at 5 °C intervals over the temperature range 240–290 °C and the populations of the free crown, its 1:1 complex, and its 2:1 complex were determined by total line-shape analysis of the spectra.[3] It was found that the K_1/K_2 ratio is *invariant* with temperature. This requires that the enthalpies of binding be the same for both steps, i.e., $\Delta H_1 = \Delta H_2 = -7.3 \pm .3$ kcal/mol. The origins of cooperativity here must therefore be entropic ($\Delta S_1 = -18.5 \pm 0.5$, $\Delta S_2 = -16.5 \pm 1$ eu).

Interpretation of these results is facilitated by reference to Figure 3. The free crown ethers enjoy a number of conformations or effective sizes defined by the dihedral angle θ. Binding of mercuric cyanide at one site of **1a** fixes this angle at the value optimal for complexation because both the benzyl oxygens are involved. The molecular rigidity of the biaryl system requires that this angle be reproduced at the remote site. To the extent that this second site is now more organized for complexation, binding of the second metal is enhanced; ΔS_2 is less negative than ΔS_1.

In the binding of mercuric trifluoromethyl to **1b**, no such restriction of θ occurs since only one of the benzyl oxygens is involved. The sites then act independently, and the result $\Delta H_1 = \Delta H_2$ and $\Delta S_1 = \Delta S_2$ leads to noncooperativity. Apparently in either case, initial binding and its attendent conformational restrictions do not alter the potential energy of the remote site.

Conclusion. In this study we have shown that allosteric cooperativity can arise from purely entropic effects in a model system. The simplicity of the model leads to interpretable data, but its relevance to biochemical systems may be remote.[4] Whether potential energy changes can result in cooperativity is the focus of our current research.

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Supplementary Material Available: Numbered drawings of complexes and tables of positional and thermal parameters for all atoms (13 pages). Ordering information is given on any current masthead page.

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(3) Stephenson, D. S.; Binsch, G. *J. Magn. Reson.* **1978**, *32*, 145–152. available as DNMR5: *QCPE*, **1978**, *10*, 365.

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Proton-Transfer Dynamics Involving the Intramolecular Charge-Transfer State of Photoexcited 1-(*p*-Aminophenyl)pyrene[1]

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The relationship between molecular structure and photophysics has been investigated with a new probe system, 1-(*p*-aminophenyl)pyrene (**1**). In particular, we have studied proton-transfer reactions in the excited state of **1** including deprotonation of the anilinium function in a locally excited π,π^* state and proton transfer quenching of the charge-transfer (CT) state. Rate parameters have now been measured for these processes.

In most solvents, a single fluorescence is observed from **1** that is highly solvatochromic (near 400 nm in nonpolar and near 500 nm in polar media). In alcohol–water (50:50), at acidic pH's, dual fluorescences are observed, which are assigned to emission from excited protonated (near 400 nm, 35 ± 2 ns) and free-base (near 500 nm, limiting lifetime 3.9 ± 0.1 ns)[2] fluorophors. We assign the shorter wavelength, structured, fluorescence to a π,π^* state wherein the excitation is localized in the pyrene moiety and the longer wavelength, structureless, fluorescence to a CT state with the aniline as donor and the pyrene as acceptor.[3] From low-temperature, time-resolved fluorescence studies in our own laboratory (to be published separately) and the work of others on closely related systems,[4] we conclude that the anilino moiety is twisted out of the plane of the pyrene ring in the CT state.

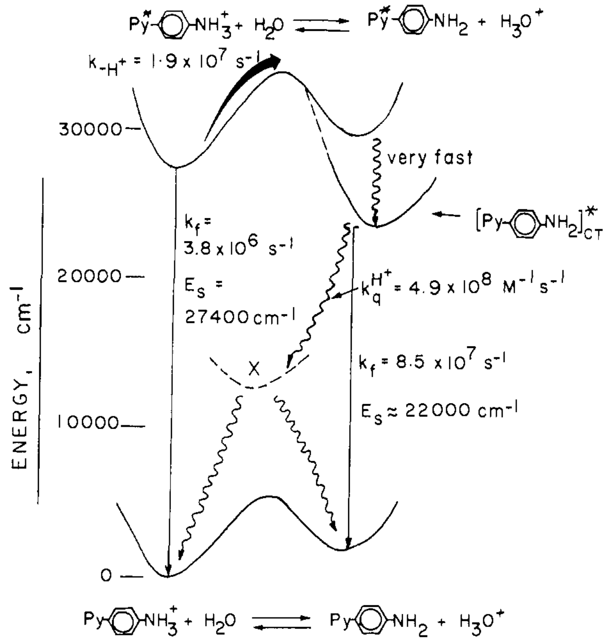

Figure 1. Comprehensive photophysical scheme for **1**. Values given are for solution in 50:50 ethanol–water and refer to the following quantities: energy of radiative singlet state (E_s), radiative rate constant (k_f), proton-transfer quenching constant ($k_q^{H^+}$), deprotonation rate constant (k_{-H^+}). X = metastable ground state of products resulting from proton-transfer quenching of CT state.

The ground-state pK_a of **1** in ethanol–water (50:50) appears in Table I along with other relevant values. The measured pK_a in alcohol–water (4.05) indicates no unusual ground-state acid–base properties for **1**.

The excited state pK_a values (pK_a*) for **1**, obtained by Forster cycle calculations[9] and fluorescence titrations,[9] are in excellent agreement and indicate only a modest enhancement in acidity of the excited state over the ground state. In contrast, systems with the amine function directly attached to an excited aromatic moiety show enhancements in acidity in the excited singlet state of many orders of magnitude (Table I).

The similarity of the pK_a and pK_a* values for **1** most likely results from similar rates of deprotonation for the conjugate acids in the ground and excited states, respectively (assuming similar and diffusion-limited protonation in both cases),[10] indicating little

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(2) Determined by the phase-plane deconvolution method. Demas, J. N. *J. Chem. Ed.* **1976**, *53*, 657.

(3) On the basis of one-electron redox potentials of pyrene and aniline, we estimate that the CT state will be 2.7 eV above the ground state in polar media compared to a locally excited π,π^* state at 3.4 eV.

(4) (a) Grabowski, Z. R.; Rotkiewicz, K.; Siemiarczuk, A.; Cowley, D.; Baumann, W. *Nouv. J. Chim.* **1979**, *3*, 443 and references therein. (b) Grabowski, Z. R.; Rotkiewicz, K.; Siemiarczuk, A. *J. Lumin.* **1979**, *18*, 420. (c) Rotkiewicz, K.; Rubaszewska, W. *Chem. Phys. Lett.* **1980**, *70*, 444. (d) Lippert, E.; Ayak, A. A.; Rettig, W.; Wermuth, G. *J. Photochem.* **1981**, *17*, 237. (e) Rettig, W. *J. Phys. Chem.* **1982**, *86*, 1970. (f) Kolos, R.; Grabowski, Z. R. *J. Mol. Struct.* **1982**, *84*, 251. (g) Kosower, E. M. *Acc. Chem. Res.* **1982**, *15*, 259 and references therein.

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(9) Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* **1976**, *12*.

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excited-state interaction between the pyrene and the anilinium fraction. In addition, the exclusive CT fluorescence from **1** in the free-base form in polar media indicates rapid conversion of the pyrene localized π,π^* state to the CT state.[11] Finally, transient data (discussed below) indicate that deprotonation of the conjugate acid, in the pyrene localized π,π^* state, also leads to formation of the CT state. These observations are consistent with the photophysical scheme shown in Figure 1.

The fluorescence decay of the short-wavelength emission (conjugate acid form) is a simple exponential under all conditions in aqueous media. At sufficiently high pH to completely deprotonate the ground state, the long-wavelength fluorescence also shows exponential decay behavior. But, in the pH range where both conjugate acid and free base are present in the ground state, the long-wavelength fluorescence is a composite of a fast and slower decay. The fast component arises from direct excitation of molecules in the free-base form to the pyrene localized π,π^* state, which rapidly relaxes to the CT state. The slow component results from excitation of molecules in the conjugate acid form which undergo excited-state deprotonation to the locally excited pyrene free-base state with subsequent rapid relaxation to the CT state (see Figure 1). This latter fluorescence component displays the lifetime characteristics of the longer lived conjugate acid fluorescence. Consistent with this scheme is the observation that even at pH values sufficient to protonate all of **1** in the ground state, a long-wavelength (CT) fluorescence is still noted. This fluorescence can only arise by the deprotonation route. There is no evidence that the CT state directly returns to the locally excited π,π^* state (either free base or protonated). This irreversibility is understandable in terms of the extreme endothermicity of this process (≥ 0.7 eV).

At sufficiently low pH values[12] that all of **1** is protonated, the efficiency of the CT state fluorescence shows a pH dependence indicating proton-transfer quenching. In alcohol-water over the pH range 1-2, a linear Stern-Volmer plot of the relative CT fluorescence yield vs. $[\mathrm{HCl}][\gamma_\pm{}^2]$[14,15] is observed with a slope indicating $k_Q = (4.9 \pm 0.8) \times 10^8$ M^{-1} s^{-1}. Proton-transfer quenching has also been observed with the aminonaphthalenes[16] and 1-aminopyrene.[17] In the methoxynaphthalenes,[16] it has been shown via H/D isotope labeling experiments that the quenching occurs with protonation of the ring carbons of naphthalene as expected for the molecule in its CT state. We believe that our observations with **1** represent the first example of proton-transfer quenching of a twisted CT state which, although geometrically different from the arylamine CT states, would also be expected to react by way of protonation of the pyrene ring.

Table I. Ground- and Excited-State Acidities

system	pK_a	pK_a*
1-(*p*-aminophenyl)pyrene	4.05	
by Forster cycle		3.3
by fluorescence titration		3.6
aniline	4.58[a]	
1-aminopyrene	2.8[b]	−1.2[c]
1-aminonaphthalene	3.9[d]	−1.0[d]
2-aminonaphthalene	4.1[d]	−0.8[d]

[a] In methanol.[5] [b] In water.[6] [c] In acetonitrile-water, 50:50.[7] [d] In acetonitrile-water, 5:95.[8]

Under conditions where all of **1** in the ground state is in the protonated form, the composite quantum yield for the short (protonated) and long (CT) wavelength fluorescences (Φ_c) was measured (relative to quinine sulfate as a standard). The intrinsic quantum efficiency ($\Phi_{CT}{}^\circ$) of the long-wavelength fluorescence was determined under pH conditions where all of **1** is in the free-base form. The expected quantum yield for the long-wavelength fluorescence under the actual experimental conditions (Φ_{CT}) was determined by correcting $\Phi_{CT}{}^\circ$ for the proton-transfer fluorescence quenching at the specific pH of the medium. The quantum efficiency for deprotonation of the excited conjugate acid (Φ_{-H^+}) can be shown to be given by

$$\Phi_{-H^+} = (\Phi_c/\Phi_{CT})(A_{CT})/A_c \qquad (1)$$

where A_c and A_{CT} are the areas of the composite and long-wavelength fluorescences, respectively. The rate constant for the deprotonation step is defined by

$$k_{-H^+} = \Phi_{-H^+}/\tau_{sw} \qquad (2)$$

where τ_{sw} is the lifetime of the short-wavelength fluorescence. In alcohol-water, $k_{-H^+} = (1.9 \pm 0.4) \times 10^7$ s^{-1} (determined at pH 1.1).

In conclusion, we wish to emphasize the special electronic and geometric features in this system, as summarized in Figure 1, that allow the relatively simple measurement of proton-transfer rates. We are currently investigating the use of **1** as a probe of the influence of the microenvironment on absolute rates of proton transfer.

Acknowledgment. We thank Mr. Mark Gorwitz for preparation of the title compound.

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[11] The similarity of the UV-visible absorption spectra of **1** in nonpolar and polar media indicates that in all media excitation occurs to a pyrene localized π,π^* state.

[12] The "pH" values, obtained with a Markson S-585 semimicro combination pH/reference glass electrode, provide a reliable measure of relative acidities of aqueous ethanol solutions.[13] The measured pH is related to the hydrogen ion activity, referenced to the standard state in aqueous ethanol, by $\mathrm{p}a_H{}^* = \mathrm{pH} - \delta$ where δ is essentially constant for a particular solvent composition. In turn $\delta = (\bar{E}_j - \log {}_m\gamma_H)$ where $\bar{E}_j$ is the residual liquid junction potential in pH units and ${}_m\gamma_H$ is the medium effect for hydrogen ion. For 50 wt% ethanol-water, δ has been variously reported as 0.17, 0.21, and 0.29,[13] which indicates the range of discrepancy between $\mathrm{p}a_H{}^*$ and pH as well as the magnitude of correction that may be applied to the pK_a values in Table I.

[13] Bates, R. G. "Determination of pH. Theory and Practice", 2nd ed.; Wiley: New York, 1973; pp 243-251 and references therein.

[14] In this quantity, $\gamma_\pm$ is the mean activity coefficient for HCl in 50% (v/v) aqueous ethanol interpolated from the data of Ivanov, A. I.; Slovetskii, V. I.; Shevelev, A. A.; Fainzil'berg, A. A.; Novikov, S. S. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1967**, 61.

[15] Harris and Selinger (Harris, C. M.; Selinger, B. K. *J. Phys. Chem.* **1980**, *84*, 891) recently pointed out that the rate of proton-transfer quenching shows a dependence on $[H^+](\gamma_\pm)^{-2Z_1}$, where Z_1 is the charge on the species being quenched, because of the influence of the ionic environment. The dependence on $\gamma_\pm{}^2$ in our system may reflect an interaction between the proton quencher and the pyrene radical anion moiety of the CT state ($Z_1 = -1$).

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Novel Syntheses of α,β-Unsaturated Cyclopentenones via Allylzincation of Alkynes[1]

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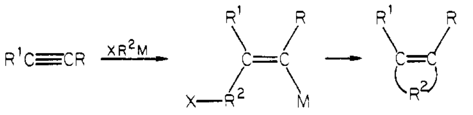
Although virtually untested, cis carbometalation of alkynes with functionally substituted organometallic reagents can produce alkenylmetal derivatives (**1**) that may serve as intermediates for cycloalkenes (eq 1). In view of the significance of α,β-unsaturated



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(1)

R, R¹ = H, C, or hetero atom group; R² = C group
X = functional group
M = metal group

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