The Fluoro(perfluoropyridine)xenon(II) Cations, $C_5F_5N\text{–}XeF^+$ and $4\text{-}CF_3C_5F_4N\text{–}XeF^+$; Novel Examples of Xenon as an Aromatic Substituent and of Xenon–Nitrogen Bonding

Adel A. A. Emara and Gary J. Schrobilgen*

Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

The fluoro(perfluoropyridine)xenon(II) cations, $4\text{-}RC_5F_4N\text{–}XeF^+$ (R = F or CF_3), have been observed in HF and BrF_5 solutions (stable up to −30 °C) and their AsF_6^- salts have been isolated from BrF_5 solutions; low temperature Raman and ^{129}Xe, ^{19}F, and ^{14}N n.m.r. spectroscopic results are consistent with planar cations in which the xenon atom is co-ordinated to the aromatic ring through the lone pair of electrons on the nitrogen.

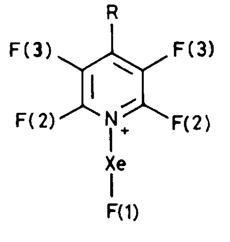
Compounds containing xenon–nitrogen bonds have only been characterized relatively recently and include the neutral species $FXeN(SO_2F)_2$,[1,2] $Xe[N(SO_2F)_2]_2$,[2,3] and $Xe[N(SO_2CF_3)_2]_2$,[4] and the cations $XeN(SO_2F)_2^+$,[5] $F[XeN(SO_2F)_2]_2^+$,[2,5] and the recently reported series of nitrile cations $R'C{\equiv}N\text{–}XeF^+$ (R′ = H, CH_3, CH_2F, C_2H_5, C_2F_5, C_3F_7, C_6F_5).[6] In this communication we report the synthesis and characterization of two novel xenon–nitrogen bonded cations which, thus far, represent unique examples of noble gas atoms functioning as aromatic ring substituents.

Equimolar amounts of $XeF^+AsF_6^-$ and the perfluoropyridine $4\text{-}RC_5F_4N$ (R = F or CF_3), react in anhydrous HF at −30

Table 1. N.m.r. parameters for the 4-RC_5F_4N–XeF^+ (R = F or CF_3) cations.[a]

	Chemical shifts/p.p.m.[b]			Coupling constants/Hz		
	$\delta(^{129}Xe)$	$\delta(^{14}N)$	$\delta(^{19}F)$	J(F–F)	$^1J(^{129}Xe–^{19}F)$	$^1J(^{129}Xe–^{14}N)$
C_5F_5N–XeF^+ (HF; −30 °C)[c]	−1871.9	−208	−148.3 F(1) −89.7 F(2) −158.0 F(3) −115.4 F(4)	24.6 F(1)F(2) −21.2 F(2)F(2) 17.6 F(2)F(3) −14.4 F(2′)F(3′) 2.0 F(3)F(3) −19.5 F(3)F(4)	5936	236
C_5F_5N–XeF^+ (BrF_5; −30 °C)[c]	−1922.5		−139.6 F(1) −88.0 F(2) −153.9 F(3) −110.1 F(4)	25.3 F(1)F(2) [d]	5926	[e]
4-$CF_3C_5F_4N$–XeF^+ (HF; −15 °C)[c]	−1802.6		−153.8 F(1) −88.7 F(2) −136.2 F(3) −60.9 CF_3	25.8 F(1)F(2) [d]	5977	238
4-$CF_3C_5F_4N$–XeF^+ (BrF_5; −50 °C)[c]	−1853.4		−144.6 F(1) −86.8 F(2) −132.6 F(3) −59.7 CF_3	25.8 F(1)F(2) −19.9 F(2)F(2) 12.5 F(2)F(3) −19.3 F(2′)F(3′) −2.7 F(3)F(3) −20.4 F(3)F(CF_3)	5963	[e]

[a] Spectra recorded without an external lock (field drift <1 Hz h^{-1}) at an external field strength B_0 = 5.8719 T using 9 mm o.d. FEP sample tubes. The corresponding spectrometer frequencies were 69.563 MHz (^{129}Xe), 18.075 MHz (^{14}N), and 235.361 MHz (^{19}F). [b] Spectra were referenced with respect to neat liquid external standards at 24 °C: $XeOF_4$ (^{129}Xe), CH_3NO_2 (^{14}N), and $CFCl_3$ (^{19}F). A positive chemical shift denotes a resonance occurring to high frequency of the reference compound. [c] For equilibrium reaction mixtures of XeF_2 and 4-$RC_5F_4NH^+AsF_6^-$ the following ^{19}F environments were also observed: (i) R = F, −30 °C, HF solvent: HF (−196.0 p.p.m.), XeF_2 [−200 p.p.m., $w_{1/2}$ 435 Hz, $^1J(^{129}Xe–^{19}F)$ 5660 Hz], AsF_6^- [−69.4 p.p.m., broad saddle-shaped resonance arising from partial quadrupole collapse of $^1J(^{75}As–^{19}F)$], and $C_5F_5NH^+$ [F(2) −100.2 p.p.m., F(3) −158.6 p.p.m., F(4) −108.6 p.p.m.]; (ii) R = F, −30 °C, BrF_5 solvent: HF (−199.4 p.p.m., $w_{1/2}$ 240 Hz), BrF_5 (quintet, 273.7 p.p.m.; doublet, 136.5 p.p.m.; ^2J(FF) 76.5 Hz), XeF_2 [δ (^{19}F) −187.4 p.p.m., $\delta(^{129}Xe)$ −1629.2 p.p.m., $^1J(^{129}Xe–^{19}F)$ 5643 Hz], AsF_6^- (−64.0 p.p.m., $w_{1/2}$ 1780 Hz), $C_5F_5NH^+$ [F(2) −96.8 p.p.m., F(3) −154.5 p.p.m., F(4) −103.2 p.p.m.]; (iii) R = CF_3, −20 °C, HF solvent: HF (−196.6 p.p.m.), AsF_6^- [−68.9 p.p.m., broad saddle-shaped resonance arising from partial quadrupole collapse of $^1J(^{75}As–^{19}F)$], 4-$CF_3C_5F_4NH^+$ [F(2) −98.5 p.p.m., F(3) −136.1 p.p.m., CF_3 −60.7 p.p.m.]; (iv) R = CF_3, −50 °C, BrF_5 solvent: HF (−193.1 p.p.m., $w_{1/2}$ 150 Hz), BrF_5 [quintet, 273.2 p.p.m.; doublet, 135.8 p.p.m.; ^2J(F–F) 76.4 Hz], XeF_2 [$\delta(^{19}F)$ −188.2 p.p.m., $\delta(^{129}Xe)$ −1589.0 p.p.m., $^1J(^{129}Xe–^{19}F)$ 5654 Hz], AsF_6^- (−63.7 p.p.m., $w_{1/2}$ 980 Hz), 4-$CF_3C_5F_4NH^+$ [F(2) −86.2 p.p.m., F(3) −131.8 p.p.m., CF_3 −59.5 p.p.m.]. [d] Although observed, intra-ring F–F couplings are not reported. [e] The spin–spin coupling $^1J(^{129}Xe–^{14}N)$ is quadrupole collapsed in BrF_5 solvent at −30 and −50 °C.



(**6**; R = F(4) or CF_3)

to −20 °C according to equation (1) and equilibria (2) and (3) to give the novel Xe–N bonded cations, 4-RC_5F_4N–XeF^+, as the AsF_6^- salts in solution. At −30 °C these solutions consisted of equilibrium mixtures of XeF_2, 4-$RC_5F_4NH^+AsF_6^-$, and 4-RC_5F_4N–$XeF^+AsF_6^-$ (determined by n.m.r. spectroscopy) (Table 1). Removal of HF solvent by pumping at −50 °C resulted in white solids which Raman spectroscopy at −196 °C also showed to be mixtures of 4-RC_5F_4N–$XeF^+AsF_6^-$, XeF_2, and 4-$RC_5F_4NH^+AsF_6^-$.

$$\underset{(\mathbf{1})}{4\text{-}RC_5F_4N} + (n+1)\,\underset{(\mathbf{2}}{HF} \rightarrow \underset{(\mathbf{3})}{4\text{-}RC_5F_4NH^+(HF)_n^-} \qquad (1)$$

$$(\mathbf{3}) + XeF^+AsF_6^- \rightleftharpoons \underset{(\mathbf{4})}{4\text{-}RC_5F_4NH^+AsF_6^-} + \underset{(\mathbf{5})}{XeF_2} + n(\mathbf{2}) \qquad (2)$$

$$(\mathbf{4}) + (\mathbf{5}) \rightleftharpoons \underset{(\mathbf{6})}{4\text{-}RC_5F_4N\text{–}XeF^+AsF_6^-} + (\mathbf{2}) \qquad (3)$$

An alternative approach which lead to isolation of the Xe–N bonded cations allowed stoicheiometric amounts of XeF_2 and the perfluoropyridinium cations, as their AsF_6^- salts, to react in HF and BrF_5 solvents at −30 °C according to equilibrium (3). The equilibria in both solvents were again monitored by ^{129}Xe, ^{19}F, and ^{14}N n.m.r. spectroscopy. In BrF_5, formation of 4-RC_5F_4N–$XeF^+AsF_6^-$ was more strongly favoured than in HF solvent; the equilibrium ratio [4-$RC_5F_4NXeF^+$]/[4-$RC_5F_4NH^+$] being 0.25 and 2.1 in HF and BrF_5 solvents, respectively, at −30 °C for R = F and 3.7 for R = CF_3 in BrF_5 at −50 °C [K_F = 4.5 at −30 °C and K_{CF_3} = 13.6 at −50 °C in BrF_5 for equilibrium (3)]. Consequently, removal of BrF_5 solvent under vacuum at −30 °C yielded white solids corresponding to 4-RC_5F_4N–$XeF^+AsF_6^-$ salts.

The Raman and n.m.r. spectroscopic findings confirm the formulations of the compounds isolated from BrF_5 solution as AsF_6^- salts possessing cation structures in which a xenon atom is co-ordinated to the aromatic perfluoropyridine ring (**6**), thus providing the first examples of compounds in which the

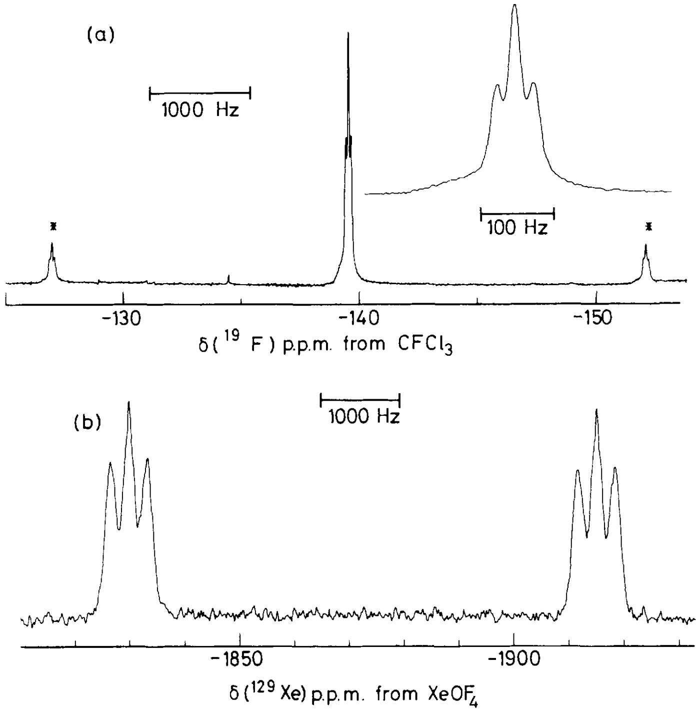


Figure 1. N.m.r. spectra of the $C_5F_5N–XeF^+$ cation at −30 °C; (a) the ^{19}F n.m.r. spectrum (235.361 MHz; solvent BrF_5) depicting the fluorine-on-xenon(II) region of the spectrum and ^{129}Xe satellites (denoted by asterisks) arising from spin–spin coupling of the terminal fluorine-on-xenon to natural abundance ^{129}Xe, $^1J(^{129}Xe–^{19}F)$ ($I = \frac{1}{2}$; 26.4%); the 1:2:1 triplet fine structure on the central line and the satellites is assigned to $^4J[F(1)–F(2)]$; (b) the ^{129}Xe n.m.r. spectrum (69.563 MHz; solvent HF) depicting the doublet arising from $^1J(^{129}Xe–^{19}F)$ and partially quadrupole collapsed 1:1:1 triplets arising from xenon directly bonded to the nitrogen of the pyridine ring, $^1J(^{129}Xe–^{14}N)$.

noble gas atoms serve as aromatic substituents. In addition to lines arising from the AsF_6^- anions [ν_1 (a_{1g}) 677, 680 cm^{-1}; ν_2(e_g) 577 cm^{-1}; ν_5(t_{2g}) 375 cm^{-1}], several key frequencies have been assigned. The Xe–N stretching frequencies can only be tentatively assigned to weak bands at 367(2) (R = F) and 367(12) (R = CF_3) cm^{-1} [*cf.* 422 cm^{-1} in $FXeN(SO_2F)_2$] while the F–Xe–N bends are assigned to moderately strong bands at 158(13) (R = F) and 162(13) (R = CF_3) cm^{-1}. The intense bands in the Raman spectra of the salts occur at 528(100) (R = F) and 524(100) cm^{-1} (R = CF_3) and are assigned to Xe–F stretching frequencies. These frequencies are higher than that of $FXe–N(SO_2F)_2$ (506 cm^{-1})[1] and lower than in the recently reported nitrile cations, $R'C{\equiv}N–XeF^+$ (564 and 565 cm^{-1} for R′ = H and Me, respectively),[6] reflecting the intermediate base strengths of $4\text{-}RC_5F_4N$: with respect to the Lewis acid XeF^+. The latter point is corroborated by comparison of the ^{129}Xe and ^{19}F chemical shifts of the Xe–F groups within a well established trend in which δ(^{19}F) increases in frequency with increasing covalency of the Xe–ligand bond, while δ(^{129}Xe) is observed to decrease. The nuclear spin–spin couplings $^1J(^{129}Xe–^{19}F)$ (doublet), $^1J(^{129}Xe–^{14}N)$ (partially quadrupole collapsed 1:1:1 triplet), and $^4J(F_1–F_2)$ (1:2:1 triplet) also support the proposed cation structures in solution (Figure 1). Owing to the higher viscosity of BrF_5, $^1J(^{129}Xe–^{14}N)$ is quadrupole collapsed at −50 and −30 °C but is observed in HF at −15 and −30 °C. The magnitude of $^1J(^{129}Xe–^{14}N)$ is consistent with a one-bond ^{129}Xe–^{14}N coupling.[1,3,5,6] On the assumption that the Fermi contact contribution to the ^{129}Xe–^{14}N spin–spin coupling is dominant, a comparison of the reduced coupling constants, $^1K(Xe–N)_F = 0.983 \times 10^{22}$ and $^1K(Xe–N)_{CF_3} = 0.991 \times 10^{22}$ N A^{-2} m^{-3}, with those in which the nitrogen atom σ-bonded to xenon is sp hybridized ($R'C{\equiv}N–XeF^+$ 1.297—1.393 × 10^{22} N A^{-2} m^{-3})[6] and sp^2 hybridized [$FXe–N(SO_2F)_2$ 0.913 × 10^{22}][1] is also consistent with bonding between the sp^2 hybridized nitrogens of the perfluoropyridines and xenon.

Other pyridine derivatives and nitrogen bases are currently being investigated as potential electron-pair donors towards noble gas cations. *X*-ray crystallographic studies of the fluoro(perfluoropyridine)xenon(II) cations are also underway in this laboratory.

This research was sponsored by the United States Air Force Astronautics Laboratory, Edwards Air Force Base, California (Contract F49620-87-C-0049) and by a Natural Sciences and Engineering Research Council of Canada (NSERCC) operating grant.

Received, 26th August 1987; Com. 1260

References

1 J. F. Sawyer, G. J. Schrobilgen, and S. J. Sutherland, *Inorg. Chem.*, 1982, **21**, 4064.

2 D. D. DesMarteau, R. D. LeBlond, S. F. Hossian, and D. Nothe, *J. Am. Chem. Soc.*, 1981, **103**, 7734.

3 G. A. Schumacher and G. J. Schrobilgen, *Inorg. Chem.*, 1983, **22**, 2178.

4 J. Foropoulos and D. D. DesMarteau, *J. Am. Chem. Soc.*, 1982, **104**, 4260.

5 R. Faggiani, D. K. Kennepohl, C. J. L. Lock, and G. J. Schrobilgen, *Inorg. Chem.*, 1986, **25**, 563.

6 A. A. A. Emara and G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.*, 1987, 1644.