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(9) We wish to thank Dr. R. L. Foltz of Battelle Columbus Laboratories for obtaining the CI–MS measurements for us.

(10) The generation of highly acidic localized sites in an electrolysis is an experimental possibility which should always be taken into consideration.

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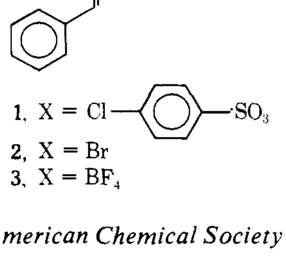
Medium Effects on Photochemical Reactions. Photochemistry of Surfactant Alkyl-4-stilbazole Salts in Solution, in the Solid State, and in Monolayer Assemblies

Sir:

A recent interest in these laboratories has been the photochemistry of surfactant molecules in different media. Since many of these compounds may be readily incorporated into monolayers, our attention has been directed toward employing the oriented, semirigid environment of monolayer assemblies to direct or modify their photochemistry.[1] In the present communication we report an investigation on the photochemistry of the *p*-chlorobenzensulfonate (**1**), bromide (**2**), and tetrafluoroborate (**3**) salts of *N*-octadecyl-*trans*-4-stilbazole.[2] These results indicate that environment can play a major role in determining photoreactivity[4] and suggest that the amphipathic nature of these molecules may modify their solution or solid-state behavior relative to nonsurfactant analogs.



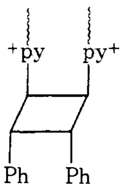
1, X = Cl–C_6H_4–SO_3

2, X = Br

3, X = BF_4

Although essentially insoluble in aliphatic hydrocarbons (hexane and hexadecane) and water, **1**–**3** were moderately soluble in polar organic solvents. Acetonitrile solutions of these salts exhibit a long-wavelength absorption maximum at 345 nm (ϵ 23,600) and a weak fluorescence with a maximum at 430 nm. The photochemistry of **1**–**3** in acetonitrile solution is unexceptional and is well-represented by that of **1**. Irradiation of acetonitrile solutions of **1** at 366 nm results in trans → cis isomerization and, eventually, establishment of a photostationary state. Upon prolonged irradiation of very dilute nondegassed solutions, slow disappearance of **1**, primarily due to cyclization, can be observed. By comparison, the properties of **1** are quite different from those of **2** and **3** in the solid state. Although excitation spectra are not significantly different, solid samples of **1** exhibit broad, intense yellow-green fluorescence with λ_{max} at 470 nm while solid samples of **2** and **3** fluoresce blue with λ_{max} at 430 nm. Irradiation (G.E. reflector flood lamp through 2 cm of H_2O and a Corning 0-52 filter) of 0.2 g of **1** spread on a watch glass for 8 hr led to essentially quantitative conversion of the starting material to a white solid product. In contrast, **2** and **3** were recovered unchanged after irradiation under identical conditions.

The solid state photoproduct of **1** can be isolated in up to 70% yield by recrystallization from 2-propanol. The uv spectrum (CH_3OH) exhibits maxima at 257 and 223 nm, and the formerly vinylic protons of **1** appear at δ 5.01 (br "d") and 4.75 (br "d") in the NMR ($CDCl_3$) of the product. Irradiation of the solid photoproduct at 254 nm reversibly regenerates the yellow-green fluorescence of **1**, consistent with a photodimer structure.[6] Thus, the most reasonable assignments of the resonances at 5.01 and 4.75 are to cyclobutane ring protons adjacent to pyridinium and phenyl, respectively, in a *trans*-**1** + *trans*-**1** photodimer. Of the four possible dimers **4**–**7**, **5** and **6** could be obtained as viscous oils by bisalkylation of the corresponding 4-stilbazole dimers[7] with octadecyl *p*-chlorobenzenesulfonate. The cyclobutane ring protons of the trans-cis-trans dimer **5** appeared as a broad unresolved 4 H resonance centered as δ 4.97. In contrast, the corresponding protons of the trans-trans-trans dimer **6** appear at δ 4.18 (br "d", 2 H) and 3.96 (br "d", 2 H), an upfield shift compatible with the pseudoequatorial disposition of the four aromatic rings.[9] These results clearly point to **4** as the structure of the solid state photoproduct of **1**.



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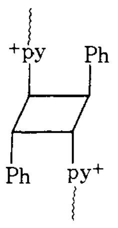

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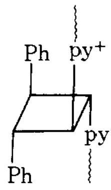

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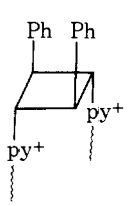

7

Both stilbazole salts **1** and **2** form monolayers and, in mixtures with tripalmitin (TP), may be incorporated into monolayer assemblies by the usual techniques.[10] Assemblies incorporating **1** or **2** have a long-wavelength absorption maximum (345 nm) comparable to that in solution, but the band is quite broad on the long-wavelength side, tailing well out past 430 nm. Analogous to the solid state of **1**, these assemblies exhibit a green fluorescence with a maximum at about 490 nm. In contrast to the solid state, the photoreac-

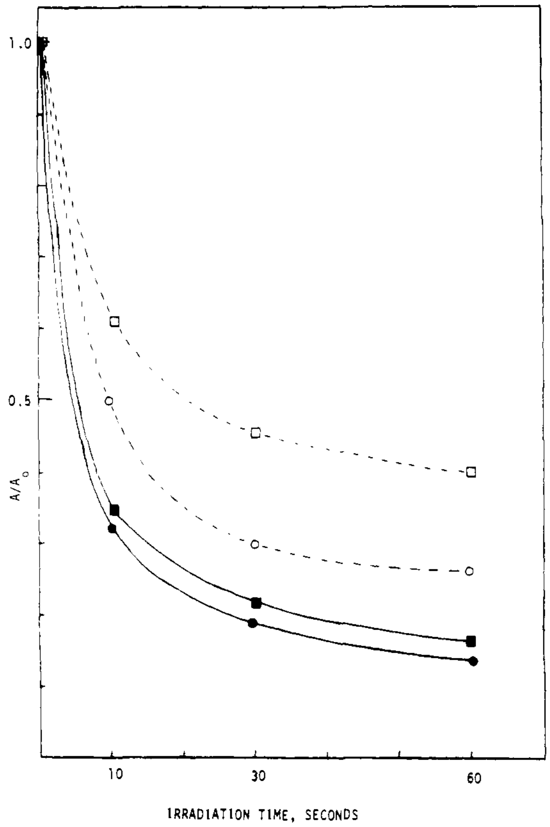

Figure 1. Plot of A/A_0 vs. irradiation time for monolayer assemblies of **1** with TP and arachidic acid: [●] six adjacent layers of **1**:TP in a 1:4 ratio; [■] six adjacent layers of **1**:TP, 1:4; [○] six layers of **1**:TP, 1:4 alternating with layers of pure TP; [□] six layers of **1** :TP, 1:8 alternating with layers of pure TP.

tivity of both **1** and **2** is comparable in the assemblies. Irradiation of assemblies incorporating **1** or **2** at 366 nm results in a decrease in the long-wavelength absorption band and fluorescence and a concomitant increase in absorption at 265 nm. By analogy to the solid state photochemistry of **1**, we infer that the photoproduct in the assemblies is a dimer.[11] This is consistent with the observation that the rate and extent of disappearance of **1** decreases at higher TP:**1** ratios. In addition, the efficiency is decreased when layers containing **1** are alternated with layers of pure TP, implying that both intra- and interlayer dimerization are important (Figure 1).

In both the solid state and in the monolayer assemblies a red-shifted (green) fluorescence is present in those systems where photodimerization takes place; the fluorescence declines in intensity as the dimer builds up. In the monolayer assemblies residual blue (apparently monomer) fluorescence persists following the initial fast reaction. These observations suggest that the green fluorescence may be due to an excimer intermediate in the photodimerization. However, the possibility that the formation of the emissive "excimer" state[12] and dimerization are competitive rather than sequential processes cannot be excluded. In contrast to the above, no solution photodimerization or excimer emission could be observed in saturated solutions of **1** (ca. 0.008 *M*) in acetonitrile; since shorter chain 4-stilbazole salts photodimerize in solution,[13] the apparent effect of the long chains is to inhibit association in solution. Although a number of polar aromatic molecules and salts of heteroaromatics are known to photodimerize in the solid state,[6] the dimers formed are almost invariably of the head-to-tail structure analogous to **5**, reflecting perhaps a minimization of steric and like-charge repulsions. In fact 2-stilbazole methiodide photodimerizes quantitatively in the solid state to yield such a product.[7,14] In contrast, the sole photodimer of **1** in the solid state has the head-to-head structure **4**; this result suggests that in the solid state preferential association of hydrophobic groups may be important enough to offset unfavorable like-charge interactions in the hydrophilic zones. This result suggests that incorporation of an orienting hydrophobic group could lead to useful directing effects on solid state photodimerization and addition reactions. We are currently exploring this possibility with several systems.

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(2) **1** and **2** were prepared by alkylation of 4-stilbazole with octadecyl-*p*-chlorobenzene sulfonate[3] and octadecyl bromide, respectively. Treatment of **2** with $AgBF_4$ provided **3**. Elemental analyses indicated that **1** was a monohydrate and that **2** and **3** were unhydrated.
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(6) W. J. Tomlinson, E. A. Chandross, R. L. Fork, C. A. Pryde, and A. A. Lamola, *Appl. Opt.*, **11**, 533 (1972).
(7) Irradiation of 4-stilbazole (1 g/100 ml) in 0.1 *M* HCl gave predominently (ca. 80%) the head-to-tail dimer corresponding to **5** as described by Abernethy.[8] In addition, a second dimer (ca. 10–15%), mp 196–196.5°, could be isolated. The dimer is assigned the structure analogous to **6** on the basis of its NMR spectrum (cyclobutane protons at δ 3.71) and the presence of a significant diazaphenanthrane peak (*m/e* 180.0711, 46%; calcd for $C_{12}H_8N_2$, 180.0687) in the mass spectrum.
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(11) The amount of photoproduct generated in the monolayer assemblies is too small to permit characterization of the dimer by other than uv spectroscopic techniques. For example a typical ten-layer assembly of **1**:TP (1:2) contains ca. 4×10^{-9} mol of **1**.
(12) The data do not allow distinction between a discrete excimer state or a more delocalized aggregate or excitonic state as a source of the red-shifted emission.
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(14) J. L. R. Williams, *J. Org. Chem.*, **25**, 1839 (1960).
(15) Alfred P. Sloan Foundation Fellow.

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Aromatic Hydroxylation by Peroxydisulfate

Sir:

Although the oxidation and cleavage of aromatic side chains by peroxydisulfate (usually in the presence of transition metal ions) is well known,[1-3] as far as we are aware, the Elbs reaction (hydroxylation of phenols in alkaline medium) provides the only example in which hydroxyl groups are efficiently introduced into the aromatic ring.[4] Oxidation of aromatics by Fenton's reagent (Fe^{2+}-H_2O_2) has also been reported to give solely side-chain oxidation of a number of aromatics,[2,3] but recently we have found that phenols