

The Fluoro(perfluoroalkylnitrile)noble-gas(II) Cations, $R_F C \equiv N - NgF^+$ ($Ng = Kr$ or Xe ; $R_F = CF_3, C_2F_5, n-C_3F_7$), and the Fluoro(trifluoro-s-triazine)xenon(II) Cation, $s-C_3F_3N_2N - XeF^+$; Novel Noble Gas-Nitrogen Bonds

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Three novel examples of Kr-N bonds derived from perfluoroalkylnitriles, the $R_F C \equiv N - KrF^+$ cations, and their xenon analogues $R_F C \equiv N - XeF^+$ ($R_F = CF_3, C_2F_5, n-C_3F_7$), have been prepared and characterized in BrF_5 solvent by ^{19}F and ^{129}Xe n.m.r. spectroscopy; the Xe-N bonded cation $s-C_3F_3N_2N - XeF^+$, synthesized as the AsF_6^- salt, is stable at room temperature and has been fully characterized by ^{129}Xe and ^{19}F n.m.r. and Raman spectroscopy.

We have previously reported that hydrogen cyanide and several classes of organic and fluoro-organic nitrogen bases are capable of forming Xe-N bonds with the hard acid XeF^+ .^{1,2} The bases include alkyl and fluoroalkyl nitriles¹ and perfluoropyridines.² We have also reported the first example of a Kr-N bond, $HC \equiv N - KrF^+ AsF_6^-$.³ All the nitrogen bases thus far found capable of bonding with NgF^+ are oxidatively resistant and possess first adiabatic ionization potentials (I.P.) close to, or exceeding, the estimated electron affinities of XeF^+ (10.9 eV) and KrF^+ (13.2 eV); e.g., the first I.P. of $HC \equiv N$ is 13.59 eV.⁴ The low basicity of the nitrogen atoms in these bases gives rise to noble gas-nitrogen bonds possessing

significant ionic character; an important criterion for thermal stability of the noble gas cation.

The measured value of the first adiabatic I.P. of $CF_3C \equiv N$ (13.90 eV)⁵ suggested that this and possibly related fluoroalkyl bases should be resistant to oxidative attack by KrF^+ and XeF^+ , and would be expected to possess nitrogen base centres conducive to the formation of correspondingly ionic noble gas-nitrogen bonds. The first I.P. (11.50 eV) for s-trifluoro-triazine, $s-C_3F_3N_3$,⁶ and the existence of $C_5F_5N - XeF^+ AsF_6^-$,² where the first I.P. of pentafluoropyridine is 10.08 eV,⁶ suggested that the $s-C_3F_3N_2N - XeF^+$ cation also ought to exist.

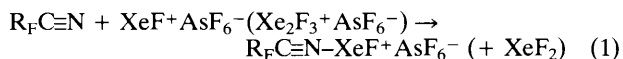
The interaction of equimolar amounts of $XeF^+ AsF_6^-$ or

Table 1. N.m.r. parameters for the $R_F C \equiv N - NgF^+$ ($R_F = CF_3, C_2F_5, n-C_3F_7$) cations^a

Cation	Chemical shift (p.p.m.) ^{b,c}		$^1J(^{129}Xe-^{19}F)/Hz$
	$\delta(^{129}Xe)$	$\delta(^{19}F)$	
$CF_3C \equiv N - KrF^+$		93.1 F-Kr- -53.9 F ₃ C-	
$CF_3CF_2C \equiv N - KrF^+$		91.1 F-Kr- -83.8 F ₃ C- ^d -108.6 -CF ₂ - ^d	
$CF_3CF_2CF_2C \equiv N - KrF^+$		91.9 F-Kr- -81.1 F ₃ C- -105.7 F ₃ C-CF ₂ -CF ₂ - -125.2 F ₃ C-CF ₂ -CF ₂ -	
$CF_3C \equiv N - XeF^+$	-1337.1	-210.4 F-Xe- -54.8 F ₃ C-	6397
$CF_3CF_2C \equiv N - XeF^+$	-1293.7	-212.9 F-Xe- -83.9 F ₃ C- -109.3 -CF ₂ -	6437
$CF_3CF_2CF_2C \equiv N - XeF^+$	-1294.2	-213.2 F-Xe- -81.9 F ₃ C- -106.6 F ₃ C-CF ₂ -CF ₂ - -125.7 F ₃ C-CF ₂ -CF ₂ -	6430

^a Spectra were recorded at 69.563 MHz (^{129}Xe) and 235.361 MHz (^{19}F) in BrF_5 solvent at -57 to $-61^\circ C$ for $R_F C \equiv N - KrF^+$ samples, and at -58 to $-68^\circ C$ (^{19}F) and $-64^\circ C$ (^{129}Xe) for $R_F C \equiv N - XeF^+$ samples. ^b Referenced externally at $24^\circ C$ with respect to the neat liquid references: $XeOF_4$ (^{129}Xe) and $CFCl_3$ (^{19}F); a positive sign denotes a chemical shift to high frequency of the reference. ^c With the exception of $C_2F_5C \equiv N - XeF^+$, no other $^3J(F-F)$ couplings could be observed owing to line broadening arising from slow chemical exchange and/or residual scalar coupling of the fluorine environments to ^{14}N . ^d $^3J(F-F) = 4.3$ Hz.

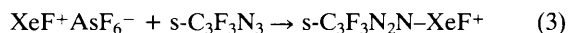
$Xe_2F_3^+ + AsF_6^-$ and $R_F C \equiv N$ ($R_F = CF_3, C_2F_5, n-C_3F_7$) in BrF_5 solvent according to equation (1) was initially studied. The syntheses of the krypton(II) analogues were also undertaken at low temperatures in BrF_5 solvent using the general synthetic approach given in equation (2).



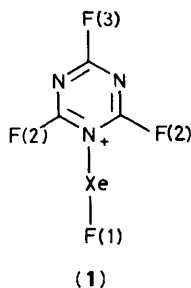
The $R_F C \equiv N - NgF^+$ cations have been characterized in BrF_5 by low-temperature (-57 to $-61^\circ C$) ^{19}F and ^{129}Xe n.m.r. spectroscopy and consist of two sets of new signals: a singlet in the F-on-Kr^{II} and in the F-on-Xe^{II} regions, and resonances in the F-on-C region with characteristic $^3J(FF)$ and $^1J(^{19}F-^{13}C)$ couplings having chemical shifts to high frequency of the parent base molecules (Table 1). In each case, the singlet assigned to F-on-Xe^{II} was flanked by natural abundance (26.44%) ^{129}Xe satellites arising from $^1J(^{129}Xe-^{19}F)$. The integrated relative intensities of the fluorine-on-noble gas environments and perfluoroalkyl group are consistent with the proposed formulations. Furthermore, the F-on-Kr^{II} resonance of $CF_3C \equiv N - KrF^+$ could be resolved to show the ^{82}Kr , ^{84}Kr , and ^{86}Kr isotopic shifts (0.0105 p.p.m./atomic mass unit, amu), which compare favourably with previously measured values for $HC \equiv N - KrF^+$ (0.0138 p.p.m./amu),³ and KrF_2 (0.0104 p.p.m./amu).⁷ In addition, the F-on-Kr^{II} resonances occur to high frequency of KrF_2 [$\delta(^{19}F)$ 68.0 p.p.m.; $-56^\circ C$; BrF_5 solvent] while the F-on-Xe^{II} resonances occur to low frequency of XeF_2 [$\delta(^{19}F)$ -184.3 p.p.m.; $\delta(^{129}Xe)$ -1685.2 p.p.m.; $^1J(^{129}Xe-^{19}F)$ 5621 Hz; $-52^\circ C$; BrF_5] (cf. Table 1). Similar, but slightly more positive ^{19}F chemical shifts have been observed for $HC \equiv N - KrF^+$ [$\delta(^{19}F)$ 99.4 p.p.m.; $-57^\circ C$; BrF_5 solvent]³ with respect to KrF_2 . This is in contrast to the $R_F C \equiv N - XeF^+$ series of cations which display significantly

more positive ^{19}F (F-on-Xe^{II}) and ^{129}Xe chemical shifts when compared with $HC \equiv N - XeF^+$ [$\delta(^{19}F)$ -198.4 p.p.m.; $\delta(^{129}Xe)$ -1552 p.p.m.; $^1J(^{129}Xe-^{19}F)$ 6150 Hz; $-10^\circ C$; HF solvent]¹ and XeF_2 . The ^{129}Xe and ^{19}F complexation shifts indicate that the Xe-N Bonds of the $R_F C \equiv N - XeF^+$ cations are significantly more ionic than in $HC \equiv N - XeF^+$ or $RC \equiv N - XeF^+$ (ref. 1) and this is further supported by significantly larger $^1J(^{129}Xe-^{19}F)$ values measured for the $R_F C \equiv N - XeF^+$ cations, which are known to increase with ionic character of the Xe-L bond in F-Xe-L type compounds.⁸ The $R_F C \equiv N - XeF^+$ cations represent the most ionic Xe-N bonded species presently known. In contrast, the analogous comparison of ^{19}F chemical shifts for $R_F C \equiv N - KrF^+$ cations indicates the Kr-N bonds are slightly more covalent than in $HC \equiv N - KrF^+$.

All three fluoro(perfluoroalkylnitrile)krypton(II) cations are thermally less stable with respect to redox decomposition than $HC \equiv N - KrF^+$ or their xenon(II) analogues, preventing their isolation and characterization in the solid state by Raman spectroscopy. Decompositions were monitored by ^{19}F n.m.r. and occurred over periods of ca. 1–2 h at -57 to $-61^\circ C$ with the assigned cation resonances decreasing while maintaining their relative intensity relationships. The major decomposition products consisted of Kr and the fluorinated products (^{19}F n.m.r. parameters listed in parentheses): CF_4 (-63.1 p.p.m.), C_2F_6 (-88.6 p.p.m.), and NF_4^+ [219.4 p.p.m., $^1J(^{19}F-^{14}N)$ 229 Hz] for all three $R_F C \equiv N - KrF^+$ cations studied, and $n-C_3F_8$ (-83.8 p.p.m., F_3C- ; -132.8 p.p.m., $-CF_2-$) for $C_2F_5C \equiv N - KrF^+$, and $n-C_3F_8$, $n-C_4F_{10}$ (-82.8 p.p.m., F_3C- ; -129.2 p.p.m., $-CF_2-$) for $n-C_3F_7C \equiv N - KrF^+$.



The interaction of liquid trifluoro-s-triazine, $s-C_3F_3N_3$, with $XeF^+ + AsF_6^-$ at room temperature for three hours followed by removal of excess of s-trifluorotriazine *in vacuo* resulted in a white powder which is stable indefinitely at room tempera-



ture. The combining ratio $\text{XeF}^+ \text{AsF}_6^- : \text{s-C}_3\text{N}_3\text{F}_3 = 1.00 : 1.00$ is consistent with equation (3). Both the ^{19}F and ^{129}Xe n.m.r. findings for the salt dissolved in BrF_5 and HF solvents are consistent with the cation formulation given by structure (1). The ^{129}Xe n.m.r. spectrum recorded in BrF_5 at -50°C consists of a doublet [$\delta(^{129}\text{Xe}) -1862.4$ p.p.m.] arising from $^1J(^{129}\text{Xe}-^{19}\text{F}) = 5932$ Hz. The $^{129}\text{Xe}-^{14}\text{N}$ coupling is quadrupole collapsed, as has been observed previously for $4\text{-CF}_3\text{-C}_5\text{F}_4\text{N-XeF}^+ \text{AsF}_6^-$ and $\text{C}_5\text{F}_5\text{N-XeF}^+ \text{AsF}_6^-$ in BrF_5 at low temperatures.² In HF solvent, however, $^1J(^{129}\text{Xe}-^{14}\text{N})$ is observed at -5°C [$\delta(^{129}\text{Xe}) -1807.9$ p.p.m.; $^1J(^{129}\text{Xe}-^{19}\text{F}) 5909$ Hz]. The magnitude, 245 Hz, compares favourably with those reported previously for the related perfluoropyridine cations (235–238 Hz). The ^{19}F n.m.r. spectra show two F-on-C environments in the ratio of 1 : 2 [F(1), -154.9 ; F(2), -27.7 ; F(3), -13.5 p.p.m. in HF solvent at -5°C and F(1), -145.6 ; F(2), -26.2 ; F(3), -8.7 p.p.m. in BrF_5 solvent at -50°C] and a F-on-Xe^{II} environment with accompanying ^{129}Xe natural abundance (26.44%) satellites arising from $^1J(^{129}\text{Xe}-^{19}\text{F})$ and a 1 : 2 : 1 triplet arising from $^4J[\text{F}(1)-\text{F}(2)] 10.9$ Hz [resolved at -50°C in BrF_5 solvent along with $^4J[\text{F}(2)-\text{F}(3)] 13.3$ Hz]. The coupling, $^4J[\text{F}(1)-\text{F}(2)]$, has also been observed for the perfluoropyridine cations $4\text{-CF}_3\text{-C}_5\text{F}_4\text{N-XeF}^+$ (25.8 Hz) and $\text{C}_5\text{F}_5\text{N-XeF}^+$ (25.0 Hz).²

A comparison of ^{129}Xe chemical shift and $^1J(^{129}\text{Xe}-^{19}\text{F})$ coupling constant values for other Xe–N bonded species studied to date reveals the following order: $\text{R}_f\text{C}\equiv\text{N} > \text{HC}\equiv\text{N} > \text{s-C}_3\text{F}_3\text{N}_3 \approx 4\text{-CF}_3\text{-C}_5\text{F}_4\text{N} > \text{C}_5\text{F}_5\text{N} > (\text{FSO}_2)_2\text{N} > (\text{CF}_3\text{SO}_2)_2\text{N}$, where the ^{129}Xe chemical shift and $^1J(^{129}\text{Xe}-^{19}\text{F})$ decrease with increasing covalent character of the Xe–N bond.

The Raman spectrum of $\text{s-C}_3\text{F}_3\text{N}_2\text{N-XeF}^+ \text{AsF}_6^-$ was recorded at -196°C using 514.5 nm excitation. In addition to modes associated with the ring, the spectrum is consistent with an ionic formulation, structure (1). Some key frequencies and their assignments follow: $\nu(\text{Xe-F})$, 544 (100), 553 (53) cm^{-1} ; $\nu(\text{Xe-N})$, 313 (0.6) cm^{-1} (tentative assignment); $\delta(\text{F-Xe-N})$, 156 (23), 159 (sh) cm^{-1} ; $\tau(\text{C}_3\text{F}_3\text{N}_2\text{N-Xe})$, 108 (6) cm^{-1} (tentative assignment) and AsF_6^- modes $\nu_1(a_{1g}) 684$ (19) cm^{-1} ; $\nu_2(e_g) 588$ (sh), 591 (4) cm^{-1} ; $\nu_5(t_{2g}) 370$ (5), 375 (4) cm^{-1} .

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