diazenium nitrogen $=NF_2^+$ compared with protonated diazenes[18] and for terminal nitrogen in the diazonium ions $FN{\equiv}N^+$ compared with $PhN{\equiv}N^+$.[19] Interestingly the upfield shift is smaller, 30 ppm, for the two-coordinate diazonium nitrogen $FN{\equiv}N^+$, and this illustrates the multiplicity of factors when fluorine is directly attached to the resonant atom. As well as the π fluoro effect, tending to increase the shielding by increasing ΔE(HOMO–LUMO), the fluoro substitution tends to increase the shielding by removing electron density from the paramagnetic circulations on nitrogen; but the increase in positive charge on nitrogen reduces the radius of the paramagnetic circulations, increasing their effect. These factors are represented (respectively) by the three terms ΔE, $\sum Q$, and $\langle r^{-3}\rangle_{2p}$ in the approximate formulation of the local paramagnetic term, restricted to electronic circulations on the observed atom A bonded to other atoms B[20]

$$\sigma_p^{AA} = \frac{-\mu_0\mu_B\langle r^{-3}\rangle_{2p}}{2\pi(\Delta E)}\left(Q_{AA} + \sum_{A\neq B} Q_{AB}\right) \qquad (1)$$

where μ_0 is the permeability of free space, μ_B the Bohr magneton, and r_{2p} the radius of the valence p electrons, and the downfield shift increases with the absolute magnitude of σ_p^{AA}. The $\sum Q$ term expresses the imbalance of electronic charge that allows the paramagnetic circulation in the magnetic field. The Q_{AA} part depends on the 2p orbital populations on the atom A, whereas $\sum Q_{AB}$ is a multiple-bond term that (with the energy term) is responsible for the large differences in chemical shift for the different bond orders. Loss of electron density (or reduction of orbital coefficients) with substitution by electronegative ligands such as oxygen or fluorine may increase the shielding, by reducing $\sum Q$. On the other hand, the radial term $\langle r^{-3}\rangle_{2p}$ and therefore the deshielding increase in proportion to the increase in (positive) atomic charge. Thus the π fluoro (ΔE) effects tend to increase the shielding, whereas the σ fluoro effects, decrease in $\sum Q$ and increase in radial terms $\langle r^{-3}\rangle_{2p}$, tend to cancel. Substituent effects are particularly influential for the lower field resonances such as those of the diazene or nitroso compounds: there is an upfield shift of 450 ppm from alkyl or aryl nitroso compounds to NOF,

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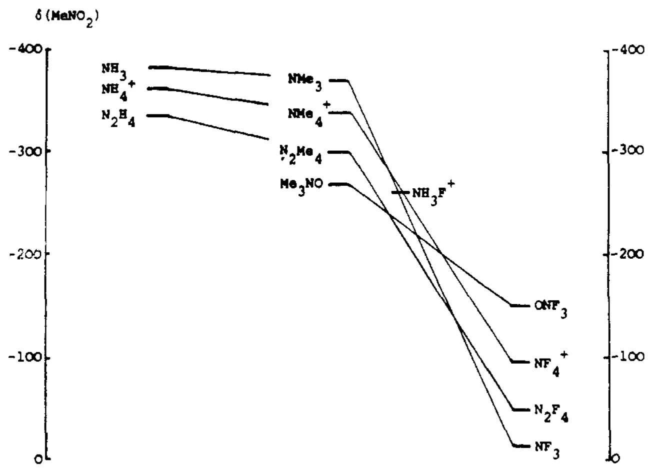

Figure 1. σ fluoro effects in nonplanar systems.

paralleled by a blue shift in $n_N \rightarrow \pi^*$ absorption from 760 to 311 nm (corresponding to an increase in ΔE from 1.6 to 4 eV, for this contribution to the appropriate component of the shielding tensor).[21]

Replacement of O$^-$ by fluorine results in upfield nitrogen shifts, of 120 ppm for NOF compared with NO_2^- and 80 ppm for NO_2F (95 ppm for NOF_2^+) compared with NO_3^- (Tables I and II); cf. the blue shift in the $n_N \rightarrow \pi^*$ absorption from 357 nm for NO_2^- to 311 nm for NOF. Again, there are σ fluoro effects of the reduction in electron density on nitrogen which tend to cancel: a CNDO/S estimate indicates a 5% increase in $\langle r^{-3}\rangle_{2p}$ from NO_2^- to NOF, corresponding to deshielding by 30 ppm or so, counteracted by effects of decrease in the constitutive terms.

σ Fluoro Effects in Nonplanar Groups. Table III and Figure 1 show the strong deshielding of nitrogen in nonplanar groups when directly bonded hydrogen or alkyl (or aryl) substituents are replaced by fluorine. The deshielding is particularly large from NH_3 to NF_3,[23a,24] and N_2H_4[25] to N_2F_4,[13] and is smaller for nitrogen bearing a positive charge (NH_4^+ to NF_4^+) or an oxygen substituent (Me_3NO[22] to NOF_3[23b]). The increase in the radial factor with fluorination now acts in the same direction as the observed shifts, on the whole; $\langle r^{-3}\rangle_{2p}$ increases by 17% from NH_3 to NF_3 and by 20% from NH_4^+ to NF_4^+. However, the line shifts upfield from NF_3 to NF_4^+ or NOF_3, despite sizable increase in the radial term. The upfield shift from NF_3 to NOF_3 has been attributed in part to the increase in the electronic symmetry around nitrogen, approaching the spherically symmetric distribution of an inert gas;[26] but nitrogen in NF_4^+ is significantly deshielded compared to NOF_3 (despite similar values of the radial term). Indeed, the deshielding in NF_4^+ compared with NH_4^+ or NOF_3 illustrates the subtlety of the concept of "imbalance of electronic charge" as it contributes to nuclear magnetic deshielding.

As to the energy terms, the electronic circulations deshielding nitrogen in these molecules are all of $\sigma \rightarrow \sigma^*$ type, including the $n_N \rightarrow \sigma^*$ circulations in NH_3, NF_3, N_2H_4, and N_2F_4, since the nitrogen lone-pair orbitals are strongly linked to the σ framework. The higher shielding of nitrogen in NOF_3 or NF_4^+ compared with NF_3 follows the normal pattern on replacement of a lone pair on nitrogen by a strong σ bond, removing the lower energy $n_N \rightarrow \sigma^*$ circulation.[5] The strong deshielding of nitrogen with fluorination of NH_3 or NH_4^+ is paralleled by that of phosphorus[27] in phosphines or phosphonium ions, carbon in alkanes, silicon in silanes,[28] and so on. It is part of a periodic trend, of increased deshielding in saturated compounds as the ligand moves across the row of the periodic table,[29] so that it might be expected to be an inductive effect influencing the energy terms, since these are usually involved when substituent effects are large. On the other hand, the evidence[1-3] from photoelectron, optical, and electron impact energy loss spectroscopy suggests that the relevant excitation energies are significantly higher overall in the fluorinated than in the unfluorinated molecules. The $n_N \rightarrow \sigma^*$ excitation energy increases from about 6.5 to 8.7 eV from NH_3 to NF_3,[2b] and there are similar increases in excitation energies with fluorination in the series of the fluoromethanes,[2c] which are isoelectronic with the fluoroammonium ions, although the CH σ orbitals are destabilized in CH_3F and CH_2F_2 (but not CHF_3) compared with CH_4. The high ionization energy of fluorine, compared with that of the other halogens, makes for better matching, and therefore mixing, of the 2p orbitals with carbon and nitrogen bonding orbitals. Whereas the halogen lone-pair orbitals are highest lying in the other halogenomethanes, the CH σ orbitals are highest lying in the fluoromethanes, and the fluorine "lone pair" and CF σ orbitals are comparable in energy. The fluorine "lone pair" electrons are extensively delocalized, and it may be that their circulations in the magnetic field help to deshield nitrogen or carbon (etc.) as well as fluorine in these molecules, reinforcing the effects of increase in the radial term.

Patterns of chemical shifts can be described in broad terms by eq 1, which is a very approximate version (with an average energy denominator) of the local term approximation, which restricts calculation to electronic circulations on the observed atom A.[20] Our use of this equation is intended to give a "chemical" picture of nuclear magnetic shielding, in terms of orbitals and bonds. More accurate calculations sum over all the excited states (or else treat the magnetic field as a perturbation on the orbital manifold) and reckon the shielding contribution from circulations on neighboring atoms by means of a dipolar (neighbor anisotropy) approximation, although this gives an underestimate, as is evident from the magnitudes of observed substituent effects.[29] The deshielding of carbon from CH_4 to CH_3F is matched quite well (slightly underestimated) by ab initio SCF methods with some extension of the basis set,[30] but further fluoro substitution would make large demands on computer time. The semiempirical methods can deal with larger molecules but cannot usually match experimental shifts without ad hoc parameterization. This has been demonstrated for the INDO method with the specific example of the deshielding of carbon from CH_4 to CH_3F.[31] The standard parameterization greatly underestimates the deshielding, but the estimate can be increased by a (drastic) reduction in the absolute value of the resonance integral β^0_{CF}, which corresponds to the splitting of CF σ and σ^* orbitals. This reduction corresponds to an increase in ionicity of the CF bond; but the fault may be with the local term approximation, which cannot take full account of the deshielding of the central atom in these nonplanar molecules by circulations of the fluorine "lone pair" electrons.

Effects of the HF Medium on the Nitrogen Shifts. The nitrogen shift of −369.9 ppm for NH_4^+ in anhydrous HF effectively doubles the range that has now been observed for

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this ion. The range previously extended from −359 or −360 ppm for the nitrate in water or aqueous nitric acid to −350 ppm for the chloride in concentrated HCl, with the bromide and iodide slightly downfield of this. Briggs and Randall[32] found that the nitrogen shifts in aqueous acid solutions of $^{15}NH_4^+$ are independent of pH and concentration of NH_4^+ but are sensitive to the nature of the counterion, depending in linear fashion on its concentration. The nitrogen shielding increases in the sequence $I^- < Br^- < Cl^- < SCN^- < SO_4^{2-} < NO_3^-$, which differs from that of the efficiency of the anion in disrupting the hydrogen bonding of water. It is the order of increasing strength of hydrogen bonding of NH_4^+ to the anion,[32] and corresponding results were subsequently found for chlorides, iodides, etc., of protonated (saturated) amines.[33] Similarly, for a given anion, the nitrogen line moves upfield with change from a chlorinated solvent to methanol or water.[33] It is pleasing to find that the HF solutions of fluoro anions lie to the extreme of the NH_4^+ series, with maximal nitrogen shielding for the strongest hydrogen bond, N–H···F. There appears to be a significant upfield shift also of the nitrogen lines in NO^+ and NO_2^+ from liquid SO_2[34] to HF as medium, with fluoro anions in each case (Table II). Hydrogen bonding to a lone pair on nitrogen in ammonia or alkylamines normally deshields the nitrogen,[33] with a sizable deshielding from gaseous to liquid NH_3 and from NH_3 to NH_4^+.[35]

Spin–Spin Coupling Constants. The NF coupling constants measured in nitrogen resonance agree with those observed in ^{19}F resonance, as shown in the tables. The $^1J_{^{14}NF}$ value of 339 Hz for $F\mathit{N}{\equiv}N^+$ is the largest known, correlating with the high s character in the nitrogen bonding orbitals, analogous to the maximal $^1J_{^{14}NH}$ value of 96 Hz (135 Hz for ^{15}N) measured for $HC{\equiv}NH^+$.[36] The new $^1J_{^{14}NF}$ value of 195 Hz for the diazene nitrogen $F_2N{=}\mathit{N}F^+$ is larger than those observed for *cis*- or *trans*-FN=NF. If the qualitative correlation with s character holds (the quantitative relation frequently fails when nitrogen bears a lone pair with s character, as here[37]), it would suggest that this diazene NNF angle is larger than in *cis*-FN=NF (114.4°,[38] $^1J_{^{14}NF} = 145$), which is larger than in *trans*-FN=NF (105.5°,[38] $^1J_{^{14}NF} = 136$ Hz).

The NF coupling constant is much smaller in NH_3F^+ than in NF_4^+, the disparity being greater than in the fluoromethanes: $^1J_{CF}$ is 158 Hz in CH_3F compared with 259 Hz for CF_4. But the factors involved are not simple, for the fluoromethane values peak at 274 Hz for CHF_3. $^1J_{NH}$ in NH_3F^+ is unexpectedly small (31 Hz, cf. 54 Hz for NH_4^+) since an electronegative substituent usually increases the magnitude of a coupling constant, regardless of sign.

Our discussion so far has been of absolute magnitudes of J_{NF}. One-bond ^{14}NF coupling constants are expected to be negative[39] (and the ^{15}NF values positive because of the negative magnetogyric ratio of ^{15}N), so that the two-bond coupling constants in the diazenes are positive.[13]

It seems that the NH coupling constants increase with the strength of hydrogen bonding in the medium, as does the nitrogen shielding. For NH_4^+, $^1J_{^{14}NH}$ increases from (+)50 Hz for chlorides in aqueous HCl to 52 Hz for nitrates in aqueous HNO_3, and this trend is continued by the value of 54 Hz that we observe for $[NH_4][AsF_6]$ in anhydrous HF (Table III). This increase is consistent with contraction of the valence s orbitals increasing the Fermi contact term, with increase in effective nuclear charge as electron density is withdrawn in hydrogen bonding.

Experimental Section

The compounds were made by published methods.[7-12] The ^{14}N spectra were measured with a Bruker WH 400 spectrometer operating at 28.9 MHz. The solution in anydrous HF was contained in a sealed 4-mm FEP Teflon tube, which was placed within coaxial 5- and 10-mm glass tubes with CD_3NO_2 between them to serve as reference and deuterium field-frequency lock. Susceptibility effects are small, since the volume susceptibility of liquid HF is close to that of $MeNO_2$. The $[NOF_2][AsF_6]$ measurements were made with a Bruker WP 60 spectrometer at 4.33 MHz. The natural-abundance $^{15}NH_3F^+$ spectra were measured on a Bruker WH 180 widebore spectrometer operating at 18.24 MHz, with a sealed tube containing the CF_3SO_3H solution and a coaxial 5-mm tube containing CD_3NO_2.

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Registry No. NOF_2^+, 43575-45-7; NF_4^+, 30494-78-1; NH_4^+, 14798-03-9; NO_2^+, 14522-82-8; NO^+, 14452-93-8; NH_3F^+, 53768-39-1; N_2F^+, 33687-51-3; $N_2F_3^+$, 39448-70-9; nitrogen, 7727-37-9; nitrogen-15, 14390-96-6.

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