limited process at 8°K. Evidence to support this view was obtained from experiments involving photolysis during deposition under identical matrix conditions. In these cases, slower deposition rates and longer photolysis times (5–8 hr) were necessary to produce appreciable amounts of FNO. After deposition, a controlled warm up of the matrix to 21°K, followed by subsequent cooling to 8°K, produced a dramatic relative increase of the NOF isomer. Since both F atoms, and to some extent NO molecules, are known to be mobile species in a cryogenic matrix,[19-21] it is suggested that their enhanced diffusion at 21°K in the absence of photolytic radiation results in greater relative yields of the NOF isomer.

The absence of the intense ir fundamentals of F_3NO, except slight traces at the higher F_2:NO ratios, suggests that postulated species such as F_2NO[22] are not present in any appreciable concentration under the experimental conditions employed. This observation, in addition to the appearance of the three infrared absorptions at 1886.6, 735.1, and 492.2 cm^{-1} (Ar matrix) in highly dilute matrices at low F_2:NO ratios, lends further credence to the postulated existence of nitrogen hypofluorite, NOF.

Acknowledgment. One of us (R. R. S.) would like to extend his gratitude to the National Research Council for support of this research under the auspices of a NRC–NRL Resident Research Associateship.

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A Novel and Versatile Fluorescence Probe for the Structure of Micelles. 11-[3-Hexyl-1-indolyl]undecyltrimethylammonium Bromide

Sir:

Fluorescent probes have been elegantly employed to map the microenvironments of biological macromolecules such as proteins and the polynucleotides[1] and to clock the dynamics of intramolecular interactions.[2] The general idea behind a fluorescent probe is that fluorescence emission is sensitive to changes in microenvironments and that a fluorescence probe in different microenvironments will display experimentally distinct fluorescence properties which will characterize uniquely each environment. Recently, fluorescence probes have been used to help understand the properties of aqueous solutions containing micelle forming detergents.[3] These latter studies have mainly utilized aromatic hydrocarbons which are assumed to remain locked into the micelle during the time period of fluorescence. More recently it has been shown that the time correlated single photon counting technique allows a simultaneous measure of a fluorescence in both aqueous and micellar environments.[4] We report here a new system, 11-[3-hexyl-1-indolyl]undecyltrimethylammonium bromide (6-I-11),[5] which shows exceptional potential as a fluorescence probe to study the properties of micellar solutions.

The fluorescence properties of indoles have been found to be highly sensitive to environment changes.[6] For example, in dilute aqueous solution, 1,3-dimethylindole (**1**) displays a broad featureless fluorescence (BWHM) $\simeq$ 66 nm, λ_{max}^{F,H_2O} 371 nm),[7] and an exponential fluorescence decay[8] with a 20 nsec lifetime.

In *n*-hexane solution, however, **1** displays a somewhat structured, narrower fluorescence ($\lambda_{max}^{F,n\text{-hexane}}$ 318 nm) and an exponential fluorescence decay with a 4 nsec lifetime. The absorption spectrum of **1** is *essentially identical* in water or *n*-hexane but mirrors the *n*-hexane fluorescence emission spectrum. Thus, one might anticipate that 1,3-dialkylindole could make powerful fluorescence probes to differentiate hydrophilic *vs.* hydrophobic environments.[9]

Dissolution of **1** in aqueous solutions of hexadecyltrimethylammonium bromide (**2**) does not affect the fluorescence characteristics of **1** (relative to those in pure water) until the critical micelle concentration (cmc) of **2** is reached. At concentrations of **2** above the cmc, the fluorescence maximum of **1** starts to shift from 371 nm (pure water value) to 355 nm and the fluorescence lifetime of **1** drops from 20 nsec (pure water value) to 9 nsec. Since the latter decay is strictly exponential, and both the fluorescence maximum of **1** and the fluorescence decay of **1** are intermediate relative to the values obtained in pure water or pure *n*-hexane,

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(5) 6-I-11 was synthesized by acylation of indolemagnesium bromide with hexanoyl chloride, followed by reduction to 3-hexylindole and alkylation of the potassium salt with 11-bromoundecanol. This alcohol was converted *via* the bromide to the desired detergent.
(6) M. Walker, T. Bednar, and R. Lumry, *J. Chem. Phys.*, **47**, 1020 (1967); R. W. Ricci, *Photochem. Photobiol.*, **12**, 67 (1970); M. S. Walker, T. W. Bednar, and F. Humphries, *ibid.*, **14**, 147 (1971); E. P. Busel, T. L. Bushueva, and E. A. Burshtein, *Opt. Spectrosc. (USSR)*, **32**, 158 (1972); T. R. Hopkins and R. Lumry, *Photochem. Photobiol.*, **15**, 555 (1972).
(7) Measurements were made in distilled water on a Hitachi-Perkin-Elmer MPF-2A spectrofluorimeter; excitation wavelength was 280 nm. Values are ± 1 nm.
(8) A single photon counting technique was used as described in W. Ware's "Creation and Detection of the Excited State," A. Lamola, Ed., Marcel Dekker, New York, N. Y., 1971. Error limits ± 1 nsec.
(9) Tryptophan fluorescence has been used previously as an indication of its environment in proteins: see J. W. Longworth, "Excited States of Proteins and Nucleic Acids," R. F. Steiner and I. Weinryb, Ed., Plenum Press, New York, N. Y., 1971, p 364 ff; S. V. Konev, "Fluorescence and Phosphorescence of Proteins and Nucleic Acids," Plenum Press, New York, N. Y., 1967, p 9; J. Eisinger and G. Navon, *J. Chem. Phys.*, **50**, 2069 (1969).

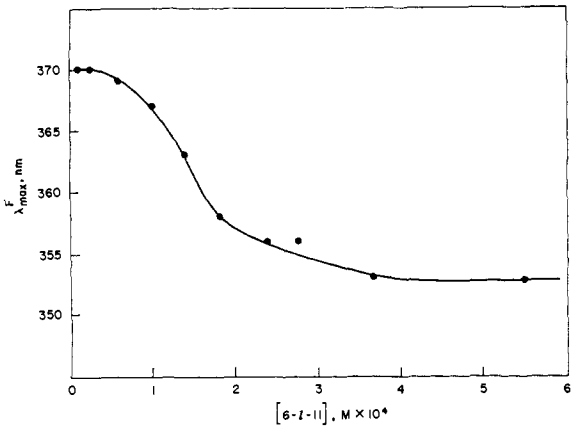

Figure 1. Variation in fluorescence λ_{max} of aqueous 6-I-11 with concentration.

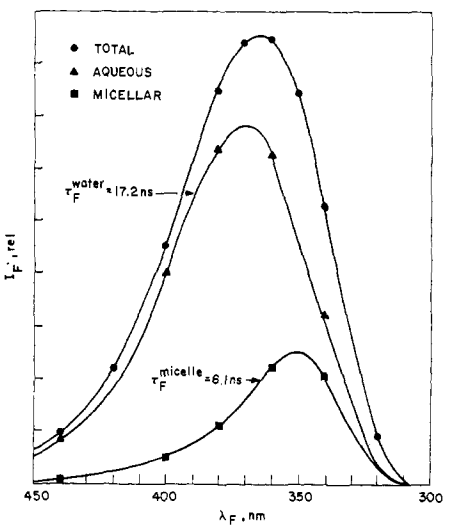

Figure 2. Components of 6-I-11 fluorescence spectrum generated by time-resolved spectroscopy using single photon counting at 1.36×10^{-4} *M*.

we conclude that **1** is either solubilized at the micelle–water interface or is rapidly transferring from the micellar interior to the bulk aqueous solution. The likelihood of the former possibility is suggested by previous measurements of naphthalene[4] solubilized in micelles of **2**. As a result of the lack of desired environmental information available from **1**, a strategy was designed to cause deeper penetration of an indole fluorophore into the micellar interior. To this effect 6-I-11 was synthesized.[5] This substance has a cmc of $\simeq 1.5 \times 10^{-4}$ *M*, as determined by standard laser light scattering experiments.[10]

Figure 1 shows that λ_{max}^{F,H_2O} of 6-I-11 depends strongly on concentration and that a shift occurs on passing from an aqueous to a less polar environment. The inflection point of Figure 2 ($\lambda_{max}^{F} \simeq 360$ nm) occurs at $\simeq 1.5 \times 10^{-4}$ *M*, coinciding with the cmc of the detergent which was independently determined. The fluorescence spectral shift upon micellization of 6-I-11 makes time-resolved spectroscopy possible through analysis of fluorescence decay as a function of wavelength. Point-by-

(10) We thank Mr. John Gether for determining this cmc value. For a related application of this technique, see S. H. C. Liu, R. K. Dewan, V. A. Bloomfield, and C. V. Moor, *Biochemistry*, **10**, 4788 (1971).

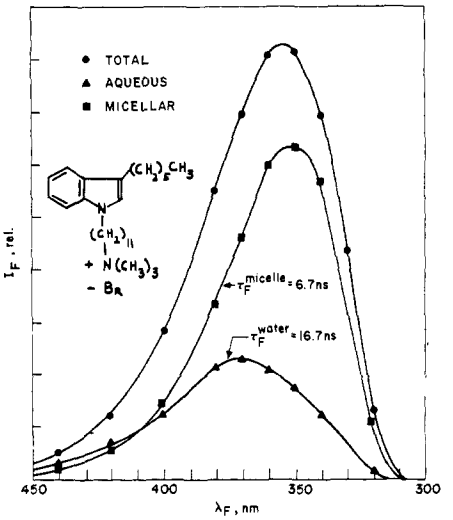

Figure 3. Components of 6-I-11 fluorescence spectrum generated by time-resolved spectroscopy using single photon counting at 4.15×10^{-4} *M*.

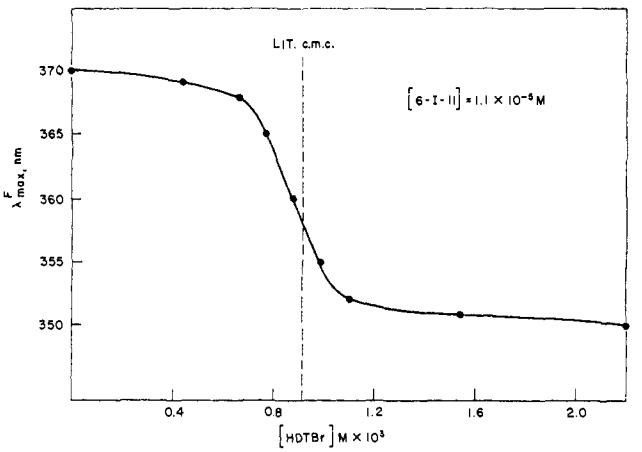

Figure 4. Variations in fluorescence λ_{max} of 6-I-11 in aqueous solution containing various concentrations of hexadecyltrimethylammonium bromide (**2**).

point fluorescence spectra were generated at several concentrations of 6-I-11 (Figures 2 and 3). The micellar component of the emission has $\lambda_{max}^{F} \simeq 350$ nm and $\tau_F \simeq 6$–7 nsec while the aqueous component has $\lambda_{max}^{F} \simeq 370$ nm and $\tau_F \simeq 17$ nsec, in accord with the data in Figure 1.

The aforementioned spectral shift can also be used to determine the cmc of a host detergent. The dependence of λ_{max}^{F} on the concentration of **2** is shown in Figure 4. The inflection point occurs at [**2**] = 8.8×10^{-4} *M* (lit. cmc[11] of **2** is 9.2×10^{-4}). Thus indole-containing probes may be useful in determining cmc values that are difficult to determine by more conventional methods.

In summary, the indole detergent **1** displays distinct fluorescence properties depending on whether it is present in a bulk aqueous environment or a micellar environment (Figure 5). Apparently, on the time scale of the measurement (tens of nanoseconds) the rate of exchange of **1** between the two environments is slow.

(11) P. Mukerjee and K. J. Mysels, "Critical Micelle Concentration of Aqueous Surfactant Systems," National Bureau of Standards NSRDS-NBS 36, Washington, D. C., 1971.

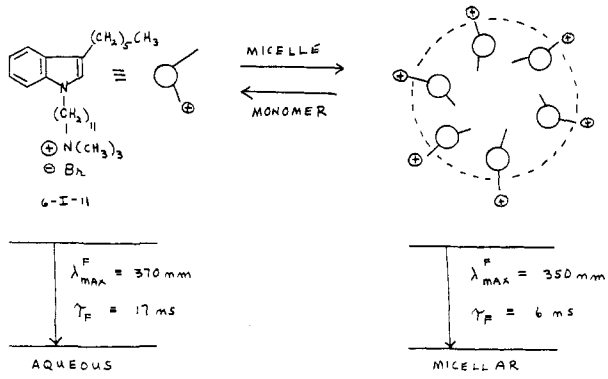

Figure 5. Schematic description of the behavior of **1** in aqueous and micellar environments.

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(12) N. I. H. Predoctoral Fellow 1970–1973.

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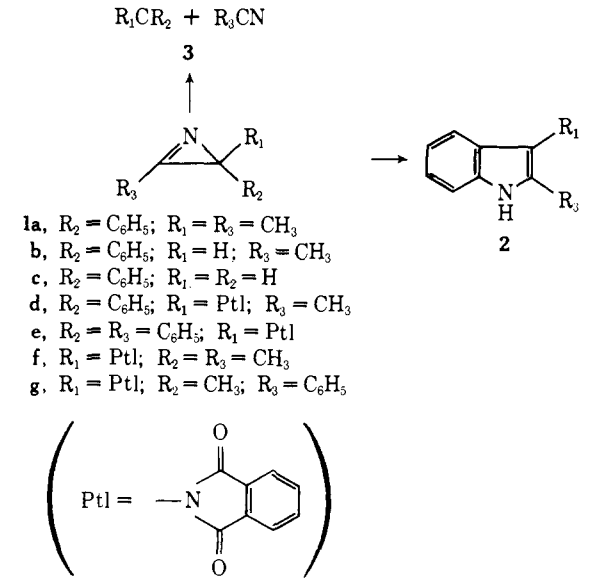
Carbon-Carbon Bond Cleavage and Iminocarbene Formation in the Thermal Decomposition of 2*H*-Azirines

Sir:

Products formed on thermal decomposition of 2*H*-azirines (**1**) appear always to involve C–N rather than C–C bond cleavage.[1] In some cases (*e.g.*, **1f, 1g**)[1a,b] this leads ultimately to fragmentation *via* carbene **3** and in other cases (*e.g.*, **1b–1e**) to indole (**2**)[1a,d] or pyrrole[1e] formation (Scheme I). We now wish to report the discovery of C–C bond cleavage in the thermolysis of 2*H*-azirines and the formation of products previously unobserved in both thermal[1] and photochemical[2] azirine decompositions. We also present an explanation for the dependence of decomposition pathway upon substitution.

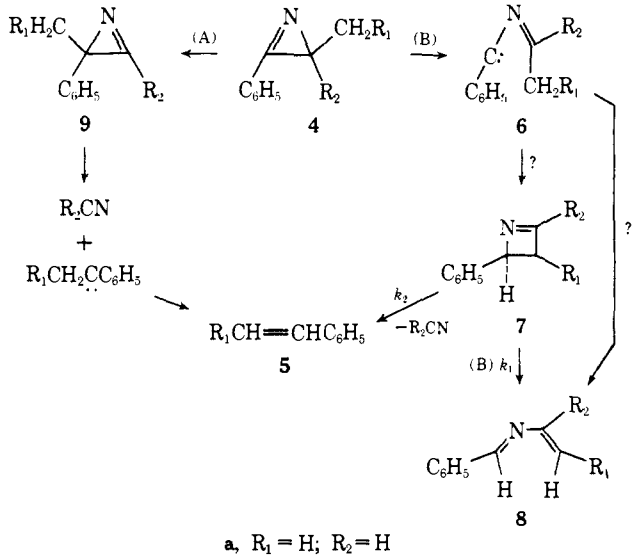
Scheme I



1a, $R_2 = C_6H_5$; $R_1 = R_3 = CH_3$
b, $R_2 = C_6H_5$; $R_1 = H$; $R_3 = CH_3$
c, $R_2 = C_6H_5$; $R_1 = R_2 = H$
d, $R_2 = C_6H_5$; $R_1 = Ptl$; $R_3 = CH_3$
e, $R_2 = R_3 = C_6H_5$; $R_1 = Ptl$
f, $R_1 = Ptl$; $R_2 = R_3 = CH_3$
g, $R_1 = Ptl$; $R_2 = CH_3$; $R_3 = C_6H_5$

2-Phenyl-3-methyl-2*H*-azirine[3] (**4a**), when subjected to flow pyrolysis in the gas phase at 565° and 1 atmosphere pressure of helium (contact time ~10 sec), gave only 2% fragmentation to benzonitrile.[1a] Rather, the major products were *styrene* (**5a**, 56% isolated yield), a reddish polymer, and (we presume) HCN. Similarly, 2-phenyl-3-ethyl-2*H*-azirine[3] (**4b**) gave only 2% benzonitrile but 42% *cis*- and *trans*-β-methylstyrene (**5b**). Formation of these products requires bonding, at some point in the reaction, between C-2 of the azirine ring and the carbon attached to C-3. However, neither of the two most obvious mechanisms for achieving this (paths A and B illustrated in Scheme II) is particularly satisfying: (a) 1,3-shift (path A) is

Scheme II



a, $R_1 = H$; $R_2 = H$
b, $R_1 = CH_3$; $R_2 = H$
c, $R_1 = H$; $R_2 = CH_3$

unprecedented in unsaturated three-membered rings; (b) hydrogen transfer in carbene **6** (path B, leading directly to **8**) should be much more favorable[4] than C–H

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