modes should give rise to very intense, sharp Raman bands with weak infrared counterparts, with the strongest Raman band representing the in-phase motion. The slight splitting observed for the 947-cm[-1] Raman band does not show the right (3:1) intensity ratio for the [35]Cl-[37]Cl isotopes and, hence, is ascribed to crystal effects.

After assigning the ClO$_3$ modes, four bands in the region 450–750 cm^{-1} remain unassigned. Based on their frequencies, these bands must represent the four skeletal stretching modes. Of the four bands the two lower frequency ones do not show a counterpart in the infrared spectrum and, therefore, must be assigned to the two A modes which do not involve a change of the dipole moment (see Table III). Based on its higher Raman intensity and lower frequency the 450-cm[-1] band is assigned to ν_{sym}(BrOCl) in phase which involves more of a Br–O stretch than a Cl–O stretch. For the two higher frequencies we prefer to assign the 720-cm[-1] band to the antisymmetric BrOCl motion based on its strong infrared intensity and large bandwidth. The two components of the 633-cm[-1] band show the correct intensity ratio of 3:1 for [35]Cl and [37]Cl isotopes and, hence, this splitting is ascribed to isotope effects.

In summary, the observed spectrum is in excellent agreement with our predictions for a covalent, monodentate perchlorato structure containing a strongly coupled and, there-fore, approximately linear OBrO configuration.[15] Except for the torsional modes and the BrO$_2$ and BrOCl in plane deformations (which are expected to be of relatively low frequency and intensity) all of the predicted fundamentals were observed. For the stretching vibrations, the strong coupling causes pronounced frequency splittings owing to in-phase and out-of-phase motions of the two ligands. For the ClO$_3$ deformation modes, such a splitting was not observed except for an 11-cm[-1] separation of the two rocking modes.

No attempts were made to compute a force field for Br-(OClO$_3$)$_2$[-] owing to the size (11 atoms) of the ion, the inavailability of the skeletal deformation frequencies, and an expected[5] strong mixing of the symmetry coordinates of the skeletal stretching modes.

(15) Quantitative computations have been carried out for M–O–M linkages containing a light central atom: I. R. Beattie and M. J. Gall, *J. Chem. Soc. A*, 3569 (1971). Qualitatively, their arguments should also be valid for our case with Br as a central atom, where the observed frequency separation of the average of the BrOCl stretches of species B from that of the corresponding A modes is 216 cm^{-1}.

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Fluorine-19 Nuclear Magnetic Resonance Studies of Some Xenon(II) Compounds

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The ^{19}F nmr spectra of solutions of XeF$_2$, FXeSO$_3$F, and Xe(SO$_3$F)$_2$ in HF and HSO$_3$F and of solutions of the adducts XeF$_2$·AsF$_5$, XeF$_2$·SbF$_5$, and XeF$_2$·2SbF$_5$ in HSO$_3$F have been studied. Spectra were also obtained for solutions of XeF$_2$ in SbF$_5$ and SbF$_5$–HSO$_3$F and for the adduct 2XeF$_2$·AsF$_5$ in BrF$_5$. Fluorine-19 chemical shifts and [129]Xe–[19]F coupling constants for the species FXeSO$_3$F, Xe(SO$_3$F)$_2$, Xe$_2$F$_3$[+], and XeF[+] have been obtained from the results.

Introduction

Although ^{19}F nmr spectroscopy is in principle capable of providing useful information concerning the structure and bonding of fluorine compounds as well as an easy and convenient method for the identification of species in solution, there has been very little work published on the ^{19}F nmr spectra of xenon–fluorine compounds in solution.

The purpose of the present work was to make an extensive study of the ^{19}F nmr spectra of xenon–fluorine compounds with a view to obtaining further information on the nature of the species present in solution and on their nmr parameters.

The present paper is concerned with xenon(II) compounds. Apart from an early study of XeF$_2$ in HF[1] the only other published work on xenon(II) compounds is a report by Cohen and Peacock[2] of the ^{19}F nmr spectrum of a solution of XeF$_2$·2SbF$_5$ in SbF$_5$. These authors observed a single line due to fluorine on xenon accompanied by satellites arising from [129]Xe–[19]F coupling. The result was tentatively interpreted as indicating that the compound XeF$_2$·2SbF$_5$ had the structure F$_5$SbFXeFSbF$_5$. Since that time the compound has been shown by X-ray crystallography to have the structure FXeFSb$_2$F$_{10}$.[3] The structure consists essentially of XeF[+] and Sb$_2$F$_{11}$[-] ions which have a rather short anion–cation contact, indicating a rather strong fluorine bridge F–Xe- - -F–Sb with presumably considerable covalent character.

We report here the results of our studies of XeF$_2$, FXeSO$_3$F, Xe(SO$_3$F)$_2$, 2XeF$_2$·AsF$_5$, XeF$_2$·AsF$_5$, XeF$_2$·2SbF$_5$, and XeF$_2$·SbF$_5$ in the solvents HSO$_3$F, HF, SbF$_5$, and BrF$_5$.

Results and Discussion

Xenon(II) Fluorosulfates. Bartlett, *et al.*,[4] showed that when xenon difluoride is allowed to react with stoichiometric amounts of HSO$_3$F at −75°, the compounds FXeSO$_3$F and Xe(SO$_3$F)$_2$ are obtained. The crystal structure of FXeSO$_3$-F has been determined and was found to consist of covalent

(1) H. H. Hyman, Ed., "Noble-Gas Compounds," University of Chicago Press, Chicago, Ill., 1963; J. H. Holloway, "Noble-Gas Chemistry," Methuen, London, 1968.

(2) B. Cohen and R. D. Peacock, *J. Inorg. Nucl. Chem.*, **28**, 3056 (1966).

(3) V. M. McRae, R. D. Peacock, and D. R. Russel, *Chem. Commun.*, 62 (1969).

(4) N. Bartlett, M. Wechsberg, F. O. Sladky, P. A. Bulliner, G. R. Jones, and R. D. Burbank, *Chem. Commun.*, 703 (1969).

Table I. ^{19}F Nmr Parameters for XeF$_2$, FXe(SO$_3$F), and Xe(SO$_3$F)$_2$

| Solute[b] | Solvent | Temp, °C | Chem shift,[a] ppm | | | | | | | $J_{^{129}\text{Xe}-^{19}\text{F}}$, Hz | |
			Xe(SO$_3$F)$_2$	HSO$_3$F	FXeSO$_3$F	S$_2$O$_6$F$_2$	HF	FXeSO$_3$F	XeF$_2$	FXeSO$_3$F	XeF$_2$
Xe(SO$_3$F)$_2$	HSO$_3$F	−80	−42.6	−40.8							
Xe(SO$_3$F)$_2$[c]	HSO$_3$F	−80		−40.8		−39.1					
Xe(SO$_3$F)$_2$	Melt	52				−39.1					
FXeSO$_3$F	HSO$_3$F	−80	−42.6	−40.8	−40.2	−39.0	180.8	193.3		6025	
FXeSO$_3$F	Melt	40			−42.1	−39.0		172.1		5835	
XeF$_2$	HSO$_3$F	−80	−42.6	−40.8	−40.2	−39.0	181.7	192.4		6025	
Xe(SO$_3$F)$_2$	HF	−68		−37.7	−37.0		195.0	196.9		6025	
FXeSO$_3$F	HF	−68		−37.7	−37.0		195.0	196.9	199.9	6025	5665
XeF$_2$	HF	−68					195.4		199.6		5665
HF	HSO$_3$F	−76		−40.1			181.7				
HSO$_3$F	HF	−68		−37.6			194.3				

[a] From external CFCl$_3$.   *[b]* Approximately 1 *m*.   *[c]* After 3 hr at room temperature.

molecules with linear F–Xe–O bonds.[4,5]   We have found that these compounds may be conveniently prepared by the reaction of XeF$_2$ with HSO$_3$F in HF solvent. No nmr data on these compounds have been previously reported. We have obtained spectra of solutions of both compounds in hydrogen fluoride and fluorosulfuric acid. The results of these measurements are summarized in Table I.

When the monofluorosulfate FXeSO$_3$F is dissolved in HSO$_3$F by briefly warming to ∼−40°, the nmr spectrum at −80° has a peak, A, with accompanying satellites in the F-on-Xe region, which may be attributed to the FXeSO$_3$F molecule (Figure 1a). Two peaks were observed in addition to the HSO$_3$F solvent peak, D, in the F-on-S region of the spectrum. The weaker of the two peaks, A, had a chemical shift of −40.2 ppm and may be attributed to the SO$_3$F group in the FXeSO$_3$F molecule while a stronger peak, C, at −42.6 ppm is assigned to Xe(SO$_3$F)$_2$. The Xe(SO$_3$F)$_2$ peak clearly arises from the reaction of FXeSO$_3$F with another mole of HSO$_3$F according to eq 1. The resonance due to HF, peak

$$\text{FXeSO}_3\text{F} + \text{HSO}_3\text{F} \rightarrow \text{Xe(SO}_3\text{F)}_2 + \text{HF} \qquad (1)$$
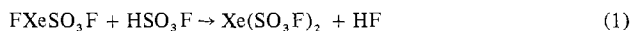
B, was also observed and occurs at 180.8 ppm. Warming of the solution to room temperature resulted in the further decomposition of FXeSO$_3$F and the appearance of a peak E due to S$_2$O$_6$F$_2$ (Figure 1b–d). Peroxysulfuryl difluoride presumably arises from the decomposition of Xe(SO$_3$F)$_2$ according to eq 2. The monofluorosulfate, FXeSO$_3$F, is

$$\text{Xe(SO}_3\text{F)}_2 \rightarrow \text{Xe} + \text{S}_2\text{O}_6\text{F}_2 \qquad (2)$$

considerably more stable than Xe(SO$_3$F)$_2$, and the molten compound at 40° had the expected nmr spectrum with a peak in the F-on-S region at −42.1 ppm.

The peak assignments for Xe(SO$_3$F)$_2$ and S$_2$O$_6$F$_2$ were confirmed by dissolving Xe(SO$_3$F)$_2$ in HSO$_3$F at −80° and recording the nmr spectrum. In addition to the solvent peak, a single peak in the F-on-S region at −40.2 ppm was observed which may be attributed to the fluorine of the SO$_3$F group. On allowing the solution to warm up to room temperature, this signal disappeared after 3 hr and was replaced by a signal at −39.1 ppm due to S$_2$O$_6$F$_2$. When the solid is melted, the same decomposition occurs and the nmr spectrum of the resulting liquid consists only of the single line due to S$_2$O$_6$F$_2$. It is clear that Xe(SO$_3$F)$_2$ is unstable in HSO$_3$F solution at room temperature and in the molten state and decomposes according to eq 2.

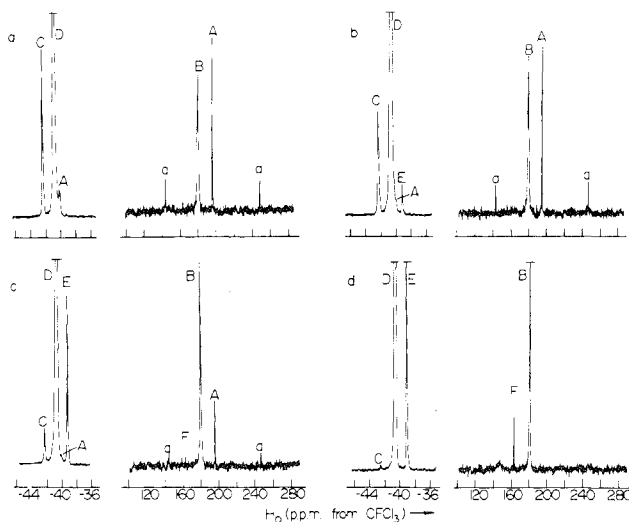When XeF$_2$ is dissolved in HSO$_3$F and the solution allowed to warm briefly to room temperature, it reacts to give a

Figure 1. ^{19}F nmr spectrum of a solution of FXeSO$_3$F (∼0.5 *m*) in HSO$_3$F solvent. Spectra were recorded at −80° in a glass tube: (a) initial spectrum; after warming to 25° for (b) 0.33 hr, (c) 3.33 hr, and (d) 6.34 hr. Peak assignments: (A) FXeSO$_3$F and (a) ^{129}Xe satellites; (B) HF; (C) Xe(SO$_3$F)$_2$; (D) HSO$_3$F solvent; (E) S$_2$O$_6$F$_2$; (F) SiF$_4$.

mixture of FXeSO$_3$F and Xe(SO$_3$F)$_2$ as shown by the nmr spectrum.

On dissolving Xe(SO$_3$F)$_2$ or FXeSO$_3$F in excess HF the nmr spectra at −68° showed that reaction occurs to give a mixture of FXeSO$_3$F and XeF$_2$ (Table I). It is clear that reaction 1 above is reversible.

Adducts of XeF$_2$ with Pentafluorides. A variety of adducts with pentafluorides have been prepared and found to have the stoichiometries 2XeF$_2$·MF$_5$, XeF$_2$·MF$_5$, and XeF$_2$·2MF$_5$.[1,6]   The adduct XeF$_2$·2SbF$_5$ has been shown by X-ray crystallography[3] to have the structure FXe$^+$--·FSb$_2$-F$_{10}$$^-$ and the adduct 2XeF$_2$·AsF$_5$ to have the structure Xe$_2$-F$_3$$^+AsF_6$$^-$.[7]   Raman spectral studies of a number of adducts with other pentafluorides show that they have similar structures and they also show that the 1:1 adducts have the structure FXe$^+$--·FMF$_5$$^-$.[6]   The adducts of XeF$_2$ with SbF$_5$ and AsF$_5$ were found to be too insoluble in HF at low temperatures to enable ^{19}F nmr spectra to be obtained but they were, however, found to have reasonable solubilities in fluorosulfuric acid.

The XeF$_2$·2SbF$_5$ adduct (*i.e.*, XeF$^+$Sb$_2$F$_{11}$$^-$) gave a spec-

(5) N. Bartlett, M. Wechsberg, G. R. Jones, and R. D. Burbank, *Inorg. Chem.*, **11**, 1124 (1972).

(6) F. O. Sladky, P. A. Bulliner, and N. Bartlett, *J. Chem. Soc. A*, 2179 (1969).

(7) F. O. Sladky, P. A. Bulliner, N. Bartlett, B. G. DeBoer, and A. Zalkin, *Chem. Commun.*, 1048 (1968).

Table II. ^{19}F Nmr Parameters for the XeF$^+$ and Xe$_2$F$_3$$^+$ Cations

Solute (molal concn)	Solvent^a	Temp, °C	Chem shift,^{b} ppm		J^{129}Xe–^{19}F, Hz	J_{FF}, Hz
XeF$^+$SbF$_6$$^-$ (0.70)	HSO$_3$F	−93	{XeF$^+$	242.5	6620	
			SbF$_6$$^-$	123.2		
XeF$^+$AsF$_6$$^-$ (0.46)	HSO$_3$F	−96	{XeF$^+$	243.8	6615	
			AsF$_6$$^-$	64.4		
XeF$_2$^{c} (1.57)	SbF$_5$	26	{XeF$^+$	291.9	7210	
			Sb$_n$F$_{5n+1}$$^-$–SbF$_5$	115.1		
XeF$_2$^{d} (0.34)	SbF$_5$	26	{XeF$^+$	289.8	7210	
			Sb$_n$F$_{5n+1}$$^-$–SbF$_5$	111.1		
Xe$_2$F$_3$$^+AsF_6$$^-$ (0.67)	BrF$_5$	−62	{Xe$_2$F$_3$$^+$ {A	184.7	4865	308
			{X$_2$	252.0	6740	
			AsF$_6$$^-$	61.8		

^{a} HSO$_3$F, −40.8 ppm; BrF$_5$, −272.8 (F$_a$) and −134.3 (F$_e$) ppm, J_{FF} = 75.2 Hz. ^{b} With respect to external CFCl$_3$. ^{c} Bright yellow solution. ^{d} Green solution.

trum in HSO$_3$F solvent which had a single line due to SbF$_6$$^-$ in the fluorine-on-antimony region of the spectrum, a doublet–quintet pattern resulting from the anion SbF$_5$SO$_3$F$^-$, a high-field quintet, a doublet of doublets, and a broad low-field peak which have previously been assigned to the Sb$_2$F$_{11}$$^-$ anion.[8,9] It is clear that the compound XeF$^+$Sb$_2$F$_{11}$$^-$ dissolves in HSO$_3$F to give the Sb$_2$F$_{11}$$^-$ anion which undergoes partial solvolysis according to the equation

$$Sb_2F_{11}^- + 2HSO_3F \rightleftharpoons SbF_6^- + SbF_5SO_3F^- + H_2SO_3F^+ \quad (3)$$
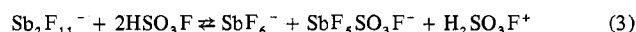
A single peak at 245.5 ppm from CFCl$_3$ accompanied by ^{129}Xe satellites was observed in the fluorine-on-xenon(II) region of the spectrum. This single fluorine resonance may reasonably be attributed to the XeF$^+$ cation. The low-temperature spectra of solutions of the XeF$_2$·AsF$_5$ and XeF$_2$·SbF$_5$ adducts (*i.e.*, XeF$^+$MF$_6$$^-$) in HSO$_3$F had the same resonance that we have attributed to XeF$^+$ together with broad lines due to AsF$_6$$^-$ and SbF$_6$$^-$ (Table II).

A solution of XeF$_2$ in SbF$_5$ solvent at room temperature gave a spectrum consisting of a single broad resonance due to (SbF$_5$)$_n$ and Sb$_n$F$_{5n+1}$$^-$ undergoing fluorine exchange and a single line with accompanying satellites which may be assigned to XeF$^+$ (Table II). At −20°, the spectrum of the solvent separated into the three peaks that have previously been observed for SbF$_5$.[10] The chemical shift and ^{129}Xe–^{19}F coupling constant for the peak attributed to XeF$^+$, however, differ considerably from the values observed in HSO$_3$F solution. In order to study this further, nmr spectra were recorded for solutions of XeF$_2$ in mixtures of SbF$_5$ and HSO$_3$F covering the whole composition range. It may be seen from Table III that there is a continuous change in the chemical shift of the XeF$^+$ ion from that observed in HSO$_3$-F to that observed in SbF$_5$ as solvent. It seems clear that the XeF$^+$ ion interacts rather strongly with the medium; in other words, it is strongly solvated, presumably by forming a single additional bond with the most basic and, hence, strongest donor molecule available. In solutions of XeF$^+$-SbF$_6$$^-$ and XeF$^+$Sb$_2$F$_{11}$$^-$ in fluorosulfuric acid, this is presumed to be the fluorosulfuric acid molecule. As the concentration of SbF$_5$ is increased, the fluorosulfuric acid solvent is presumably replaced by the anions Sb$_2$F$_{11}$$^-$ and SbF$_5$SO$_3$F$^-$ which are, in turn, replaced by the more weakly basic larger polymeric anions Sb$_n$F$_{5n+1}$$^-$. As the XeF$^+$ cation becomes more weakly bonded to the less basic accompanying anions, its chemical shift and the ^{129}Xe–^{19}F coupling constant both increase.

Table III. Variation of ^{19}F Chemical Shift and ^{129}Xe–^{19}F Coupling Constant for the XeF$^+$ Ion with Solvent Composition

[XeF$^+$], m	Mole ratio SbF$_5$:HSO$_3$F	Chem shift, ppm	J^{129}Xe–^{19}F, Hz
~1^a	0.00	245.5	6710
0.57	0.11	245.2	6710
0.86	0.17	245.8	6710
0.33	1.02	249.5	6730
0.58	1.50	256.9	6860
0.27	2.17	273.0	7035
0.47	3.53	284.0	7140
0.88	SbF$_5$	290.2	7230

^{a} XeF$^+$Sb$_2$F$_{11}$$^-$ dissolved in HSO$_3$F.

The Xe$_2$F$_3$$^+$ cation is of particular interest since it contains a bridging fluorine atom. The ^{19}F nmr spectrum of Xe$_2$F$_3$$^+$ cannot be obtained in HSO$_3$F solution as it is immediately decomposed; its reaction with HSO$_3$F will be discussed in a subsequent paper.[11] The complex 2XeF$_2$·AsF$_5$, however, was found to give a stable solution in BrF$_5$ and the low-temperature ^{19}F nmr spectrum shows that the solution contains the Xe$_2$F$_3$$^+$ cation. In addition to the single broad line due to AsF$_6$$^-$ and the AX$_4$ spectrum of the solvent, the Xe$_2$-F$_3$$^+$ spectrum, which is shown in Figure 2, consists of an AM$_2$ pattern arising from species I overlapped by an AM$_2$X pattern arising from species II. The AM$_2$X$_2$ spectrum of species III was too weak to observe because of the low concentration of this species.
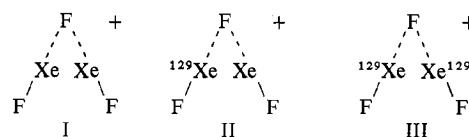
The areas of the various peaks are in good agreement with the values expected on the basis of the natural abundance of ^{129}Xe (26.24%). The chemical shifts and coupling constants derived from the spectra are summarized in Table II. The fluorine–fluorine coupling constant (308 Hz) is the largest so far observed in any xenon species, the other values being 174 Hz for XeF$_3$$^+$,[12] 176 Hz for XeF$_5$$^+$,[13,14] and 103 Hz for XeOF$_3$$^+$.[13] The fluorine–fluorine coupling constant of the recently characterized krypton analog, Kr$_2$F$_3$$^+$, is also large and has a similar value (351 Hz).[15] The large difference

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(9) J. Bacon, P. A. W. Dean, and R. J. Gillespie, *Can. J. Chem.*, 47, 1655 (1969).
(10) J. Bacon, P. A. W. Dean, and R. J. Gillespie, *Can. J. Chem.*, 48, 3413 (1970).

(11) R. J. Gillespie and G. J. Schrobilgen, *Inorg. Chem.*, in press.
(12) R. J. Gillespie, B. Landa, and G. J. Schrobilgen, *Chem. Commun.*, 1543 (1971).
(13) R. J. Gillespie, B. Landa, and G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.*, 607 (1972).
(14) R. J. Gillespie and G. J. Schrobilgen, *Inorg. Chem.*, 13, 765 (1974).
(15) R. J. Gillespie and G. J. Schrobilgen, *J. Chem. Soc., Chem. Commun.*, 90 (1974).

Table IV. Correlations among the ^{19}F Nmr Parameters, Xe-F Bond Distances, and Xe-F Stretching Frequencies

Species	Solvent	Chem shift, ppm	$J^{129}Xe^{-19}F$, Hz	r_{Xe-F},[a] A	ν_{Xe-F}, cm^{-1}
$(FXe)_2F^+$	BrF_5	184.7	4865	2.14	409[a]
XeF_2	HF	199.6	5665	2.01	526[a]
$FXeSO_3F$	HF	196.9	6025	1.94	533[a]
	HSO_3F	193.3	6025		
$(FXe)_2SO_3F^+$ [b]	BrF_5	221.9	6470		568
$(FXe)_2F^+$	BrF_5	252.0	6740	1.90	593[a]
XeF^+	HSO_3F	245.5	6710	1.84	619[a]
	SbF_5	290.2	7230		

[a] R. J. Gillespie and B. Landa, *Inorg. Chem.*, 12, 1383 (1973), and references therein. [b] Reference 12.
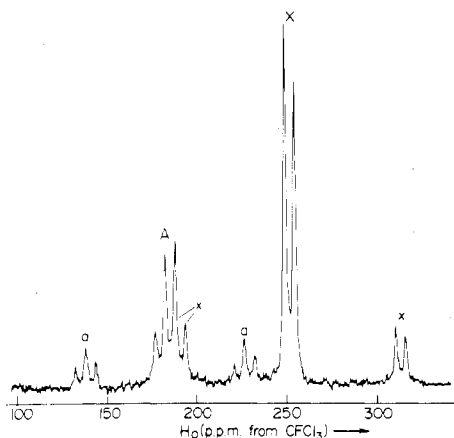
Figure 2. ^{19}F nmr spectrum of the $Xe_2F_3^+$ cation (0.67 m $Xe_2F_3^+$-AsF_6^-), recorded at $-62°$ in BrF_5 solvent: (A) bridging fluorine and (a) ^{129}Xe satellites; (X) terminal fluorines and (x) ^{129}Xe satellites.

between the values for $Xe_2F_3^+$ and $Kr_2F_3^+$ and those for the other cations may reasonably be associated with the fact that the F-Ng-F angle is ~180° in $Xe_2F_3^+$ and $Kr_2F_3^+$ but is only ~90° in the other cations.

Empirical Correlations. It may be seen in Table IV and Figure 3 that except for XeF_2 and the bridging fluorine of $Xe_2F_3^+$, there is a near-linear correlation between the ^{19}F chemical shift and the $^{129}Xe^{-19}F$ coupling constant. As the XeF group becomes more ionic, there is a continuous increase in the $^{129}Xe^{-19}F$ coupling constant and the ^{19}F chemical shift from the covalent $FXeSO_3F$ molecule through to the essentially "free" XeF^+ cation in SbF_5 solution. In the latter case, though, there is almost certainly some covalent interaction between XeF^+ and the $Sb_nF_{5n+1}^-$ anion (Table III). There are also good correlations among the $^{129}Xe^{-19}F$ coupling constant, the Xe-F bond length, and the Xe-F stretching frequency (Table IV). As the Xe-F bond length increases and the bond becomes more polar, the stretching frequency and the coupling constant both decrease.

Experimental Section

Materials. Xenon difluoride was prepared by mixing equimolar quantities of xenon (Matheson) and fluorine (Matheson) in a Pyrex vessel followed by exposure to ultraviolet radiation, according to the method described previously.[16] The XeF_2 obtained was checked for purity by recording the ^{19}F nmr spectrum in HF solution and the laser Raman spectrum on the solid.

Antimony pentafluoride (Ozark-Mahoning Co.) was purified by double distillation in an atmosphere of dry nitrogen using an all-glass apparatus and stored in glass vessels in a drybox.

Fluorosulfuric acid (Allied Chemical Co.)[17] and anhydrous hydrogen fluoride (Harshaw)[18] were purified by the standard literature methods.

(16) S. M. Williamson, *Inorg. Syn.*, 11, 67 (1968).
(17) J. Barr, R. J. Gillespie, and R. C. Thompson, *Inorg. Chem.*, 3, 1149 (1964).
(18) R. J. Gillespie and D. A. Humphreys, *J. Chem. Soc. A*, 2311 (1970).
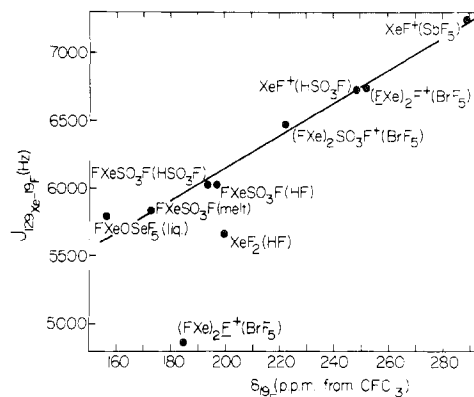
Figure 3. Correlation of the ^{19}F chemical shift ($\delta^{19}F$) and the ^{129}Xe-^{19}F coupling constant ($J^{129}Xe^{-19}F$) for some xenon(II) compounds.

Arsenic pentafluoride (Ozark-Mahoning Co.) was used without further purification.

Bromine pentafluoride (Matheson) was vacuum distilled into a Kel-F trap fitted with Teflon valves, and purified by passing fluorine at atmospheric pressure through the liquid until all the Br_2 and BrF_3 had reacted. After degassing several times, the BrF_5 was then vacuum distilled into a Kel-F storage trap containing dry sodium fluoride.

Sample Preparation. All manipulations were carried out under anhydrous conditions on a vacuum line constructed from Monel, Kel-F, and Teflon, or in a drybox. All preparative work was done in 15 cm × 2 cm o.d. Kel-F tubes (Argonne National Laboratory) equipped with Kel-F heads and Teflon valves.

Nmr samples were prepared and vacuum sealed in 5-mm o.d. medium-wall Pyrex nmr tubes or, in the case of HF samples, in Kel-F tubing. Kel-F sample tubes were sealed under vacuum by heating with a small electrical heating coil. Hydrogen fluoride and bromine pentafluoride samples were prepared by distilling an appropriate quantity of the solvent into a sample tube containing the solute. Fluorosulfuric acid and antimony pentafluoride samples were prepared in a drybox by syringing the solvent into a sample tube containing the solute. Owing to their reactivity with HSO_3F and HF solvents, samples involving $FXeSO_3F$ and $Xe(SO_3F)_2$ were prepared at liquid nitrogen temperature in these solvents, warmed to $-78°$ to effect solution and stored at $-78°$ until the spectra could be recorded. All sample concentrations were *ca.* 0.5 m unless indicated otherwise.

^{19}F **Nmr Spectra.** Fluorine nmr spectra were measured using a Varian DA-601 L spectrometer operating at 56.4 MHz and modified as described previously[19] to record spectra in the field sweep unlock mode. The spectra were calibrated by the usual audio side band method, using a Muirhead-Wigan D-890-A decade oscillator. Side band frequencies were checked with a General Radio Type 1191 frequency counter. Low-temperature spectra were obtained using a Varian V4540 temperature controller with the low-temperature probe. Fluorine chemical shifts were measured from external $CFCl_3$ by sample tube interchange.

Preparation of $XeF_2 \cdot SbF_5$ and $XeF_2 \cdot 2SbF_5$. A quantity of SbF_5 (*ca.* 10 mmol) was transferred to a Kel-F reaction vessel in a drybox. The required amount of XeF_2 was transferred to another Kel-F reaction vessel and dissolved in about 10 ml of HF at room temperature. The XeF_2-HF solution was transferred through an

(19) P. A. W. Dean and R. J. Gillespie, *J. Amer. Chem. Soc.*, 91, 7260 (1969).

evacuated Kel-F T piece onto the SbF₅ that had been cooled to −196°. The SbF₅-XeF₂-HF mixture was then warmed to and kept at room temperature for 5 min to ensure complete reaction. The mixture was then cooled to −64° and HF solvent removed under vacuum at this temperature.

Preparation of 2XeF₂·AsF₅ and XeF₂·AsF₅. A weighed amount of AsF₅ was distilled onto an XeF₂-HF mixture kept at −196° (*ca.* 10 mmol of XeF₂ in 10 ml of HF). The procedure was then exactly the same as for the preparation of the XeF₂-SbF₅ compounds.

Preparation of Xe(SO₃F)₂ and FXeSO₃F. Both compounds were prepared from HSO₃F and XeF₂ by the same procedure as was used for the XeF₂-SbF₅ compounds. Approximately 10 mmol of HSO₃F was used in each case. The products were stored under dry nitrogen at −78°.

Registry No. Xe(SO₃F)₂, 25523-77-7; FXeSO₃F, 25519-01-1; XeF₂, 13709-36-9; ¹²⁹Xe, 13965-99-6; XeF⁺SbF₆⁻, 30864-32-5; XeF⁺AsF₆⁻, 26024-71-5; Xe₂F₃⁺AsF₆⁻, 21308-45-2.

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# Cyclic Borane Derivatives of Amino Acids[1]

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New five- and six-member heterocycles which are formally cyclized amino acid boranes have been characterized as air-stable volatile solids. The markedly different hydrolysis rates for the two five-membered heterocycles is interpreted as arising from different mechanisms. The chemistry of the ring systems has been explored and new types of boranes have been synthesized, including cations and the novel strong base
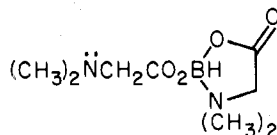

A study of the chemistry of the cyclic borane I was begun

I
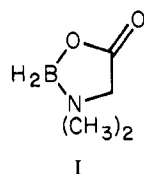
after it was isolated and characterized as an intermediate in the hydrolysis of (ethyl dimethylglycine)trimethylamine-boron(1+) cation.[2] New types of boranes and several new transformations have emerged from the study and these are described in two sections, one dealing with the parent hetero-cycles and the other with derivatives.

Heterocyclic Amino Acid Boranes

The heterocycle I may be considered to be the cyclized product by hydrogen loss of the borane adduct of *N,N*-dimethylglycine and as such would be the first in a potentially large new class of heterocycles derivable from amino acids. Three parent homologous cyclic systems with dimethylated nitrogens have now been made, related to glycine, 2-amino-isobutyric acid, and 3-aminopropionic acid, compounds I-III.

II   III
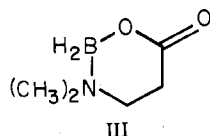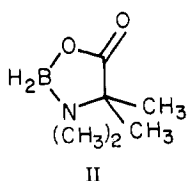
These three are white crystalline materials, sublimable with-out decomposition near 100° under high vacuum. Char-acterizations by analysis, molecular weight, ir, nmr, and mass spectral patterns are given in the experimental details and Tables I-III. The cyclic structures are supported by the mass spectral molecular weight (P − 1 peaks), volatility, and solu-tion molecular weight (for I). While some puckering of the ring in III might be expected, there is no nmr evidence for it. *N*-CH₃ resonance is a singlet down to −30°, explicable by planar or rapidly inverting configurations.

The methylenic protons of I are sufficiently acidic to undergo rapid exchange in D₂O solution when mildly basic as shown by the collapse of the methylene proton nmr singlet in aqueous trimethylamine. This exchange was substantiated as reversible by isolation of the deuterated material and re-converting it to the normal hydrogen compound. The time scale for the nmr signal collapse was about 4 min at 37° in 10% aqueous trimethylamine, corresponding approximately to a half-life of 0.5 min. It is remarkable that the cyclization by borane can enhance the methylenic protons of dimethyl-glycine from no exchange in 1 *M* hydroxide[3] to that ob-served for I. Inductive effect of the borane normally re-leases electrons and decreases acidity; consequently, an ex-planation must be found elsewhere, perhaps in solvation and π-bonding stabilizations of the anion of I produced by proton abstraction.

The acid nature of the methylenic protons in I was employed in the first synthesis of II wherein excess sodium hydride was slurried with a solution of methyl iodide and I in dimethylformamide (eq 1). Because the product was free

(1) Presented in part at the 8th Midwest Regional Meeting of the American Chemical Society, Columbia, Mo., Nov 8-10, 1972.
(2) N. E. Miller, *J. Amer. Chem. Soc.*, 92, 4564 (1970).

(3) W. E. Thompson, R. J. Warren, I. B. Eisdorfer, and J. E. Zaremba, *J. Pharm. Sci.*, 55, 857 (1966).