Photochemistry of a Surfactant Stilbene in Organized Media: A Probe for Hydrophobic Sites in Micelles, Vesicles, and Other Assemblies[1,2]

Sir:

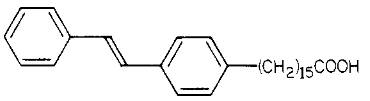
The rich array of photochemical and photophysical phenomena—cis–trans isomerization, photocyclization, cyclodimerization and addition, photoreduction and fluorescence—associated with stilbene and related 1,2-diarylethylenes has made these compounds among the most widely investigated of all organic chromophores.[3-8] Despite widespread investigation, there are still areas of controversy and uncertainty. One of the more striking features of stilbene photochemistry is its strong dependence on medium viscosity and temperature; the competition between fluorescence and trans → cis isomerization has been shown to be extremely sensitive to medium viscosity in an evidently well-understood fashion.[9-11]

An area of active investigation concerns the specific properties of the various microenvironments associated with organized media such as micelles, vesicles and liposomes, protein–lipid natural and synthetic membranes, and monolayer films and supported multilayers constructed therefrom. Much recent work has involved the use of probes whose properties in the medium can be monitored by various spectroscopic techniques to furnish a detailed picture of the medium microenvironment.[12-17] Although several studies using a variety of probes have undoubtedly furnished highly useful information, questions have been frequently raised concerning the likelihood that the specific properties of many probes tend to alter or create a special microenvironment such that the results obtained with different probes may be quite probe dependent. In recent work, we have been particularly interested in probing the microenvironment of the hydrophobic regions of various organized assemblies.[18-20] The stilbene chromophore appeared to be an attractive probe since it is a more or less linear hydrocarbon which should be both hydrophobic and relatively compatible in size and shape with the extended hydrocarbon chains of linear saturated hydrocarbons, fatty acids in phospholipids. Earlier work by Turro,[21] in fact, involved studies of *trans*-stilbene fluorescence in dipalmitoyllecithin vesicles; in these investigations, it was found that there was a substantial effect on the fluorescence intensity and its temperature dependence above and below the phase transition temperature, T_c. Although these studies clearly indicated the sensitivity of the stilbene chromophore as a probe for organized media, the precise site of the stilbene chromophore in these vesicles could not be determined. In the present manuscript, we report results of a study of the fluorescence and photoisomerization behavior of the surfactant stilbene **1** in a number of different media. Our preliminary results suggest that **1** and other similar surfactant stilbenes can in fact be highly sensitive probes for the microenvironment in a variety of different organized media and especially for vesicles and other bilayer structures.

Table I. Quantum Yields and Decay Factors for Photoreaction of Surfactant *trans*-Stilbene **1** in Different Media

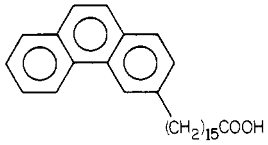
medium	temp, °C	$\phi_{t\rightarrow c}$	ϕ_f	R
CH_2Cl_2	22	0.50 ± 0.02	0.04	0.52
CTAB[a]	22	0.39 ± 0.02	0.18	0.48
DDAB[b]	22	0.38 ± 0.01	0.23	0.49
	0	0.28 ± 0.01	0.32	0.41
DCP/Lec[c]	22	0.38 ± 0.02	0.23	0.49
	0	0.28 ± 0.01	0.35	0.43
DDAB/DCP[d]	22	0.27 ± 0.02	0.30	0.39
	0	0.14 ± 0.03	0.48	0.27

[a] Micelles composed of 0.05 M cetyltrimethylammonium bromide in water. [b] Vesicles composed of 0.005 M didodecyldimethylammonium bromide in water. [c] Mixed vesicles composed of 50:50 (molar ratio) dicetyl phosphate/egg lecithin–total surfactant concentration 0.005 M. [d] Mixed vesicles composed of 50:50 (molar ratio) didodecyldimethylammonium bromide/dicetyl phosphate–total surfactant concentration 0.005 M.



1

The surfactant stilbene **1** was prepared by Wittig synthesis similar to that used with other functionalized fatty acids.[19,20,22] The similarity of **1** in its surfactant properties was demonstrated by examining its surface pressure area isotherms in spread films on water and other aqueous subphases. It was found that pure **1** shows "condensed film" behavior, rapidly compressing to a molecular area of 20 Å^2, which is nearly the same as that for unsubstituted fatty acids of similar chain length (20–24 carbons).[18] This indicates that the spread films have an extended structure into which the stilbene unit packs well such that its effective area is little different from that of a polymethylene chain. In contrast, it was found that films of *cis*-**1** or the phenanthrene **2** obtained by photocyclization of **1** gave expanded films with much greater limiting areas.



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It was found that films of **1** could readily be transferred to form multilayer assemblies on rigid supports such as glass or quartz slides.[23,24] Not surprisingly, it was found that irradiation of *trans*-**1**

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(22) The methyl ester of 16-oxotolylhexadecanoic acid was prepared as in ref 20. This was brominated at the aryl methyl group by NBS in CCl_4, then coupled by means of the Wittig reaction, using triphenylphosphine, to benzaldehyde. The keto group was reduced with zinc amalgam in HCl in the presence of benzene, yielding the methyl ester of 1 which was saponified by refluxing in aqueous acetone with KOH. Anal. Calcd: C, 82.90; H, 9.74. Found: C, 81.52; H, 10.09.

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in these assemblies leads to rather inefficient isomerization with $\phi \leq 0.0015$.[25] The products recovered included *cis*-**1** and the phenanthrene derivative **2**, which was formed in other media only upon prolonged irradiation. Evidently in this medium, the quantum yield for formation of **2** from *cis*-**1** is higher than that for *trans*-**1** to *cis*-**1**. Phenanthrenes are known to form from *cis*-stilbenes by way of the photogenerated dihydrophenanthrene in the presence of an oxidizing agent.[26] Usually this occurs with a quantum yield much lower than that for trans to cis isomerization. With the assumption that photoisomerization of *cis*- to *trans*-**1** is more hindered than that of *trans*- to *cis*-**1**, the likelihood of *cis*-**1** cyclizing is probably high enough to prevent much of the intermediate *cis*-**1** from being seen in the analysis.

We have measured quantum yields for both fluorescence and trans to cis isomerization of **1** in a variety of media.[27,28] Table I shows that in homogeneous solution these values are very similar to those of *trans*-stilbene. Generally, photoisomerization of **1** decreases from CH_2Cl_2 solution to CTAB micelles to lipid vesicles above T_c to lipid vesicles below T_c, while fluroescence increases over the same range. This trend is expected since the range of media investigated represents an increase in viscosity seen by the stilbene group. In general, the observation that isomerization quantum yields are much higher in all the "liquid" media than for the supported multilayers is in accord with other evidence that suggests even for "well-organized" bilayer systems there is little order or alignment of the terminal ends of the alkyl chains above T_c.

The fluorescence and photoisomerization quantum yields obtained in liquid media (CH_2Cl_2) were used to calculate a decay ratio, (R), that is, the fraction of twisted intermediate states which isomerize to the cis form. The values of R show somewhat more complex behavior. In solution, micelles, and vesicles above T_c, R is the same within experimental error. In vesicles below T_c, R decreases noticeably. There are two possible explanations for this. First, the effective viscosity of the highly organized medium in vesicles below T_c may slow the motion of the stilbene to the twisted state to the extent that radiationless decay occurs before it has reached the totally twisted configuration. This would favor decay to the starting material. Alternatively, the excited stilbene may reach the twisted configuration, but then be forced back to the trans form by the more organized alkyl chains of the host surfactant which had been deformed by the twisting.

The results suggest that in vesicles above T_c the orderliness, or degree of alignment, of surfactant alkyl groups in the bilayer midsection near the alkyl terminus is similar to that in micelles. Little order is present, but there is sufficient viscosity to noticeably increase the fluorescence of **1**. Below T_c, this region appears to become considerably more highly ordered. That this is not simply a temperature effect can be seen by examination of the results for vesicles of DDAB/DCP, which at room temperature are similar to those for the other vesicles at 0 °C. This mixed vesicle is composed of surfactants, one containing a cationic and the other an anionic head group. Such a vesicle would be expected to have very tightly packed alkyl chains, and should be in the "gel" phase even at relatively high temperatures.

The results of this work are consistent with those of Czarniecki and Breslow,[15] who photolyzed a series of surfactant benzophenones in vesicle solutions. They found patterns of hydrogen abstractions from the surfactant alkyl chains which suggested considerable disorder in the vesicles above T_c. We feel, however, that due to the smaller perturbational effects and lower concentrations used, our probe is more appropriate for investigating conditons in vesicle solutions. We are currently engaged in further investigtions with shorter chain homologues of **1**, which should provide information about conditions at various positions along the surfactant chain, as well as in the central region. We hope to use this information to develop an order parameter similar to that found with deuterium quadrupole splitting studies.[29]

Acknowledgments. We are grateful to the National Science Foundation (Grant CHE 7823126) for support of this work.

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[25] This represents the combied yield of *cis*-**1** and **2**. The maximum quantum yield for disappearance of *trans*-**1** is 0.007, which probably includes dimer formation as the major reaction.

[26] See, for example: Mallory, F. B.; Wood, C. S.; Gordon, J. T.; Lindquist, L. C.; Savitz, M. L. *J. Am. Chem. Soc.* **1962**, *84*, 4361, and references therein.

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[28] Incorporation into micelles was done by slowly dropping an appropriate amount of benzene stock solution of **1** into a warm stirred solution of 0.05 M CTAB. The solution was stirred overnight to evaporate the benzene. Incorporation into vesicles was done by mixing appropriate amounts of stock solutions of **1** and surfactant in benzene to give a ratio of 1:100. The mixture was evaporated to form a film on the sides of a vial, triply distilled water was added, and the mixture was sonicated with the immersible probe of a Heat Systems Model 220-F ultrasonicator until a clear solution resulted. This was centrifuged to remove titanium particles. Monolayers and multilayer assemblies were prepared by the method of Kuhn.[23] Solutions were degassed by passing N_2 purified by bubbling through chromous solution over stirred samples of the solution in an absorbance cell fitted with a stopcock. Irradiations were with a Schoeffel 1000-W Hg-Xe lamp fitted with a Bausch and Lomb monochromator set at 313 nm. Actinometry was with an Aberchrome reversible actinometer previously calibrated by ferrioxalate actinometry. Absorbance and fluorescence spectroscopy were performed with a Perkin-Elmer model 576 ST UV-vis spectrophotometer and a Hitachi MPF 2A spectrofluorimeter. Quantum yields were determined by analysis of the absorbance spectra before and after irradiation and supported by high-pressure liquid chromatography by using a Whatman 10/25 PAC column and Varian Varichrome UV-vis detector set at the isosbestic point for the trans to cis conversion of **1**.

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ESR Study of X-Irradiated $[HP(OCH_2CH_2)_3N]BF_4$: Phosphorus in a Trigonal-Bipyramidal Configuration with the Unpaired Electron in Apical Position

Sir:

Numerous studies concerning the structure of phosphoranyl radicals in solution have been published. Usually, a trigonal-bipyramidal (TBP) structure with the unpaired electron in an equatorial position has been assigned. However, these assignments cannot be conclusive since they are based on isotropic hyperfine coupling constants and theoretical predictions. The studies dealing with oriented phosphoranyl radicals in solid matrixes are very scarce, and from these studies conflicting ideas arise about the location of the unpaired electron. For $Ph_3\dot{P}Cl$, the unpaired electron is assumed to reside in an antibonding P–Cl orbital.[1] On the other hand, for $\dot{P}F_4$ and $Cl_3\dot{P}O^-$, a TBP structure has been found with the unpaired electron located in the axial axis.[2,3]

We now report the single-crystal study of the radical derived from $[HP(OCH_2CH_2)_3N]BF_4$ (**1**). In this compound, the phosphorus atom possesses a TBP configuration with the adjacent

(1) (2)

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