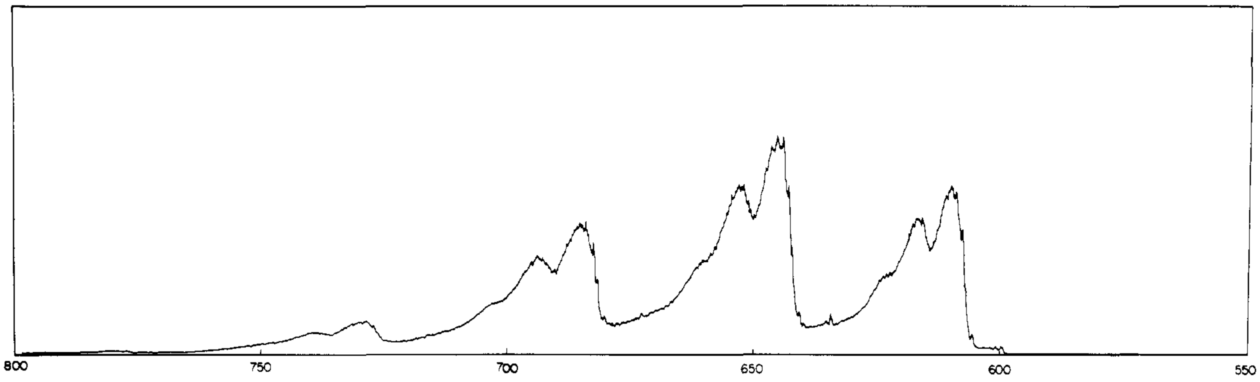

Figure 1. Emission spectrum of crystalline *trans*-[$ReO_2(py)-d_5)_4$]BPh_4 at 4.5 K (436-nm excitation, uncorrected for spectrometer response).

Table I. Photophysical Data for *trans*-$ReO_2L_4{}^z$ Complexes

complex	conditions[a]	$\lambda_{max}{}^{em}$, nm	τ, μs[b]
$K_3[ReO_2(CN)_4]$	crystal (300)	*c*	330
	crystal (30)	*c*	700
$[ReO_2(py)_4]BPh_4$	crystal (300)	*c*	32
	crystal (30)	*c*	66
	py soln (300)	655	17 (0.03)
	THF soln (300)	645	13 (0.03)
	CH_2Cl_2 soln (300)	670	4
$[ReO_2(py\text{-}d_5)_4]BPh_4$	crystal (300)	*c*	140
	THF soln (300)	645	9 (0.04)
$[Re^{18}O_2(py)_4]BPh_4$	crystal (300)	*c*	36
	py soln (300)	655	15 (0.03)
$[ReO_2(4\text{-pic})_4]BPh_4$	crystal (300)	*c*	11
	THF soln (300)	665	17 (0.02)
$[ReO_2(4\text{-}t\text{-Bu(py)})_4]BPh_4$	crystal (300)	*c*	11
	THF soln (300)	660	21 (0.03)

[a] Temperature (K) is given in parentheses. [b] Lifetimes measured with the second harmonic (532 nm) from a Nd:YAG laser (pulse width 8 ns fwhm). In parentheses are quantum yields measured relative to $[Ru(bpy)_3]Cl_2$ in degassed H_2O (Φ_{em}(436 nm) = 0.042 ± 0.002: van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* 1976, *98*, 4853. [c] Near 650 nm.

Several dioxorhenium(V) complexes also luminesce in aprotic solutions. The emission quantum yields measured with 436-nm excitation are about 0.03 for *trans*-$ReO_2(py)_4{}^+$ and its isotopically substituted derivatives. The excited-state lifetimes of these ions in solution vary from 4 to 17 μs, down by at least a factor of 2 from the solid-state values. Our observation that *trans*-$ReO_2(py\text{-}d_5)_4{}^+$ has a lifetime in THF solution nearly equal to that of the protonated form suggests that the dominant nonradiative solution decay pathway differs markedly from the one that is operative in crystals. Solvation of the cation as well as equatorial ligand dissociation[15] may contribute significantly to the observed decay rate.

None of the dioxorhenium(V) ions luminesces in aqueous solution. Addition of water to a pyridine solution of *trans*-$ReO_2(py)_4{}^+$ shifts both the absorption and emission bands to lower energy, decreases the emission quantum yield, and shortens the luminescence lifetime. Deuterated water produces identical spectral changes but reduces the excited-state lifetime less efficiently than H_2O. Methanol and ethanol also shorten the dioxorhenium(V) excited-state lifetime. The efficiency of the lifetime quenching by these alcohols is sensitive to deuteration at the hydroxyl though not at the alkyl positions. A cationic proton source, pyridinium ion, however, does not alter the absorption nor the emission spectrum of *trans*-$ReO_2(py)_4{}^+$ in pyridine solution, nor does it appreciably reduce the excited-state lifetime. These data suggest that protic media solvate the dioxorhenium(V) ions (perhaps via hydrogen bonding) to produce species that luminesce less efficiently and have shorter excited-state lifetimes than the isolated complexes.

In summary, we have found that the ${}^3E_g$ state of dioxorhenium(V) complexes lives 10–100 μs in crystalline samples and ~10 μs in aprotic solvents. Such relatively long-lived, highly energetic (~2-eV excited states) oxometal species are of potential interest as oxygen atom transfer agents in oxygenation reactions, and we are exploring this area at the present time.

Acknowledgment. J.R.W. thanks the Sun Company for a graduate fellowship. This research was supported by National Science Foundation Grants CHE78-10530 and CHE81-20419.

Registry No. $K_3[ReO_2(CN)_4]$, 19439-48-6; $[ReO_2(py)_4]BPh_4$, 84417-09-4; $[ReO_2(py\text{-}d_5)_4]BPh_4$, 84417-11-8; $[Re^{18}O_2(py)_4]BPh_4$, 84417-13-0; $[ReO_2(4\text{-pic})_4]BPh_4$, 84472-13-9; $[ReO_2(4\text{-}t\text{-Bu(py)})_4]BPh_4$, 84417-15-2.

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Host–Guest Interactions in Amylose Inclusion Complexes: Photochemistry of Surfactant Stilbenes in Helical Cavities of Amylose[1]

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Received October 6, 1982

The control and modification of reactivity through incorporation of molecules into organized assemblies, functionalized polymers, and interfacial sites at solution–solid or gas–solid interfaces remain an area of considerable interest. A specific subarea that has been the focus of several recent investigations concerns reactivity of molecules incorporated into "host–guest" complexes, using as hosts such varied systems as zeolites, cyclodextrins, and various cryptates or crown ethers.[3-7] Most of the aforementioned reagents offer guest sites of relatively restricted dimensions; modifications of reactivity can occur for a variety of reasons including restriction of molecular motion, limited access of potential reaction partners, or hydrophilic–hydrophobic effects.

It has recently been shown that various amyloses and (carboxymethyl)amyloses can form inclusion compounds with a variety

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(2) Visiting scientist from Shanghai Institute of Organic Chemistry, Academia Sinica, People's Republic of China.

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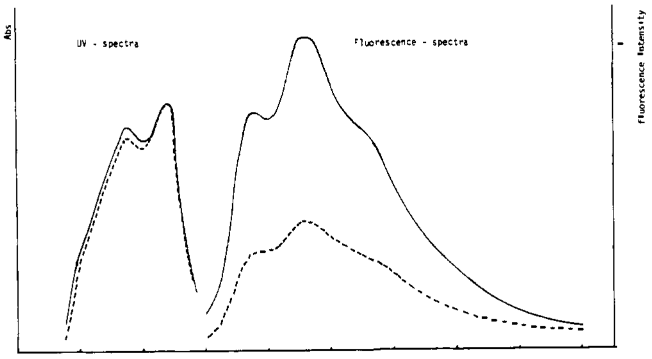
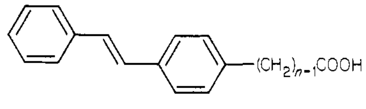


Figure 1. UV and fluorescence spectra of S_6 in 1:1 Me_2SO–water mixture with and without(—)amylose, 30 °C; concentration of $S_6 = 5 \times 10^{-5}$ M; concentration of amylose = 7.21×10^{-5} M.

of molecules.[8-13] Measured binding constants suggest that the host provides a cavity with characteristics similar to those of the cyclodextrins but with more flexibility in the size and length of the guest binding sites. The binding sites provided by amylose appear relatively hydrophobic; for example, studies with the fluorescent probe 2-(*p*-toluidinyl)naphthalene-6-sulfonate in low molecular weight amylose–water showed a fluorescence enhancement on forming amylose inclusion complexes similar to that observed in organic solvents or hydrophobic sites of protein.[9] It has been suggested that the amylose chains exist as an extended coil in the absence of guests but rearrange to helical segments when the inclusion complexes are formed;[10] evidently both the conformation of the amylose macromolecule and its binding properties are strongly dependent upon the solvent composition.[12]

The photophysics and photochemistry of the *trans*-stilbene chromophore have been thoroughly investigated in a number of careful studies.[14-21] The behavior of the lowest excited singlet state has been shown to be quite sensitive to temperature and to properties of the microenvironment, especially viscosity.[19-21] For this reason stilbene and related derivatives have been used as probes for several organized assemblies such as micelles,[22,23] vesicles,[24] and cyclodextrins.[25] Recently we have synthesized a series of substituted stilbenes, S_n, in which the stilbene chromophore is incorporated into a surfactant molecule. We have found these stilbenes sensitive structural probes for organized media.[22,24,26] The present paper describes the behavior of three of the surfactant stilbenes in the presence of amylose in aqueous dimethyl sulfoxide. The results reveal several interesting features of amylose host–guest interaction, including a clear indication that, at least for the stilbenes, the guest is held in a reasonably constrained site similar to that provided by various bilayer structures.



S_n

Table I. Dissociation Constants, Free-Energy Changes, and α (the Fraction of Complexed Probes of the Inclusion Complexes Formed between Amylose and Surfactant Stilbenes) in 1:1 (v/v) Me_2SO-Water Mixture (30 °C)

probe	K_d*, 10^{-3} M	K_d,[a] 10^{-4} M	α,[b] %	$-\Delta G/CH_2$,[c] kcal/mol
S_4	20.0	2.70	18	0.17
S_6	9.68	1.51	26	0.17
S_{12}	0.648	0.138	70	0.20

[a] $K_d = K_d^*/n$, the dissociation constant of inclusion complexes based on the macromolecules, where *n* is the number of binding sites per macromolecule. [b] Concentration of amylose = 7.21×10^{-5} M. [c] Corresponding number of methylene groups for surfactant stilbenes are $S_4 = 14$, $S_6 = 16$, $S_{12} = 22$.

The surfactant stilbenes S_4, S_6, and S_{12} and stilbene itself were studied in 50% (v/v) dimethyl sulfoxide–water in the presence and absence of soluble amylose having DP = 857.[27] As shown in Figure 1 for S_6, addition of amylose produced virtually no change in the absorption spectrum; however, for the surfactant stilbenes S_4, S_6, and S_{12} there is a pronounced increase in the fluorescence intensity without any apparent spectral alteration. The increase is monotonic with increasing amylose concentration and follows the order $S_4 < S_6 < S_{12}$. For the concentrations [(stilbene) = 5×10^{-5} M, (amylose) ≤ 1.0% (7.21×10^{-5} M)] there was no detectable change in fluorescence for *trans*-stilbene.

The increase in fluorescence observed upon addition of amylose to solutions of the surfactant stilbenes is attributed to formation of inclusion complexes between stilbenes and amylose as described by eq 1, where S = surfactant stilbenes, $\bar{A}$ is a binding segment

$$S + \bar{A} \underset{1/K_d^*}{\overset{K_a^*}{\rightleftharpoons}} \bar{A}S = C \qquad (1)$$

of the amylose, and $\bar{A}S$ is the inclusion complex C. The change in fluorescence can be related to the equilibrium for complex formation if it is assumed that the echange in eq 1 is much slower than fluorescence. A modification of a method designed by Bender and co-workers for absorption changes on complex formation can be applied as follows.[28] Here initial concentrations are $S = S_0$ and $\bar{A} = nA_0$ (A_0 is the initial concentration of amylose, and *n* is the number of binding sites), and a 1:1 stoichiometry between A and S to form C is assumed. This yields an expression (eq 2)

$$\frac{1}{K_a^*} = K_d^* = \frac{(\bar{A} - C)(S_0 - C)}{C} = \frac{(nA_0 - C)(S_0 - C)}{C} \qquad (2)$$

that upon expansion and use of the assumption that the term C^2 can be neglected[29] gives eq 3. The variation in total fluorescence

$$C = \frac{(nA_0)(S_0)}{(nA_0) + S_0 + K_d^*} \qquad (3)$$

yield $\Delta\phi_f$ is related to the concentration of C by eq 4, where ϕ_f^C

$$C = \Delta\phi_f[S_0]/(\phi^C{}_f - \phi_f{}^S) \qquad (4)$$

and $\phi_f{}^S$ are the quantum yields for pure complexed and uncomplexed stilbene derivatives, respectively. Substitution of eq 4 into

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eq 3 leads to eq 5, which predicts a linear relationship between

$$\frac{1}{\Delta\phi_{\mathrm{f}}} = \frac{1}{\phi_{\mathrm{f}}{}^{\mathrm{C}} - \phi_{\mathrm{f}}{}^{\mathrm{S}}}\left(1 + \frac{\mathrm{S}_0 + K_{\mathrm{d}}{}^*}{nA_0}\right) \tag{5}$$

the reciprocals of $\Delta\phi_{\mathrm{f}}$ and A. Reasonable plots were obtained for all three of the surfactant stilbenes; values for $K_{\mathrm{d}}{}^*$ and α, the degree of complex formation, as listed in Table I, were extrapolated from these plots.[30]

The trans → cis photoisomerization of S_6 was also investigated in the presence and absence of amylose. As might be anticipated from the enhancement of fluorescence, the isomerization was retarded by addition of amylose. It was found, for example, that at $A_0 = 7.21 \times 10^{-5}$ M the $\phi_{\mathrm{t}\to\mathrm{c}}{}^{\mathrm{obsd}}$ for S_6 in the inclusion complex is approximately 0.22 or about 44% of that in homogeneous $\mathrm{Me_2SO}$–water.

These results reveal several features of the amylose inclusion complexes. First of all, the extrapolated values for stilbene fluorescence yields in the complexes, $\phi_{\mathrm{f}}{}^{\mathrm{C}} \simeq 0.230$ (for S_4 and S_6) and $\phi_{\mathrm{t}\to\mathrm{c}}{}^{\mathrm{C}} = 0.22$ are very similar to those obtained for these and other surfactant stilbenes incorporated into various bilayer vesicles below or near the phase-transition temperature.[22] These values indicate a reasonably restricted environment for the stilbene chromophore or a relatively high effective "microviscosity" in the amylose complexes. The similarity to results obtained with vesicles is interesting since the microstructures of the two assemblies must be quite different. The amylose has the glucopyranose units in the C1 chair conformation[31] and can form helical cavities (6-helix, 7-helix) with approximate internal diameters of 4.5 and 7.0 Å, respectively.[32,33] The cross-sectional areas for the helical cavities are 16 and 38 Å^2, respectively. The 6-helix is the most stable form and apparently the cavity used for incorporation of benzene and several aliphatic derivatives; however, the flexibility of the amylose is such that larger cavities can be formed to accommodate somewhat larger molecules.[32] The cavity size for the 6-helix is somewhat smaller than the indicated cross-sectional area for the S_n compounds—20–22 Å^2 in compressed monolayer films at the air–water interface.[22] In the latter phase photoisomerization of the stilbenes is virtually eliminated. Thus the present results suggest that the stilbene chromophore may exist in a cavity somewhat between a 6-helix and 7-helix in which molecular motion is restricted but not prohibited to the extent in condensed monolayers or crystals.

The relatively high sensitivity of the fluorescence of stilbene S_4, S_6, and S_{12} to complex formation suggests that these or similar probes can be useful to measure amylose binding constants for nonfluorescence molecules or even molecules without a characteristic chromophore. Indeed this is the case; we find addition of several surfactants results in a decrease in the stilbene fluorescences, presumably due to competitive binding to the amylose.

That formation of the amylose inclusion complexes is governed largely by hydrophobic effects is indicated by the pronounced variation in dissociation constants $K_{\mathrm{d}}{}^*$, observed for the different stilbene derivatives. Thus stilbene does not form a detectable complex in the concentration ranges employed while the surfactant stilbenes complex with decrease in $K_{\mathrm{d}}{}^*$ paralleling increase in hydrophobicity. As shown in Table I, there is a reasonable correlation for the surfactant stilbenes between $-\Delta G$ and the effective number of methylene groups; similar incremental $-\Delta G/\mathrm{CH_2}$ values have been observed for quite different molecules such as carboxylic esters of p-nitrophenol, suggesting that this may be a fairly general phenomenon.[13]

Acknowledgment. We are grateful to the U.S. Department of Energy (Contract DE-A505-81ER10815.A000) for support of this research.

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(29) Although it is true that for S_{12}, the term CS $\simeq$ C^2, for each of the surfactant stilbenes, analysis of the data in Table I confirms that the term C^2 is negligible compared with the other terms in the expansion developed from eq 2.

(30) By use of the σ-C (surface tension–concentration of substrate) curve, the n value can be determined experimentally. In the present case, n values were calculated from the DP of amylose used and the lengths of surfactant stilbenes based on the previousd data presented in ref 12.

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Synthesis and Structure of 8-Carboxy[6]paracyclophane

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Received November 1, 1982

Central to the interest in the chemistry of [n]paracyclophanes with small bridges (n = 6[1] or 7[2]) is the distortion of the aromatic ring from planarity and the effect of the distortion on its physical and chemical properties. The smallest [n]paracyclophane thus far obtained has been the [6] isomer, first reported by Jones et al. in 1974.[1a] However, the crystal structure determination of this system has not been done due to the inaccessibility of either the parent hydrocarbon or suitable derivatives. We report herein the novel and efficient synthesis and single-crystal X-ray structure determination of 8-carboxy[6]paracyclophane (**2**), which has, to our knowledge, the most highly deformed benzene ring (α_{av} = 20.7°, β_{av} = 18.8°) obtained to date.

The synthesis of **2** takes advantage of the facility of Dewar benzene → benzene valence isomerization of [6.2.2]propelladiene to [6]paracyclophane[1b] (Scheme I). Ring contraction of the propellanone **3**,[3] prepared from the bicyclic α,β-unsaturated ketone, by employing photo-Wolff rearrangement of the α-diazo ketone derived from **3** in methanol afforded a mixture of two epimeric [6.2.2]propellanes, **4X** and **4N** (**4X**/**4N** = 2), in 47% yield. Treatment of either **4X** or **4N** with LDA/diphenyl diselenide at −70 °C furnished a mixture of two isomeric α-selenides, **5X** and **5N** (**5X**/**5N** = 6–10), in 89% yield. Oxidation of the major isomer **5X** in dichloromethane with $\mathrm{H_2O_2}$ at room temperature yielded the propelladiene **6** in 72% yield. Valence isomerization of **6** took place smoothly at 60 °C leading to the formation of the cyclophane **1** quantitatively. Hydrolysis of **1** gave the crystalline **2**, mp 123–125 °C, in 87% yield.

A single-crystal X-ray analysis of **2** gave precise information about the deformation of the benzene ring of the [6]paracyclophane system.[4,7] Figure 1 is an ORTEP drawing[8] of **2**. The

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[†] Department of Petroleum Chemistry.

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(3) All new compounds showed satisfactory spectral properties. Satisfactory elemental analyses were obtained on all new compounds except for **6** and **8**, which are readily converted to **1** and **7**, respectively. Details are recorded in the supplementary material.

(4) Crystal data of **2**: $\mathrm{C_{13}H_{16}O_2}$, M_{r} 204.3, tetragonal, space group $P4_2/n$, a = 16.646 (1) Å, c = 7.987 (1) Å, U = 2213.3 (3) Å^3, D_x = 1.226 g cm^{-3}, Z = 8. Intensity measurements were made on a Rigaku four-circle diffractometer using nickel-filtered Cu Kα radiation. A total of 1395 reflections was collected up to 2θ = 110°, among which 1185 were nonzero reflections. The structure was solved by the direct method (MULTAN-78)[5] and refined by the block-diagonal least squares (HBLS-V)[6] to the R index of 0.123 (non-hydrogen atoms anisotropically, hydrogen atoms of benzene ring isotropically). The fractional atomic parameters are listed in Table S1.