

Registry No. GEsBP, 106762-80-5; GPhBP, 56956-53-7; GEsBP-HCl, 106762-81-6; GPhBP-HCl, 106762-82-7; Ru(NH₃)₅GEs, 106762-75-8; Ru(NH₃)₅GPh, 106762-76-9; Ru(bpy)₂(GEsBP)₂, 106762-77-0; Ru(bpy)₂(GPhBP)₂, 106762-78-1; Ru(OEP)(GPhBP)₂, 106798-74-7; Ru(TPP)(GPhBP)₂, 106762-79-2; styrene, 100-42-5; butyl acrylate, 141-32-2.

Photodynamic Macrocycles

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The cyclodextrins and other synthetic macrocycles have been the subject of extensive studies directed toward the synthesis of enzyme model systems.^{2,3} With regard to the critical issues of product release and catalytic turnover, a conformationally dynamic system could have important advantages over these relatively static binding cavities, since the binding properties of substrate, transition state, and product could be different in the different components of a dynamic system.⁴ We report herein our preliminary results with a new class of compounds that we call photodynamic macrocycles, which incorporate a spiro[pyranindoline] moiety into a carbocyclic ring. The spiro[pyranindoline]s are an important class of photo- and thermochromic compounds whose unusual properties can be attributed to the equilibrium shown in Scheme I.^{5,6} The

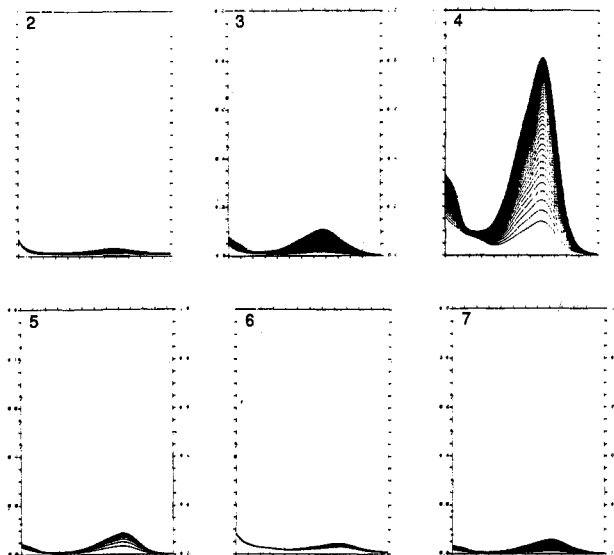


Figure 1.

Scheme I

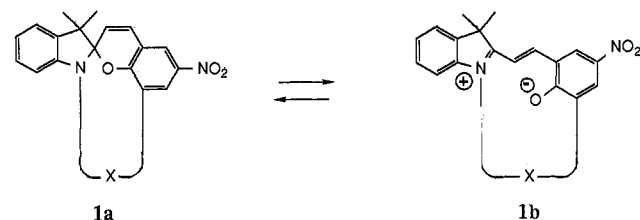
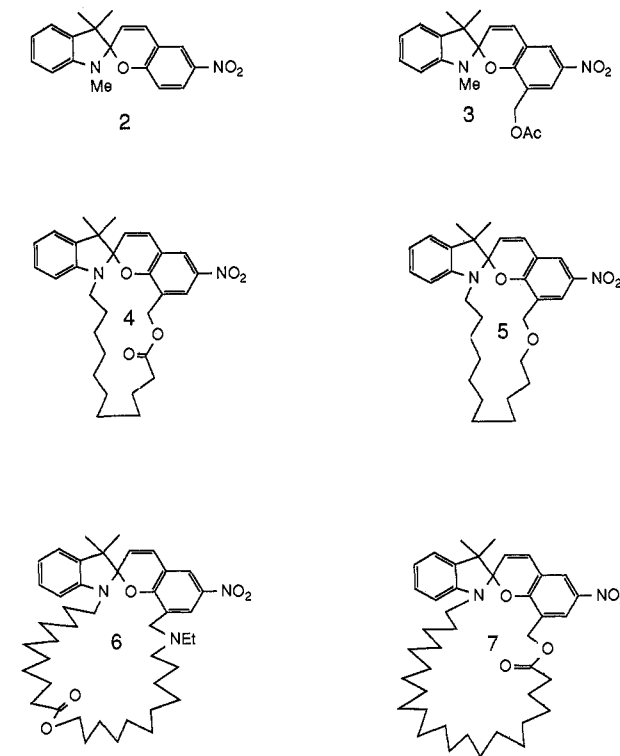


Chart I



remarkable effect of the size of the carbocyclic ring on the thermodynamics of the **1a** ⇌ **1b** interconversion is the subject of this paper.

To determine the effect of "X" in Scheme I on the thermal equilibrium, **1a** ⇌ **1b**, we prepared six spiro[pyranindoline]s, **2-7** (Chart I), to compare the behavior of **2** and **3** with the macrocyclic compounds, **4-7**.⁷

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Table I

	ΔG , kcal/mol	ΔH , kcal/mol	ΔS , cal/K·mol
2a \rightleftharpoons 2b	2.6	0.8	-6.2
3a \rightleftharpoons 3b	1.6	-0.5	-6.7
4a \rightleftharpoons 4b	-0.4	-3.6	-10.2
5a \rightleftharpoons 5b	1.7	-0.6	-7.5
6a \rightleftharpoons 6b	2.4	1.8	-2.0
7a \rightleftharpoons 7b	2.0	-0.6	-8.4

Monitoring the absorbance for the open, zwitterionic forms **2b**-**7b** (λ_{\max} at 560 nm) of **2a** \rightleftharpoons **2b**, **3a** \rightleftharpoons **3b**, **4a** \rightleftharpoons **4b**, **5a** \rightleftharpoons **5b**, **6a** \rightleftharpoons **6b**, **7a** \rightleftharpoons **7b** (3×10^{-5} M in dimethyl sulfoxide at 25 °C) as the systems reach thermal equilibrium leads to the spectra shown in Figure 1.⁸ Under conditions (25 °C in dimethyl sulfoxide) where **2**, **3**, **5**, **6**, and **7** exist predominantly in the closed form, i.e., very little absorbance at 560 nm is observed, there is a considerable absorbance at 560 nm for **4**.

The equilibrium constant and therefore ΔG for the **1a** \rightleftharpoons **1b** equilibrium for each system can be determined,⁹ and these values are shown in Table I. For the parent compound, **2**, the equilibrium constant is 1.2×10^{-2} , which corresponds to a ΔG between **2a** and **2b** (only the closed spiro[pyranindoline] forms of **2**-**7** are shown in Chart I) of 2.6 kcal/mol. Under these conditions, 99% of the mixture remains in the closed spiro pyran form, **2a**. In a similar manner, the ΔG for **3** is ca. 1.5 kcal/mol, so that this compound also exists predominantly in the closed form (**3a**). In dramatic contrast to the thermal behavior of **2** and **3**, we have found that **4** exists predominantly (65%) in the open form, **4b** (not shown), with a thermal equilibrium constant of 1.8, representing a ΔG of -0.4 kcal/mol between **4a** and **4b**. The free energy difference between the open and closed forms of the spiro[pyranindoline] systems **2a** \rightleftharpoons **2b** and **4a** \rightleftharpoons **4b** is ca. 3.0 kcal/mol. The effect of the macrocycle in this system is to increase the concentration of the zwitterionic form of the spiro[pyranindoline] \rightleftharpoons merocyanine equilibrium by a factor of 54, from 1.2% (**2a** \rightleftharpoons **2b**) to 65% (**4a** \rightleftharpoons **4b**). We predicted that the effect of the macrocycle on the **1** \rightleftharpoons **2** equilibrium would diminish on increasing ring size, and that is indeed observed. The thermal behavior of **6** and **7** closely parallels that of the parent nonmacrocylic compounds **2** and **3** (Figure 1). The equilibrium constants for **6a** \rightleftharpoons **6b** and **7a** \rightleftharpoons **7b** are 1.8×10^{-2} and 3.5×10^{-2} , respectively, at 25 °C in dimethyl sulfoxide, corresponding to a free energy difference of 2.4 and 2.0 kcal/mol, so that once again >96% of the spiro[pyranindoline] exists in the closed form. However, the 18-membered ring appears to be a necessary but not sufficient condition for this remarkable thermochromic behavior. The thermal behavior of **5**, in which the lactone of **4** is replaced by an ether linkage, exists predominantly in the closed form, **5a** ($K_{\text{eq}} = 5.6 \times 10^{-2}$).

The relative contributions of enthalpy and entropy to the 3 kcal/mol $\Delta\Delta G$ between **2a** \rightleftharpoons **2b** and **4a** \rightleftharpoons **4b** were determined by plotting $\ln K_{\text{eq}}$ against $1/T$. The results are summarized in Table I. Only the opening of the smaller macrocycle, **4a** \rightleftharpoons **4b**,

(7) Compounds **4**, **6**, and **7** were prepared from the corresponding hydroxy acids by macrolactonization using the method of Mukaiyama (cf.: Mukaiyama, T.; Usui, M.; Saigo, K. *Chem. Lett.* 1976, 49), and NMR, IR, and FAB-MS data were compatible with the assigned structures. The hydroxy acids were in turn prepared by condensation of the appropriate indolines and salicylaldehydes. Compound **5** was prepared by intramolecular displacement of the corresponding chloromethyl spiro[pyranindoline] alcohol (potassium *tert*-butoxide, tetrahydrofuran, 45 °C), and **2** and **3** are described in ref 5.

(8) For a similar treatment, see ref 6k.

(9) The determination of the equilibrium constant requires a knowledge of ϵ , which we have calculated for the open form of the spiro[pyranindoline] from the equilibrium constant for **4a** \rightleftharpoons **4b** that can be obtained by NMR. Integration of the peak heights of the singlet at δ 1.7 for the methyl protons of **4b** (six protons) and the signal (AB quartet) at δ 4.8 for the benzylic protons of **4a** gives a K_{eq} of 1.8, from which $\epsilon = 51\,000$ can be obtained from the equation

$$K_{\text{eq}} = \frac{A/\epsilon}{[S_T] - (A/\epsilon)}$$

where A = absorbance, ϵ = extinction coefficient, and S_T = starting concentration of the closed spiro[pyranindoline], **4a**.

is significantly (>1 kcal/mol) exothermic. The relative differences between ΔS values are much smaller, so that enthalpy is the primary source of the difference in ΔG between **4** and the other spiro[pyranindoline]s. We attribute this difference in large part to ring strain in the unusually constrained 18-membered ring of **4**. A critical role, however, must be ascribed to the conformation of the lactone, since **5**, in which the lactone is replaced by an ether linkage, no longer exhibits this unusual thermal behavior. While reports on the qualitative effects of metals on the **1a** \rightleftharpoons **1b** equilibrium have appeared,^{6m,n} we are not aware of any studies that have quantitatively demonstrated a change of this magnitude in the **1a** \rightleftharpoons **1b** equilibrium. The further effect of added ligands on this equilibrium and the incorporation of the spiro[pyranindoline] into macrocycles that are capable of inclusion complex formation are currently being pursued in our laboratory.

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Ferromagnetic Alternating Spin Chains

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The study of the magnetic properties of heteronuclear species has shown that ferromagnetic coupling is much more common than it was suspected before,^{1,2} because by using different metal ions, or in general different spins, it is much easier to bring into interaction orthogonal magnetic orbitals. These results have been very stimulating, because they have suggested possible strategies to assemble ferromagnetic materials starting from pairs of different spins. The interest for such materials is bound both to the wish to make what has been called the magnetic zoo³ as complete as possible and also to the possibility of determining which are the conditions under which molecular ferromagnets can be obtained.

The design of low dimensional materials is relatively simple using molecular building blocks, and chains are the systems for which more examples are available.^{4,5} As regards the magnetic properties, either antiferro-, ferro-, or ferrimagnetic behavior has been reported. In particular, recently there have been reports in the literature concerning structurally ordered bimetallic chains in which a sequence of the type $-M-M'-M-M'-$ has been obtained.⁶⁻⁸ The coupling in these chains has been found to be antiferromagnetic in nature, but since different spins are coupled,

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