Fluoro[imidobis(sulphuryl fluoride)]xenon. An Example of a Xenon–Nitrogen Bond

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Summary The reaction of xenon difluoride with imidobis(sulphuryl fluoride) in dichlorodifluoromethane at 0° yields the new compound, fluoro[imidobis(sulphuryl fluoride)]xenon, $FXeN(SO_2F)_2$, the first example of xenon bonded to an element other than oxygen or fluorine under ordinary laboratory conditions.

Previously reported compounds of xenon contain either xenon–fluorine or xenon–oxygen bonds. While a variety of xenon(II) compounds has been obtained by substitution reactions of xenon difluoride,[1] all these contain the substituent bound to xenon through oxygen. In order to form reasonably stable xenon compounds of this type, a primary requirement is that the substituent should have a high group electronegativity and be resistant to degradative fluorination and oxidation. We have been exploring the possibility of forming xenon compounds with xenon bonded to an element other than oxygen or fluorine, and we chose the $N(SO_2F)_2$ group as a likely substituent in forming such a compound, and now report the synthesis of $FXeN(SO_2F)_2$, which contains a xenon–nitrogen bond.

Reaction of $HN(SO_2F)_2$,[2] and XeF_2 in CF_2Cl_2 at 0° forms HF and $FXeN(SO_2F)_2$ in high yield. In a typical reaction, XeF_2 (2·66 mmol) is transferred into the bottom of 7 ml Kel-F tube reactor, followed by $HN(SO_2F)_2$ (1·18 mmol), which is condensed on the upper walls of the reactor. CF_2Cl_2, sufficient to cover the $HN(SO_2F)_2$, is then added and the mixture is maintained at 0° for 4 days. The long reaction time is necessary since neither reactant is very soluble in CF_2Cl_2 and both are solids at 0°. Thus the

Table

Raman spectra of $XN(SO_2F)_2$ derivatives[a]

$HN(SO_2F)_2$	$CsN(SO_2F)_2$	$FXeN(SO_2F)_2$
292 (70)	295 (43·0	110 (27·4
335 (100)	333 (14·0)	130 (27·4)
378 (6)	361 (54·2)	180 (5·8)
388 (6)	438 (5·6)	214 (45·1)
417 (6)	463 (22·4)	338 (3·5)
460 (32)	488 (14·0)	474 (0·6)
485 (22)	525 (10·0)	504 (100
528 (40)	568 (18·7)	554 (0·5)
560 (24)	587 (9·3)	582 (0·4)
578 (6)	730 (75·7)	655 (3·7)
639 (15)	745 (30·8)	798 (2·6)
813 (90)	777 (5·6)	825 (2·2)
839 (10)	842 (22·4	880 (3·8)
914 (6)	1170 (7·5)	1223 (10·0)
1217 (12)	1218 (100·0)	1428 (2·4)
1242 (90)	1360 (21·5)	1450 (4·6)
1350 (4)	1395 (13·1)	
1462 (6)	1428 (11·2)	
1474 (8)		

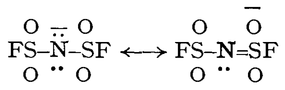
[a] Values in cm^{-1} with most intense band given an intensity of 100; relative intensities in parentheses.

reaction proceeds only slowly, but this is a prime requirement in obtaining good yields. Reaction in the absence of CF_2Cl_2 or using HF or $CFCl_3$ as solvents, does not form the compound in appreciable yield. After reaction is complete, as judged by the disappearance of solid $HN(SO_2F)_2$, CF_2Cl_2 and HF are removed *in vacuo* at 0°. If the HF and CF_2Cl_2 are not removed together, considerable decomposition will occur as the HF concentration is effectively increased. The white solid product is then kept under high vacuum at 22° for 30 min to yield 1·05 mmol of purified product (89·5%).

Hydrolysis of $FXeN(SO_2F)_2$ yields the theoretical amount of xenon and quantitative thermal decomposition at 70° follows equation (1). The stability of $FXeN(SO_2F)_2$ is

$$2FXeN(SO_2F)_2 \rightarrow Xe + XeF_2 + [N(SO_2F)_2]_2$$

similar to that of $FXeOSO_2F$ and the formation of $[N(SO_2F)_2]_2$[3] upon decomposition is analogous to the formation of $S_2O_6F_2$ from $FXeOSO_2F$. The Raman spectrum of $FXeN(SO_2F)_2$ (Table) is very similar to that of $CsN(SO_2F)_2$ and $HN(SO_2F)_2$ except for a very intense band at 504 cm^{-1}, readily assignable to $\nu(XeF)$. The low value for this vibration,[4] and also shifts in the N–S and S–F region compared to $CsN(SO_2F)_2$, indicate that there is considerable covalent interaction between FXe^+ and $N(SO_2F)_2^-$. The possibility of xenon–oxygen bonding due to resonance structures of the type (A) and (B) is discounted owing to the simplicity of the observed S=O vibrations and their similarity to those in covalent $XN(SO_2F)_2$ derivatives [X=H, Cl, $N(SO_2F)_2$[2]]. If oxygen bonding were involved, a unique $\nu(S=O)$ somewhere between the antisymmetric and symmetric $\nu(S=O)$ frequencies of a typical covalent $XN(SO_2F_2)$ derivative would be expected.



$$\overset{O}{\underset{O}{FS}}-\overset{-}{\underset{\cdot\cdot}{\ddot{N}}}-\overset{O}{\underset{O}{SF}} \longleftrightarrow \overset{O}{\underset{O}{FS}}-\underset{\cdot\cdot}{N}=\overset{\overline{O}}{\underset{O}{SF}}$$

(A) (B)

The ^{19}F n.m.r. spectrum of $FXeN(SO_2F)_2$ in BrF_5 at $-40°$ consists of two 3-line multiplets each having intensities of *ca.* 1:6:1, with relative areas of 1·0:2·06. One at δ 127 (external $CFCl_3$) is assigned to FXe– with the characteristic large ^{129}Xe–F coupling of 5600 Hz. The other, at δ $-57·7$, is assigned to $-XeN(SO_2F)_2$ with ^{129}Xe–F coupling of 18 Hz. The latter is the first reported long range ^{129}Xe–F coupling and provides strong support for the presence of a xenon–nitrogen bond.

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