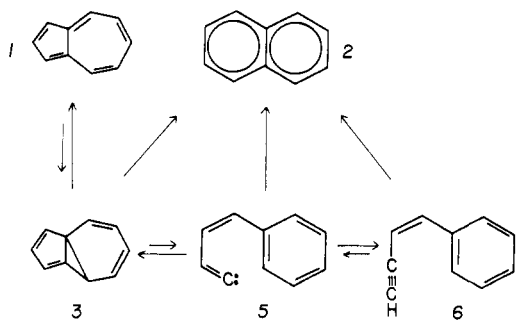
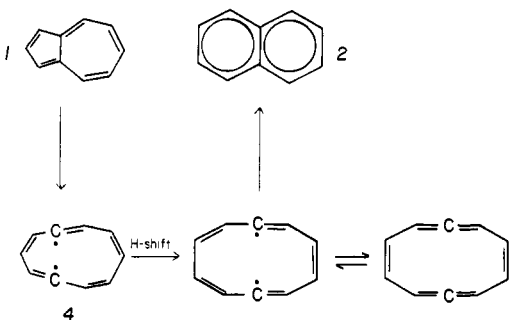


Scheme I



Scheme II



**Table I.** Heats of Formation (kcal/mol) Calculated by MNDO for Molecules and Transition States (TS)

compd	RHF	UHF	TS	RHF	UHF
1	77.1	56.7	1-3	135.3	
2	38.1	30.9	1-4		131.9
3	134.0	124.7	3-11		145.6
4	<sup>a</sup>	131.5	3-8	153.0	
5	116.6	108.0	4-5		181.3
6	158.1	155.0	3-9		131.5
7			6-8	169.8	
8	140.5		6-9		163.0
9		104.3	8-2	155.6	
11		128.5	9-2		144.7

<sup>a</sup>Does not exist on the MNDO surface.

calculate  $\Delta H_f^\ddagger$ 's that are too low by 20–25 kcal/mol for biradicals.<sup>9</sup> Applying this correction to the calculated  $\Delta H_f^\ddagger$  of **9** gives a  $\Delta H_f^\ddagger$  of ca 130 kcal/mol.

The last step involves conversion of **9** (or **8**) to **2** by 1,2 migration of hydrogen. Since MNDO is known<sup>7</sup> to overestimate  $E_a$  for hydrogen migrations (see above), the calculated  $E_a$  is probably too large. Indeed, since the reaction here is very exothermic, it may well take place without activation. Our calculations also indicate that **6** should cyclize to **8** almost without activation (11.7 kcal/mol see Table I). This accounts for the results reported by Becker et al.<sup>5</sup>

Opening of the three-membered ring in **3** can take place in a third way, leading to a spiro diradical (**11**) whose calculated heat of formation is less positive than that of **3**. However, since the corresponding  $E_a$  was very large, it seems unlikely that **11** can play a significant role in the AN reaction.

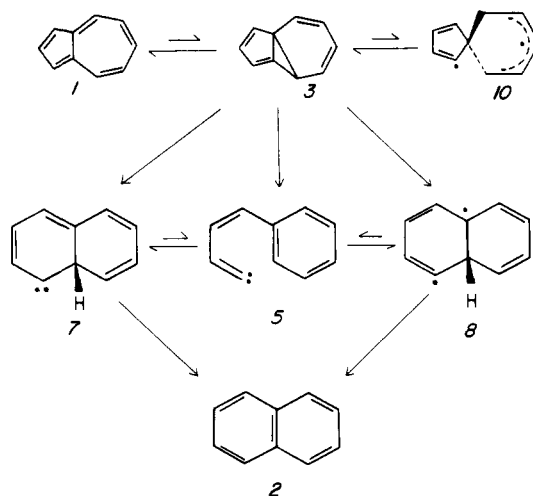
Heilbronner<sup>10</sup> has reported, with some reservations, an  $E_a$  for the AN reaction of  $48.8 \pm 0.8$  kcal/mol, approximately 26.5 kcal/mol less than the MNDO values (**1-8**  $E_a = 75.9$  kcal/mol; **1-9**,  $E_a = 74.8$  kcal/mol). MNDO, however, gives an  $E_a$  for the electrocyclic conversion of cyclobutene to butadiene that is also too large by a comparable amount (16.88 kcal/mol<sup>11</sup>) so our results are consistent with Scheme I, assuming the second step is rate-determining.

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Scheme III



The mechanism presented here generally agrees with the available labeling data,<sup>5,6,12</sup> accounting for 80–90% of the labeled products. Indeed, other intramolecular mechanisms have also been able to account for 80–90% of the observed labeled products, but our calculations have now eliminated these as possibilities. A detailed search of the potential surface, which will be reported elsewhere, indicated that the remaining species are probably not formed from **1** by intramolecular rearrangement because the  $E_a$  for all reasonable routes were too large.

**Acknowledgment.** This work was supported by the Air Force Office of Scientific Research (Contract F49620-83-C-0024), the Robert A. Welch Foundation (Grant F-126), the National Science Foundation (Grant CHE82-17948), and the Tektronix Foundation.

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### Intramolecular Photochemical Electron Transfer. 3. Solvent Dependence of Fluorescence Quenching and Electron Transfer Rates in a Porphyrin-Amide-Quinone Molecule<sup>†</sup>

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Synthetic porphyrins covalently linked to quinones have received much attention as models of the primary electron transfer in photosynthesis.<sup>1</sup> As an extension of our own work<sup>2</sup> in this area

<sup>†</sup> Publication 342, Photochemistry Unit, Department of Chemistry, University of Western Ontario.

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Table I

solvent	$\epsilon^a$	$n^a$	$\Delta E_{\text{solvent}}^-$ $\Delta E_{\text{ether}}^-$ eV	$\tau_1/$ ns <sup>f</sup>	$\tau_2/$ ns <sup>f</sup>	$k_{\text{CT}}/$ $10^8$ s <sup>-1g</sup>
ethyl ether	4.33	1.352	0.00	10.77	12.77	0.14
1,2-DME <sup>b</sup>	7.20	1.380	-0.17	10.05	12.41	0.19
<i>p</i> -dioxane	2.21	1.422	-0.17	8.34	11.92	0.36
MTHF <sup>c</sup>	7.60	1.406 <sup>d</sup>	-0.28	9.43	11.69	0.20
acetone	20.7	1.359	-0.17	8.92	12.15	0.30
ethyl acetate	6.02	1.372	-0.12	9.52	11.9	0.21
CH <sub>3</sub> CN	37.5	1.344	-0.13	7.39	11.89	0.51
<i>n</i> -PrCN	20.3	1.384	-0.27	7.12	11.31	0.52
<i>n</i> -BuOH	17.5	1.399	-0.32	3.15	12.38	2.4
CH <sub>3</sub> CHCl <sub>2</sub>	10.0	1.416	-0.34	1.92	10.5	4.3
CH <sub>2</sub> Cl <sub>2</sub>	9.14	1.424	-0.36	1.09	9.14	8.1
CHCl <sub>3</sub>	4.81	1.446	-0.38	0.424	9.05	23
CH <sub>2</sub> CCl <sub>3</sub>	7.53	1.438	-0.40	1.69	10.55	5.0
CH <sub>2</sub> ClCH <sub>2</sub> Cl	10.60	1.445	-0.46	1.56	9.61	5.4
CH <sub>2</sub> BrCH <sub>2</sub> Br	4.78	1.539	-0.71	0.521	1.54 <sup>h</sup>	13
benzene	2.27	1.501	-0.47	3.63	11.2	1.9
toluene	2.38	1.497	-0.46	4.77	11.7	1.2
chlorobenzene	5.62	1.525	-0.68	1.15	11.0	7.8
anisole	4.33	1.517	-0.62	2.45	11.9	3.2
benzyl ether	4.3	1.541	-0.70	3.45	11.7	2.0
benzonitrile	25.6	1.527	-0.80	2.08	11.7	3.9
Cl-naph <sup>e</sup>	5.04	1.633	-1.03	1.16	10.6	7.7

<sup>a</sup>All values are at 20 °C, taken from: Murov, S. L. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973; p 85. Riddick, J. A.; Bunger, W. B. "Techniques of Chemistry, II, Organic Solvents", 3rd ed.; Wiley: New York, 1970. Unless otherwise indicated. <sup>b</sup>1,2-Dimethoxyethane. <sup>c</sup>2-Methyltetrahydrofuran. <sup>d</sup>"Handbook of Chemistry and Physics"; 63rd ed.; Weast, R., Ed.; Chemical Rubber Company: Boca Raton, FL, 1982-1983; p C-304. <sup>e</sup>1-Chloronaphthalene. <sup>f</sup>Lifetimes > 2 ns were measured by using excitation from a hydrogen flash lamp with a pulse width of 2 ns. Shorter lifetimes were detd. by using a pulsed argon ion rhodamine-6G dye laser with a response time of 300 ps. Error in the lifetimes is estimated at  $\pm 5\%$ . <sup>g</sup>Error in  $k_{\text{CT}}$  is estimated at  $\pm 10\%$ .

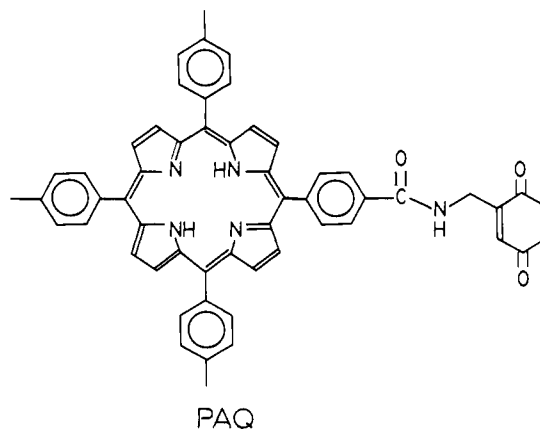
we have synthesized PAQ<sup>3a</sup> (see structure) and its hydroquinone derivative PAQH<sub>2</sub> and have investigated their photophysical properties. Fluorescence lifetime and optical flash photolysis results<sup>3b</sup> suggest that intramolecular electron transfer is a major

(3) PAQ and PAQH<sub>2</sub> were prepared and characterized in the following way: 5-(4-carboxyphenyl)-10,15,20-tri(*p*-tolyl)porphyrin<sup>4</sup> (TTPa) was coupled via its acid chloride with 2,5-dimethoxybenzylamine,<sup>5</sup> giving an amide compound, mp >300 °C. Exact mass: observed 849.361, calculated for C<sub>57</sub>H<sub>47</sub>N<sub>5</sub>O<sub>3</sub> 849.368. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz)  $\delta$  8.90-8.76 (8 H, s superimposed on AB quartet  $J = 4$  Hz,  $\beta$ -pyrrole), 8.31-8.14 (4 H, AB quartet  $J = 8$  Hz, 4-benzoyl aromatic), 8.11 (6 H, d,  $J = 8$  Hz, tolyl aromatic closest to porphyrin ring), 7.57 (6 H, d,  $J = 8$  Hz, tolyl aromatic farthest from porphyrin ring), 7.10, 6.89, (3 H, m, aromatic of 2,5 dimethoxyphenyl), 7.03 (1 H, t,  $J = 6$  Hz, shown by homo decoupling to be coupled to benzyl methylene signal at 4.81, N-H), 4.81 (2 H, d,  $J = 6$  Hz, benzyl methylene), 3.95 (3 H, s, methoxy), 3.84 (3 H, s, methoxy), 2.72 (9 H, s, tolyl methyl), 2.78 (2 H, s, br, pyrrole N-H). Elemental analysis: obsd C 80.54%, H 5.32%, N 8.22%. Calcd C 80.54%, H 5.57%, N 8.24%. This amide compound was treated with BBr<sub>3</sub> to give the hydroquinone PAQH<sub>2</sub>, m.p. > 300 °C. Exact mass: observed: 821.340, calculated for C<sub>55</sub>H<sub>43</sub>N<sub>5</sub>O<sub>3</sub>: 821.337. <sup>1</sup>H NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>, 200 MHz)  $\delta$  9.32 (1 H, t,  $J = 6$  Hz, shown by homo decoupling to be coupled to doublet signal at 4.56, amide N-H), 8.90 (1 H, s, signal disappears on treatment with D<sub>2</sub>O, hydroquinone O-H), 8.85 (8 H, m,  $\beta$ -pyrrole), 8.74 (1 H, s, signal disappears on treatment with D<sub>2</sub>O, hydroquinone O-H), 8.38 (4 H, m, 4-benzoyl aromatic), 8.11 (6 H, d,  $J = 8$  Hz, tolyl protons closest to porphyrin ring), 7.64 (6 H, d,  $J = 8$  Hz, tolyl protons farthest from porphyrin ring), 6.80 (1 H, d,  $J = 2$  Hz, 6-proton on hydroquinone ring), 6.71 (1 H, d,  $J = 6$  Hz, 3-proton on hydroquinone ring), 6.55 (1 H, doublet of doublets,  $J = 2$  Hz and 6 Hz, 4-proton on hydroquinone ring), 4.56 (2 H, d,  $J = 6$  Hz, benzyl methylene), 2.68 (9 H, s, tolyl methyl), -2.92 (2 H, s, br, pyrrole N-H). PAQ was freshly prepared before each experiment by shaking a solution of PAQH<sub>2</sub> with PbO<sub>2</sub>. The formation of the quinone was confirmed by the presence of its characteristic optical absorption at 246 nm.<sup>4a,b</sup> (b) Results from optical flash photolysis experiments are consistent with the formation of a porphyrin radical cation following excitation of the porphyrin. These will be described in a future publication.

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decay path of the porphyrin excited singlet state of PAQ. Here we report that the forward electron-transfer rate constant (as determined from time-resolved fluorescence experiments) is characterized by a strong dependence on the solvent refractive index.

The fluorescence decay times for PAQ and PAQH<sub>2</sub> in a variety of solvents were determined by the single photon counting technique, as previously described.<sup>2b</sup> The results are listed in Table I.  $\tau_1$  and  $\tau_2$  are the decay times for PAQ and PAQH<sub>2</sub>, respectively.  $\epsilon$  is the static dielectric constant and  $n$  is the refractive index of the solvent. The shortening of the PAQ fluorescence lifetime, relative to that of PAQH<sub>2</sub>, is assumed to be entirely a consequence of intramolecular electron transfer from singlet excited porphyrin to quinone.<sup>7</sup> The electron-transfer rate constant is then given by<sup>2b</sup>

$$k_{\text{CT}} = \tau_1^{-1} - \tau_2^{-1} \quad (1)$$

The observed rate constants  $k_{\text{CT}}$  vary over about 2 orders of magnitude. They do not appear to be related in any simple way to the dielectric constant of the solvent; however, there appears to be a correlation with the refractive index (see Table I). The optical dielectric constant ( $n^2 = \lim_{\omega \rightarrow \infty} \epsilon(\omega)$  where  $\omega$  is the frequency of the electric field) is related to polarization under conditions where nuclear and orientational motions are frozen. The  $n$  dependence of  $k_{\text{CT}}$  suggests that the final charge-separated state has characteristics of a Franck-Condon state.

We interpret our results within the following model. The relative positions of the reactant and product surfaces are shifted by solvent interactions, giving rise to a solvent-dependent activation barrier. In terms of Marcus electron-transfer theory<sup>9,10</sup> this results from variations in the solvent reorganization energy and from the solvent dependence of the reaction free energy. Further, we suggest that the solvent dependence of a Franck-Condon transition from the reactant surface to the product surface should reflect the solvent dependence of the activation barrier. The expression

$$\Delta E = E_2^0 - E_1^0 - \mu_1 \mu_2 (f_\epsilon - f_n) - \frac{1}{2} \mu_2^2 f_n + \mu_1^2 (f_\epsilon - f_n / 2) \quad (2)$$

where

$$f_\epsilon = 2/a^3(\epsilon - 1)/(\epsilon + 2) \quad (3)$$

$$f_n = 2/a^3(n^2 - 1)/(n^2 + 2) \quad (4)$$

has been derived,<sup>11</sup> to describe the energy separation between a thermally equilibrated state 1 and a Franck-Condon state 2 (i.e., an optical transition),<sup>12</sup> in a solvent of static dielectric constant

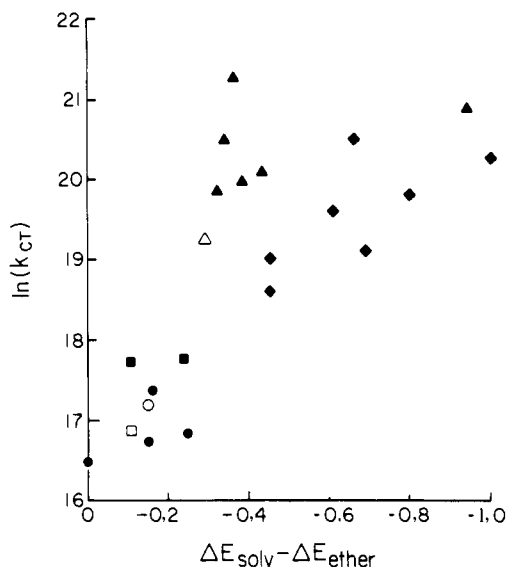
(7) Electron transfer from the porphyrin S<sub>1</sub> state to hydroquinone is highly endergonic while electron transfer to quinone is exergonic,<sup>8</sup> thus PAQH<sub>2</sub> is an ideal control compound for this study.

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**Figure 1.** Plot of  $\ln(k_{CT})$  vs. energy separation arising from solvent interactions,  $\Delta E_{solv} - \Delta E_{ether}$ , as calculated from eq 5: (●) ether solvents; (■) nitrile solvents; (○) acetone; (△) 1-butanol; (▲) halocarbons; (□) ethyl acetate; (◆) aromatic solvents.

$\epsilon$  and refractive index  $n$ .  $E_1^\circ$ ,  $E_2^\circ$  and  $\mu_1$ ,  $\mu_2$  are the gas-phase energies and dipole moments of states 1 and 2, respectively. In this treatment, solute-solvent interactions are described by the Onsager reaction field model.<sup>13</sup> The molecule is approximated by a point dipole at the center of a spherical cavity of radius " $a$ ", usually taken as the molecular radius. This spherical cavity is immersed in the solvent, considered to be a homogeneous dielectric of dielectric constant  $\epsilon$ . For PAQ, space-filling molecular models give a maximum porphyrin-quinone center-to-center distance of  $\approx 15 \text{ \AA}$  (hence  $a \approx 7.5 \text{ \AA}$ ),<sup>14</sup> which generates a dipole moment  $\mu_2 \approx 72 \text{ D}$  in the charge-separated state. The porphyrin excited singlet state is essentially nonpolar; for this we assumed  $\mu_1 \approx 2 \text{ D}$ . With these parameters the change in energy separation of the two states arising from solvent interactions is given by the last three terms of eq 2,

$$\Delta E_{solv} = -90(f_\epsilon - f_n) - 1600f_n + 2.5(f_\epsilon - f_n/2) \quad (5)$$

A factor of  $0.622 \text{ eV/D}^2 \text{ \AA}^{-3}$  is incorporated into the constants of (5) so that  $\Delta E_{solv}$  is in electronvolts if " $a$ ", the molecular radius, is in angstroms. The dominance of the term involving  $f_n$  is a consequence of the large dipole moment in the  $P^+Q^-$  state.

Table I lists the solvation energies relative to that for diethyl ether, where little electron transfer occurs. A plot of  $\ln(k_{CT})$  vs. the energy separation resulting from solvent interactions (Figure 1) shows a good qualitative correlation between these two quantities. The actual  $P^+Q^-$  molecular radius, and therefore the optimal values of " $a$ " and  $\mu_2$ , is probably somewhat solvent-dependent. Thus, using a constant value of the molecular radius to determine " $a$ " and  $\mu_2$  limits the usefulness of this model to qualitative predictions of solvent effects.

These results are significant because they suggest that in linked donor-acceptor molecules, solvent effects on the energy of the Franck-Condon charge-transfer state can have a profound effect

(12) The electron transfer does not occur via a vertical transition to the Franck-Condon coordinates of the product potential energy surface. However, a change in the energy of the Franck-Condon transition should reflect a qualitatively similar change in the activation energy.

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(14) The choice of the center-to-center distance of the "stretched" conformation to evaluate  $\mu_2$  and " $a$ " is arbitrary. Ring current calculations<sup>15</sup> (from 500 MHz NMR results) for a similar porphyrin-quinone molecule suggest that a conformation with a separation of  $\approx 11 \text{ \AA}$  might be more appropriate. Such a change does not affect the qualitative results of our model.

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on the rate of intramolecular electron transfer.

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### Organic Reactions in Liquid-Crystalline Solvents. 3. Substituted $\beta$ -Phenylpropiophenones as Photochemical Probes of Solute-Solvent Interactions in Liquid Crystals

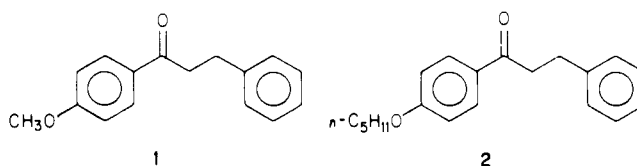
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There has been considerable recent interest in the possible effects of liquid-crystalline order on the unimolecular reactivity of dissolved solutes.<sup>2,3</sup> Cyclization reactions have received particular attention,<sup>2</sup> effects on reactivity being expected to the extent that for a rodlike solute, such a process might involve disruption of local solvent order as the transition state is approached. With a few interesting exceptions,<sup>2b,k,l</sup> only small or negligible effects on reactivity have been observed, even with the highly ordered smectic liquid crystals. We wish to report one of the largest effects observed to date of smectic solvents on the energetics of a unimolecular reaction. Furthermore, our results indicate that the ability of smectic phases to inhibit cyclization of even a highly oriented solute may depend critically on structural features defining the "fit" of the solute into the smectic array.

We have measured the triplet lifetimes ( $\tau_T$ ) of two  $\beta$ -phenyl-4-alkoxypropiophenones **1** and **2**<sup>4</sup> between 30 and 95 °C in



*trans,trans*-4'-butylbicyclohexyl-4-carbonitrile (BCCN) and the 4'-ethyl homologue (ECCN) by nanosecond laser flash photolysis.<sup>6</sup>

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(4) Laser excitation of 1.0 mol % (ca. 0.02 M) solutions of **1** and **2** in these two solvents yields transients that decay with clean first-order kinetics and whose UV absorption spectra ( $\lambda_{max} = 395 \text{ nm}$ ) are similar to that previously reported for the triplet state of **1**.<sup>5a,b</sup>

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