

reaction may, therefore, result from the oxidation of HCOOH, which would be produced in the course of reactions, because the reaction of $[4\text{-Fe}]^{2-}$ with excess HCOOH in an aqueous suspension of pH 7.0 at room temperature has evolved a stoichiometric amount of CO_2 (based on $[4\text{-Fe}]^{2-}$) for 4 h. This result suggests that the $[4\text{-Fe}]^{2-}$ cluster is a possible model compound to formate dehydrogenases.²⁴

Acetonitrile was similarly reduced in an aqueous suspension²⁵ of $[4\text{-Fe}]^{4-}$ or $[\text{Mo-Fe}]^{5-}$ formed electrochemically at pH 7.0 to produce C_2H_6 , C_2H_4 (0.1 or 0.05 to C_2H_4), and NH_3 . The amount of NH_3 produced in the reaction was 95% or 96% of the number of total moles of C_2H_6 and C_2H_4 , and no $\text{C}_2\text{H}_5\text{NH}_2$ has been detected in the reaction systems. In addition, $[4\text{-Fe}]^{4-}$ and $[\text{Mo-Fe}]^{5-}$ were completely inactive to the reduction of $\text{C}_2\text{H}_5\text{NH}_2$ under the same conditions. These results indicate that the reduction of CH_3CN in the present reaction does not proceed by a stepwise mechanism, which requires two electrons in each step and should produce $\text{C}_2\text{H}_5\text{NH}_2$ as an intermediate.

Registry No. CH_3NC , 593-75-9; $[4\text{-Fe}]^{4-}$, 66213-39-6; $[4\text{-Fe}]^{3-}$, 52627-89-1; $[\text{Mo-Fe}]^{5-}$, 76125-83-2.

(24) Thauer, R. K.; Fuchs, G.; Jungerman, K. "Iron-Sulfur Proteins"; Academic Press: New York, 1977; Vol. III, p 121.

(25) $[4\text{-Fe}]^{2-}$ (39 μmol) or $[\text{Mo-Fe}]^{3-}$ (34 μmol) was dispersed as fine particles by adding a CH_3CN (2 cm^3) solution of the cluster to H_2O .

Bis[bis(trifluoromethanesulfonyl)imido]xenon: A New Compound Possessing Xenon-Nitrogen Bonds

Jerry Foropoulos, Jr., and Darryl D. DesMarteau*¹

Department of Chemistry, Clemson University
Clemson, South Carolina 29631

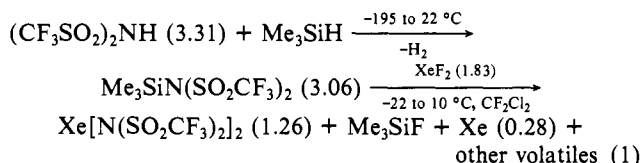
Received March 22, 1982

Since the first report of the synthesis of a stable xenon-nitrogen compound,² no other compound of this type has been successfully prepared with a different nitrogen ligand. Until now, only $\text{FXeN}(\text{SO}_2\text{F})_2$, $\text{Xe}[\text{N}(\text{SO}_2\text{F})_2]_2$, and $[(\text{FSO}_2)_2\text{NXe}]_2\text{F}^+\text{AsF}_6^-$ were known.^{3,4} In this communication, we report a new xenon-nitrogen compound utilizing a new ligand designed expressly for this purpose.

Reflection on the properties of the $\text{N}(\text{SO}_2\text{F})_2$ group led us to conclude that a likely ligand for formation of a bond to xenon would be $\text{N}(\text{SO}_2\text{CF}_3)_2$ from the bis(perfluoroalkylsulfonyl)imides, $\text{HN}(\text{SO}_2\text{R})_2$.⁵ Several examples of these were known, but the parent member of the series, $(\text{CF}_3\text{SO}_2)_2\text{NH}$, had not been isolated. This compound was of particular interest because of the obvious comparisons one can make with $(\text{FSO}_2)_2\text{NH}$ and the fact that the CF_3SO_2 group is probably the most electron-withdrawing group in chemistry. This acid was subsequently prepared by us^{6,7} and found to give a xenon-containing product upon reaction with XeF_2 . This product was postulated to be $\text{Xe}[\text{N}(\text{SO}_2\text{CF}_3)_2]_2$, but there were several problems in characterizing the material. The same xenon-containing species was observed regardless of initial reaction stoichiometry. Attempts at the synthesis of a 1:1 product only resulted in poorer yields of the postulated disubstituted compound. The best xenon analyses were only 80-90% of the expected values. The product always seemed to be contaminated

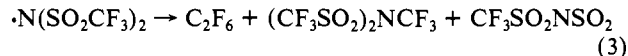
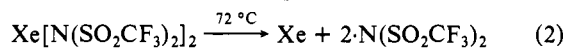
with the starting acid, and the best yields never exceeded 50%.

As an alternate approach to obtaining the pure compound, we investigated the use of a trimethylsilyl group to replace the acid proton. An expected advantage of this approach was the elimination of product HF, which was thought to be a major problem in promoting side reactions. Reaction of $(\text{CF}_3\text{SO}_2)_2\text{NH}$ with an excess of trimethylsilane afforded the appropriate reagent. Reaction of the silylimide with XeF_2 afforded the desired compound in high yield, as shown in the eq 1 (mmol).



The other products include unreacted XeF_2 and small amounts of N_2 , CF_4 , and SO_2 -containing materials. The yield of the xenon compound is 75% starting from the acid, including purification of the intermediate silyl compound via pumping under dynamic vacuum for 0.5 h at 22 $^\circ\text{C}$. The xenon product is purified by pumping under dynamic vacuum at 22 $^\circ\text{C}$ for 3 h. This illustrates the first successful use of a silyl derivative to form a bond to xenon. The reactivity can be compared to $\text{B}(\text{OTeF}_5)_3$ in the preparation of TeF_5O derivatives of xenon from xenon fluorides. The Si-N and B-O bonds have comparable reactivity and Me_3SiF and BF_3 are relatively innocuous byproducts.⁸

$\text{Xe}[\text{N}(\text{SO}_2\text{CF}_3)_2]_2$ is a fine white solid, stable at 22 $^\circ\text{C}$ under nitrogen or vacuum for several days without appreciable decomposition. A small sample exposed to the air decomposed after ~ 1 h. A quantitative xenon analysis for the formula $\text{Xe}[\text{N}(\text{SO}_2\text{CF}_3)_2]_2$ was realized after heating 0.327 g in a glass vessel to 72 $^\circ\text{C}$, at which point it cleanly and abruptly decomposed. The products obtained were xenon, C_2F_6 , a volatile solid and liquid, and a very small amount of a nonvolatile oil. The separation of the Xe from the C_2F_6 was difficult. Repeated transfers through a $-172 \text{ }^\circ\text{C}$ trap gave a xenon value greater than 95 mol%. Mass spectral analysis showed little C_2F_6 in the Xe but considerable Xe in the C_2F_6 , and the total Xe is nearer 99%. The volatile liquid was shown to be $(\text{CF}_3\text{SO}_2)_2\text{NCF}_3$ by its mass spectrum (CI, base m/e 350 amu) and its ^{19}F NMR. The volatile solid displays a singlet in the ^{19}F NMR, and its IR and mass spectrum indicate it is a form of the previously reported dimer $(\text{CF}_3\text{SO}_2\text{NSO}_2)_2$.⁹ No evidence was found for $[\text{N}(\text{SO}_2\text{CF}_3)_2]_2$, a theoretical product.³ These decomposition products are easily rationalized by eq 2 and 3. The instability of the $\cdot\text{N}(\text{SO}_2\text{CF}_3)_2$ radical compared to



$\cdot\text{N}(\text{SO}_2\text{F})_2$ ³ is surprising, but this has been confirmed by the photolysis of $\text{ClN}(\text{SO}_2\text{CF}_3)_2$ ⁷ which forms CF_3Cl and $\text{CF}_3\text{SO}_2\text{NSO}_2$ quantitatively.

The mass spectrum of $\text{Xe}[\text{N}(\text{SO}_2\text{CF}_3)_2]_2$ by direct solid inlet shows no parent ion or xenon-containing fragment other than xenon. Analysis of the products evolving from a gradually heated sample by direct gas inlet gave the parent ions of Xe, $\text{CF}_3\text{SO}_2\text{NSO}_2$, and $\text{CF}_3\text{N}(\text{SO}_2\text{CF}_3)_2$ along with the expected fragments as observed in independent spectra of each product.

The Raman spectrum clearly shows the bands of a covalent $(\text{CF}_3\text{SO}_2)_2\text{NX}$ group,¹⁰ with no evidence of XeF bonds. However, a band at 826 cm^{-1} is of surprising intensity relative to other covalent $(\text{CF}_3\text{SO}_2)_2\text{NX}$ derivatives.

(8) The use of $\text{B}(\text{OTeF}_5)_3$ with other xenon fluorides and oxyfluorides is known, as well as with other nonmetal fluorides: Lentz, D.; Seppelt, K. *Angew. Chem., Int. Ed. Engl.* **1978**, *5*, 356. Jacob, E.; Lentz, D.; Seppelt, K.; Simon, A. *Z. Anorg. Allg. Chem.* **1981**, *472*, 7.

(9) Roesky, J. W.; Aramaki, M.; Schonfelder, L. *Z. Naturforsch., B* **1978**, *338*, 1072.

(10) The Raman spectrum in general is very similar to other covalent $(\text{CF}_3\text{SO}_2)_2\text{NX}$ derivatives that we have made, including $(\text{CF}_3\text{SO}_2)_2\text{NH}$ and $(\text{CF}_3\text{SO}_2)_2\text{NCl}$ and dissimilar to ionic derivatives such as $\text{CsN}(\text{SO}_2\text{CF}_3)_2$.

(1) Work done at Kansas State University, Manhattan, KS 66506.

(2) LeBlond, R. D.; DesMarteau, D. D. *J. Chem. Soc., Chem. Commun.* **1974**, 555.

(3) DesMarteau, D. D.; LeBlond, R. D.; Hossain, S. F.; Nothe, D. *J. Am. Chem. Soc.* **1981**, *103*, 7734.

(4) The existence of an Xe-N bond in $\text{FXeN}(\text{SO}_2\text{F})_2$ has been confirmed by X-ray crystallography: Sawyer, J. F.; Schrobilgen, G. J.; Sutherland, S. J. *Chem. Commun.*, in press. Schrobilgen, G. J., private communication.

(5) Meussdorffer, J. N.; Niederprum, H. *Chem.-Ztg.* **1972**, *96*, 582.

(6) Foropoulos, J., Jr.; DesMarteau, D. D. 2nd Chemical Congress of the North American Continent, Las Vegas (San Francisco), Aug. 25-29, 1980, Abstract Fluo 14.

(7) Foropoulos, J., Jr.; DesMarteau, D. D., to be submitted for publication.

The ^{19}F NMR of the compound at $\sim 10^\circ\text{C}$ in SO_2ClF shows a single CF_3 peak at -73.42 ppm relative to external CFCl_3 . As the sample was warmed to 35°C , successive spectra showed a decrease in the signal for the xenon compound and a subsequent growth of two other singlets, one due to CF_3Cl (-28.27 ppm) and the other at -76.34 ppm. The latter does not correspond to previously observed decomposition products for the compound, and along with the CF_3Cl , this indicates a reaction with the solvent upon decomposition.

Further structural characterization of $\text{Xe}[\text{N}(\text{SO}_2\text{CF}_3)_2]_2$ to provide direct physical evidence for the xenon-nitrogen bond is in progress, and extension of this now reaction type to other systems is planned.

Acknowledgment is made to the National Science Foundation for the support of this research and to the NSF and the U.S. Army Research Office for funds to purchase the mass spectrometer.

Registry No. $\text{Xe}[\text{N}(\text{SO}_2\text{CF}_3)_2]_2$, 82113-64-2; $(\text{CF}_3\text{SO}_2)_2\text{NH}$, 82113-65-3; $\text{Me}_3\text{SiN}(\text{SO}_2\text{CF}_3)_2$, 82113-66-4; XeF_2 , 13709-36-9.

Drastic Fluorescence Enhancement of Cyanine Dyes Bound to Synthetic Bilayer Membranes. Its High Sensitivity to the Chemical Structure and the Physical State of the Membrane¹

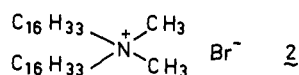
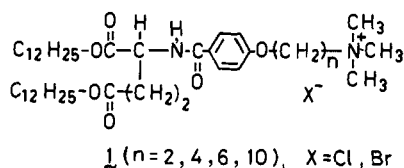
N. Nakashima and T. Kunitake*

Department of Organic Synthesis
Faculty of Engineering, Kyushu University
Fukuoka 812, Japan

Received February 22, 1982

We describe herein that the fluorescence intensity of cyanine dyes is markedly enhanced by binding to synthetic bilayer membranes and that the enhancement is strongly affected by the chemical structure and fluidity of the membrane. Cyanine dyes have been known as sensitizers in the photographic process.² Recent attempts to use these dyes as probes for the physical state and the membrane potential of liposomes and interfacial monolayers³⁻⁵ and as chromophores in organic solar cells⁶ and dye lasers⁷ called for widespread attention to their fluorescence behavior.

Dialkylammonium amphiphiles **1** and **2** produce stable bilayer



aggregates (vesicles and lamellae) upon dispersion in water by sonication.⁸⁻¹¹ These bilayer membranes possess physicochemical

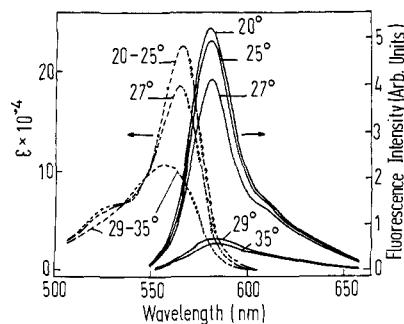


Figure 1. Absorption (dotted line) and fluorescence (solid line) spectra of cyanine dye **3** bound to aqueous bilayer **1**, $n = 4$ ($\text{X} = \text{Cl}$; $[\mathbf{1}] = 2 \times 10^{-3}$ M, $[\mathbf{3}] = 5 \times 10^{-7}$ M).

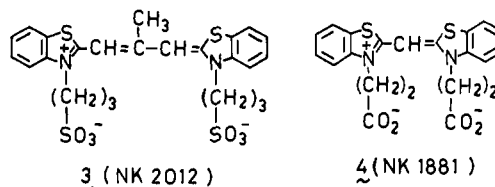
Table I. Quantum Yield of Cyanine Dye **3** in Various Media

media	Φ_F		P , (20°C)
	20°C	35°C	
1 , $n = 2$, ($\text{X} = \text{Br}$)	0.40		0.47
1 , $n = 4$, ($\text{X} = \text{Cl}$) ^a	0.64	0.08	0.47
1 , $n = 6$, ($\text{X} = \text{Br}$)	0.60		0.47
1 , $n = 10$, ($\text{X} = \text{Br}$)	0.64		0.46
2	0.063	0.047	0.43
CTAC	0.035	0.019	0.39
water	~ 0.0025	~ 0.0018	0.40
methanol	~ 0.0024	~ 0.0017	0.39
glycerol	0.24		0.47

^a Φ_F is almost the same when Cl is replaced by Br.

characteristics common to those of biolipid bilayers such as the crystal-to-liquid crystal phase transition.¹²

Figure 1 shows absorption and fluorescence spectra of cyanine dye **3** bound to aqueous bilayers of **1** ($n = 4$) (counterion, Cl^-).¹³



The molar ratio of the dye and the membrane is 1:4000, and self-quenching of fluorescence is not observed in this range. Both the absorption and fluorescence spectra show remarkable temperature dependence. Although the absorption spectrum is not sensitive to temperature at 20 – 25°C with λ_{max} at 565 nm (ϵ_{max} 220 000), its intensity diminishes drastically at 27 – 29°C , becoming constant again at 30 – 35°C (λ_{max} 555 nm, ϵ_{max} 110 000). In contrast, the spectrum is virtually invariable in the whole temperature range in methanol (λ_{max} 542 nm), in water (λ_{max} 541 nm), and in aqueous cetyltrimethylammonium chloride (CTAC) micelles (λ_{max} 565 nm). These results are to be discussed elsewhere in terms of organization of dye molecules at the membrane surface.¹⁴

The fluorescence spectrum shows temperature dependence similar to that of the absorption spectrum in that a drastic intensity change is observed at 27 – 29°C . The fluorescence intensity, I_F , in the low-temperature range is ca. 8 times larger than that in

- (1) Contribution No. 658 from the Department of Organic Synthesis.
- (2) Helz, A. H. *Adv. Colloid Interface Sci.* **1977**, *8*, 237–298.
- (3) Onuki, K.; Kurihara, K.; Toyoshima, Y.; Sukigara, M. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1914–1917.
- (4) Möbius, D. *Acc. Chem. Res.* **1981**, *14*, 63–68.
- (5) Waggoner, A. S.; Grinvald, A. *Ann. N.Y. Acad. Sci.* **1977**, *303*, 217–241.
- (6) Morel, D. L. *Mol. Cryst. Liq. Cryst.* **1979**, *50*, 127–138.
- (7) Schäfer, F. P., Ed.; "Dye Lasers"; Springer-Verlag: Berlin, 1973.
- (8) Kunitake, T.; Okahata, Y. *J. Am. Chem. Soc.* **1977**, *99*, 3860.
- (9) Okahata, Y.; Ihara, H.; Kunitake, T. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2072–2078.
- (10) Kunitake, T.; Nakashima, N.; Shimomura, H.; Okahata, Y.; Kano, K.; Ogawa, T. *J. Am. Chem. Soc.* **1980**, *102*, 6642–6644.
- (11) Nakashima, N.; Fukushima, H.; Kunitake, T. *Chem. Lett.* **1981**, 1207–1210, 1555–1558.

(12) Okahata, Y.; Ando, R.; Kunitake, T. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 789–798.

(13) Aqueous solutions of cyanine dyes (5.0×10^{-7} M, purchased from Nippon Kanko-shikiso Co.), were added to aqueous bilayer aggregates (2.0×10^{-3} M) and subjected to aging at 20°C for 20 min. The absorption spectra were obtained with a Hitachi 200 spectrophotometer. Fluorescence spectra were obtained with a Hitachi 650-10S spectrofluorimeter and corrected by using *m*-(dimethylamino)nitrobenzene as reference. The excitation wavelength (545 nm) was set at the isobestic point of the absorption spectra. The measurement was done in the air. Virtually the same fluorescence intensity was observed when O_2 -saturated or N_2 -saturated solutions were used.

(14) Nakashima, N.; Kunitake, T. *J. Chem. Soc., Chem. Commun.*, in press.