

Photoaddition of Water and Alcohols to the Anthracene Moiety of 9-(2'-Hydroxyphenyl)anthracene via Formal Excited State Intramolecular Proton Transfer

Mitchel Flegel, Matthew Lukeman, Lawrence Huck, and Peter Wan*

Contribution from the Department of Chemistry, Box 3065, University of Victoria,
British Columbia, Canada, V8W 3V6

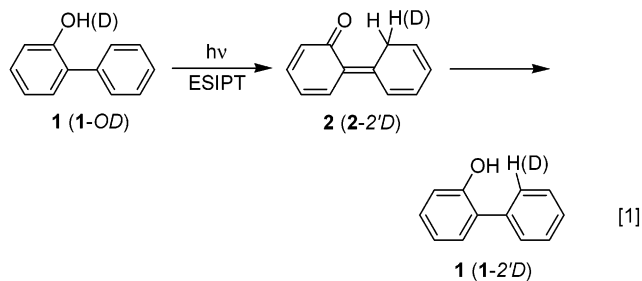
Received October 15, 2003; E-mail: pwan@uvic.ca

Abstract: The title compound undergoes efficient photoaddition of a molecule of a hydroxylic solvent (H₂O, MeOH, (Me)₂CHOH) across the 9- and 10-positions of the anthracene moiety to give isolable triphenylmethanol or triphenylmethyl ether type products. The reaction is believed to proceed via a mechanism involving water-mediated formal excited state intramolecular proton transfer (ESIPT) from the phenolic OH to the 10-position of the anthracene ring, generating an *o*-quinone methide intermediate that is observable by nanosecond laser flash photolysis, and is trappable with nucleophiles. A “water-relay” mechanism for proton transfer seems plausible but cannot be proven directly with the data available. Irradiation in deuterated solvents led to incorporation of one deuterium atom at the methylene position in the photoaddition product, and partial deuterium exchange of the 10-position of recovered starting material, consistent with the proposed formal excited state proton transfer mechanism. The deuterium exchange and photoaddition reach maximum quantum efficiency at ~5 M water (in CH₃CN or CH₃OH), with no reaction observed in the absence of a hydroxylic solvent, demonstrating the sensitivity of this type of ESIPT to solvent composition.

Introduction

Excited state intramolecular proton transfer (ESIPT) processes continue to be a subject of widespread research efforts, years after the field was opened up with the pioneering work of Weller.^{1,2} ESIPT arises when a molecule contains both acidic and basic functionalities that experience simultaneous enhancement in both their acidity and basicity, respectively, when electronically excited, permitting the transfer of a proton from the acidic group to the basic group. The systems that have received the most attention are those in which the acidic group is an OH or NH acid and the basic group is a heteroatom, such as a carbonyl oxygen or heterocyclic nitrogen atom. The key feature of these systems is that both the forward proton transfer (to give the tautomer) and the subsequent reverse proton transfer (to regenerate the starting material) are extremely fast processes, usually occurring on the subpicosecond time scale.

More recently, we have reported a new type of ESIPT (from a phenol OH) to a carbon atom that is part of an aromatic ring.³ ESIPT in **1-OD** gave quinone methide **2-2'D**, which underwent reverse proton transfer to give **1-2'D** (eq 1). The reaction was observed to proceed in a variety of solvents and in the solid state, indicating that the proton transfer is intrinsic (water is



not required to mediate the proton transfer). Since this discovery, we have reported a similar ESIPT that is operative in systems in which the proton acceptor is a 1-naphthyl group.⁴ In these systems, dihydrobenzoxanthene products were photogenerated. For example, ESIPT from the phenol OH to the 7'-aromatic carbon atom in **3** led to formation of quinone methide **4**, which underwent electrocyclic ring closure to give the isolable **5** with reasonably high quantum efficiency ($\Phi = 0.20$). In addition to this pathway, ESIPT to the 2'-carbon is operative, as evidenced by deuterium incorporation in recovered starting material. Both routes required that a sufficient amount of water in the solvent mixture (~5 M) to reach maximum efficiency.

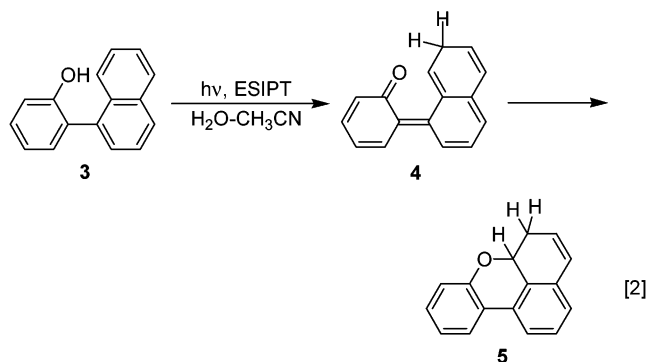
Our current interest in the photochemistry of *o*-hydroxybiaryls led us to consider derivatives bearing an anthracenyl substituent. Hydroxy-substituted phenylanthracenes have received considerable attention recently for their ability to form hydrogen-bonded networks with cavities capable of including guest molecules.⁵

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The interest in using these derivatives in the engineering of such crystals is primarily because the 90° twist angle between the two aryl rings leads to predictable and well-defined crystal geometries. Potential photoreactivity in these systems could lead to a disruption of the geometry of the crystal networks and their guest binding properties. We chose to study 9-(2'-hydroxyphenyl)anthracene (**6**), which was readily prepared from commercially available 9-bromoanthracene. It was anticipated that a formal ESIPT from the phenol OH to one or more aromatic carbon positions of the anthracenyl moiety might lead to similar reactivity as observed for **1** and **3**, namely deuterium incorporation and photocyclization. We report that a formal ESIPT in **6** does not give rise to ring-closed products as expected, but instead gives products resulting from photoaddition of either a water or an alcohol molecule across the 9- and 10-positions of the anthracene ring system. While the photohydration of alkenes and alkynes via ESIPT is well-known,⁶ to our knowledge, this is the first report of the photoaddition of a hydroxylic solvent to an aromatic ring system resulting from an ESIPT process.

Results and Discussion

Product Studies. We first probed the photoreactivity of **6** by UV-vis spectrophotometry, by irradiating quartz cells containing the substrate ($\sim 10^{-6}$ M) in 1:9 (v/v) H₂O-CH₃CN (deoxygenated) in a Rayonet RPR-100 reactor (350 nm lamps). Traces were recorded at regular time intervals throughout the course of the irradiation, with representative traces shown in Figure 1. Irradiation led to a decrease in the intensity of the absorption maxima at 384, 364, 346, 330, and 254 nm, indicating loss of the anthracene chromophore. The absorption bands associated with the phenol chromophore (220 and 280 nm) remain, suggesting that this moiety is not lost in the transformation. No new absorption bands were observed to grow in, suggesting that benzoxanthene-type products that would arise from photocyclization⁴ are not formed. Irradiation of **6** in anhydrous CH₃CN did not lead to any observable changes in the absorption spectrum. Irradiation in neat CH₃OH led to

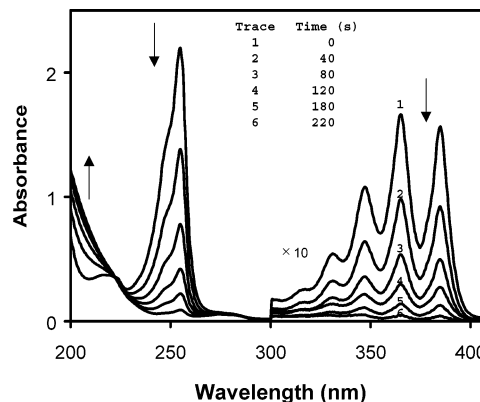
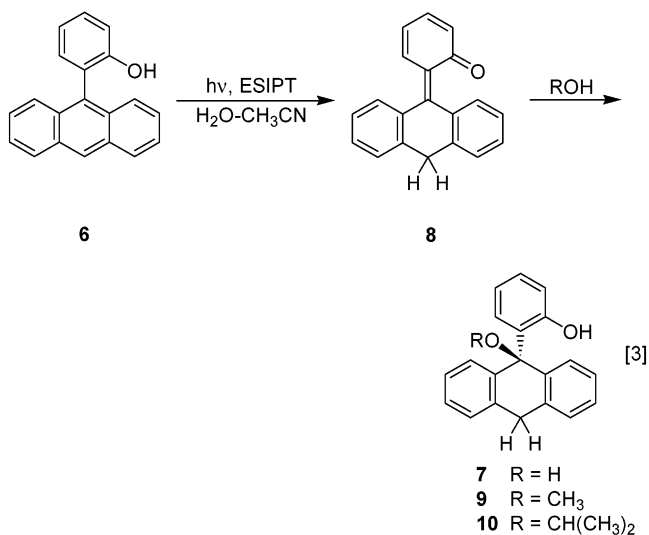


Figure 1. UV-vis spectra showing loss of anthracene chromophore (250 and 365 nm) of **6** with photolysis time. Photolysis was carried out in a Rayonet RPR-100 reactor with 16 lamps (350 nm) (1:9 H₂O-CH₃CN, argon saturated). Representative traces are shown with the corresponding irradiation times given in the figure. Spectral data for wavelengths longer than 300 nm are expanded 10-fold.

similar changes as observed in aqueous CH₃CN, indicating that the reaction requires the mediation of a hydroxylic solvent. Addition of 5 M water to the CH₃OH solution led to a 25% enhancement of the reaction that gives rise to the absorption loss, indicating that water is better at mediating the reaction than CH₃OH.

In an effort to isolate and characterize the products of the photoreaction, a preparatory scale photolysis was carried out ($\sim 10^{-3}$ M, 1:9 H₂O-CH₃CN, for solubility a higher ratio of CH₃CN cosolvent was used; 350 nm). A single photoproduct was formed in 58% yield and was chromatographically separated from the unreacted starting material. NMR analysis is consistent with assignment of this to the photohydration product **7** (eq 3).

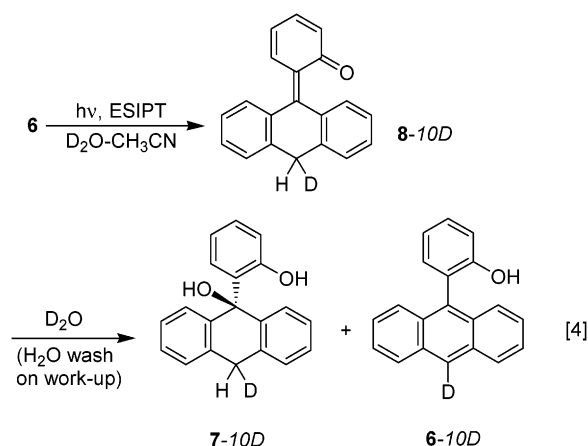


This product would arise from nucleophilic trapping (by water) of quinone methide **8** formed by an envisioned formal ESIPT process from the phenol OH to the 10-position. The addition of water to the anthracene ring essentially converts this chromophore into three isolated phenyl rings, explaining the loss of the characteristic anthracene absorption (and growth in absorption at wavelengths shorter than 220 nm) observed in the UV-vis studies. Extending the irradiation time allowed quantitative generation of **7**, with no observable side products.

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Quantitative dehydration of **7** (to refurnish **6**) was achieved by 12 h reflux in toluene. Irradiation of solutions of **6** in methanol or 2-propanol (in 1:2:5 ROH:H₂O:CH₃CN) gave ethers **9** and **10**, respectively, with high efficiency. These reactions could also be taken to quantitative conversion with shorter photolysis times than those used for the quantitative formation of **7**. This is likely due to the enhanced nucleophilicity of the alcohols relative to water⁷ which allows for more efficient trapping of **8**, minimizing thermal tautomerization back to **6**. Trapping of **8** by hydride was also achieved: irradiation of **6** in the presence of NaBH₄ gave **11** in good yield (>50%). No reaction was observed when **6** was irradiated in neat CH₃CN.

ESIPT processes for **1** and **3** that did not give isolable products were implicated by irradiating the substrates in D₂O and analyzing the recovered starting material for deuterium exchange. To probe whether such processes are also available for **6**, irradiations were carried out as described above, but with the H₂O portion replaced with D₂O. Irradiation of **6** (~10⁻⁴ M, 10 min) gave **7** with one deuterium incorporated at the methylene position (7-10D) in 70% yield (eq 4). Starting



material from this run which constituted the remaining 30% of the material present showed deuterium exchange (~70%) at the carbon atom at the 10-position (**6-10D**) with no exchange observed at any other position. This suggests that the formal ESIPT in **6** can only occur to the 10-position to give **8** (or **8-10D**). Therefore, formation of **6-10D** most likely occurs via tautomerization of **8-10D**.

The methyl ether derivative **12** was studied in a manner similar to that for **6**. This derivative lacks an acidic proton and thus cannot undergo excited state proton transfer (ESPT) or ESIPT processes. Solutions of **12** irradiated under the same conditions as described for **6** did not yield any photohydration products, and the recovered substrate did not show deuterium exchange when D₂O was used as the cosolvent. Thus, an acidic phenolic proton is required for reaction in these systems, consistent with the operation of a formal ESIPT process.

The study of the effect of water concentration on previously reported ESIPT reactions in our group has uncovered important mechanistic details. For example, the absence of any water effect on the efficiency of ESIPT of **1** led to the conclusion that the ESIPT in this system was intrinsic,³ whereas the ESIPT of **3** required water mediation.⁴ To probe the effect of water content on the proposed ESIPT of **6**, solutions containing varying

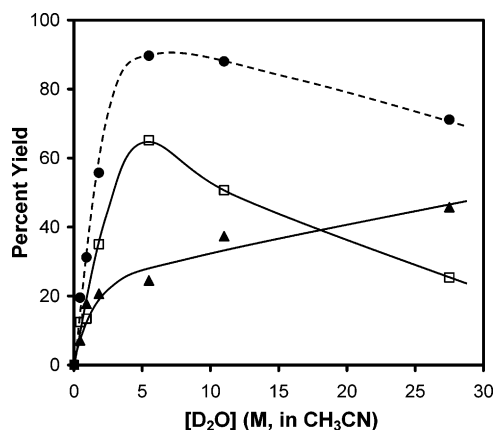


Figure 2. Plot showing percent yield of 7-10D (□), 6-10D (▲), and 8-10D (●) present in photolysate following irradiation of **6** in solvents of varying D₂O concentration (~10⁻³ M, argon saturated, 350 nm lamps, 10 min). The yield of 8-10D was calculated as the sum of 7-10D and 6-10D.

amounts of D₂O (in CH₃CN) were irradiated. The yields of **6-10D** and **7-10D** generated in these runs were determined by ¹H NMR, and results are presented in Figure 2. Since both of these products arise most likely from intermediate **8-10D**, the sum of the yields of these two products (also included in the plot in Figure 2) can be taken as a measure of the yield of formation of this intermediate. The efficiency of quinone methide generation (formation of **8-10D**) shows a strong dependence on water content, with minimal reaction at low water concentrations. The yield of **8-10D** increased sharply as more D₂O was added to the solvent mixture, reaching a maximum at approximately 5 M D₂O. Addition of more D₂O beyond 5 M led to a gradual decrease in the yield of quinone methide, probably due to the enhancement of competing processes, such as ESPT to water to yield the phenolate **6⁻**. The partitioning of intermediate **8-10D** to **6-10D** and **7-10D** is also apparently influenced by the concentration of D₂O; as the water concentration is increased past 5 M, the quinone methide gives more of the deuterium-exchanged starting material **6-10D** at the expense of the photohydrated product **7-10D**. This result is in keeping with expectations since formation of **6-10D** is expected to proceed via a water-catalyzed tautomerization mechanism involving several molecules of water, whereas the nucleophilic attack of **8-10D** to give **7-10D** in principle only requires a single water molecule.

The quantum yield for photogeneration of **8-10D** in 10 M D₂O-CH₃CN was estimated by comparison with the deuterium incorporation reaction of dibenzosuberene.⁸ The sum of **7-10D** and **6-10D** was used to approximate the quinone methide efficiency, and a value for the quantum yield of 0.09 ± 0.01 was obtained (Table 1). This value is similar to efficiencies of quinone methide formation estimated for **1³** and **3**.⁴ The quantum efficiency in H₂O would be expected to be somewhat higher due to the operation of a primary isotope effect in the proton transfer to obtain **8**.

Fluorescence Measurements. The anthracene chromophore is well-known to exhibit strong and structured fluorescence emission;¹⁰ thus use of fluorescence spectrophotometry was expected to be a valuable tool for probing the photoreactivity

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Table 1. Photophysical and Photochemical Parameters for **6**

solvent	Φ_f^a	Φ_f^b	τ_f^c
neat CH ₃ CN	0.00	0.50 ± 0.03	5.9
4 M D ₂ O (in CH ₃ CN)	0.09	~0.25	

^a Quantum yield for formation of **7**-10D and **6**-10D (number shown is sum) from **6** in the solvent indicated. Estimated error is ±10% of the quoted value. Measured relative to the quantum yield for deuterium incorporation reported for dibenzosuberene.⁸ ^b Fluorescence quantum yield measured relative to the reported fluorescence quantum yield of quinine bisulfate in 0.1 N H₂SO₄.⁹ ^c Fluorescence lifetime as measured by single photon counting. Fluorescence decay was first order. Estimated error is ±0.2 ns.

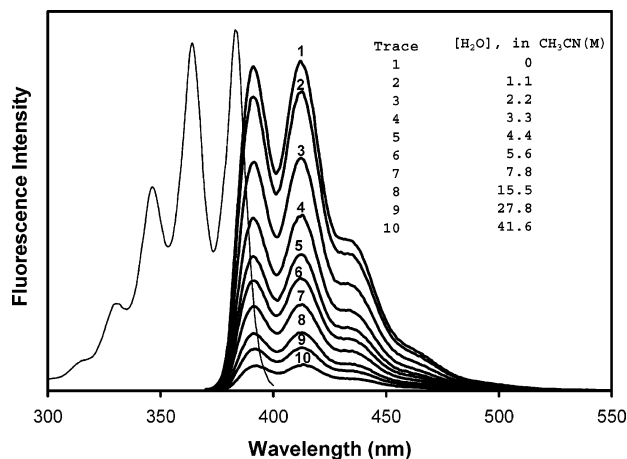
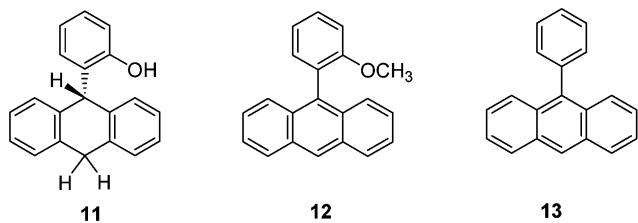


Figure 3. Representative traces for **6** showing quenching of fluorescence emission (in CH₃CN) with added water ($\lambda_{ex} = 365$ nm). Concentrations are given in the figure.

of **6**. Representative fluorescence excitation and emission spectra are shown in Figure 3. Strong and structured emission was observed for **6** with maxima at 391 and 412 nm and shoulders at 435 and 465 nm. The Stokes shift in the fluorescence emission is very slight, and is much smaller than that observed for the unsubstituted parent 9-phenylanthracene (**13**).¹⁰ It has been



shown for **13** through both free-jet laser induced fluorescence studies¹¹ and ab initio molecular orbital calculations¹² that the equilibrium biaryl twist angle changes from 90° in the ground state to 55–60° in S₁. It is this twisting on excitation that is largely responsible for its sizable Stokes shift. The minimal Stokes shift observed for **6** suggests that little or no twisting takes place on excitation, presumably because of the additional steric crowding imparted by the hydroxyl substituent (of the phenol). Thus, the emission is essentially that of unsubstituted anthracene, indicating that the emissive state is not influenced by the phenol moiety.

Addition of water to the solvent led to efficient quenching of the fluorescence emission (Figure 3). A Stern–Volmer plot of the quenching of the steady-state fluorescence by water is

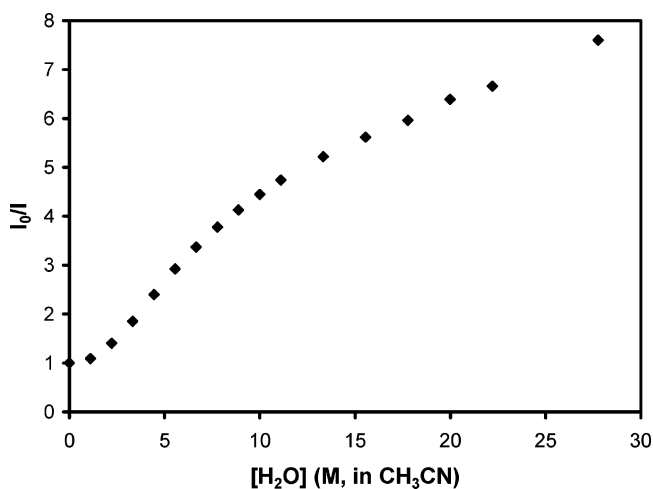


Figure 4. Stern–Volmer plot of fluorescence quenching vs water concentration (in CH₃CN) for **6**.

shown in Figure 4. At low water concentrations, the fluorescence quenching appears to show a squared dependence on water concentration. Nonlinear fluorescence quenching by water has been previously shown for related phenols that can undergo water-mediated ESIPT processes, and has been associated with the involvement of water clusters in the ESIPT process.^{6c,d} At water concentrations above 5 M, there is significant negative deviation from the binomial behavior. This deviation is indicative of a change in the mechanism of fluorescence quenching. It is important to note that the water concentration at which the deviation becomes pronounced (5 M) coincides with the concentration of water at which the formation of **8** reaches maximum efficiency, as described in the product studies. On the basis of this correlation, we assign the fluorescence quenching at concentrations lower than 5 M as due to the increasing efficiency of the formal ESIPT reaction to give **8**. The quenching of the fluorescence at higher water concentrations is probably due to competitive formation of phenolate **6**[−] via ESPT to solvent (a known process for phenols at high water content). No new emission band is observed at high water concentrations indicating that **6**[−], if formed, shows only anthracene emission like the normal form, or is nonemissive. To test for these possibilities, we attempted to record directly the fluorescence spectrum of **6**[−] (formed by dissolving **6** in 1:1 H₂O–CH₃CN, pH 12). This solution gave only weak fluorescence that is identical to the neutral form with no other emission bands, supporting our assertion that **6**[−] does not give unique fluorescence.

The fluorescence quantum yield for **6** (in neat CH₃CN) was measured to be 0.50 ± 0.03 (Table 1), which is essentially the same as for **13** ($\Phi_f = 0.49$ in cyclohexane).¹⁰ The fluorescence lifetime of **6** in neat CH₃CN was measured to be 5.9 ± 0.2 ns (Table 1), also similar to that reported for **13** ($\tau_f = 6.5$ ns in cyclohexane).¹⁰ Both results indicate that addition of the hydroxyl group to the 9-phenylanthracene chromophore does little to affect its photophysical characteristics *unless* water is added to the solvent mixture.

Nanosecond Laser Flash Photolysis (LFP). We have been able to successfully characterize a large variety of photogenerated quinone methide intermediates by LFP. For example, LFP of **14** in 1:1 H₂O–CH₃CN allowed direct detection of *o*-quinone

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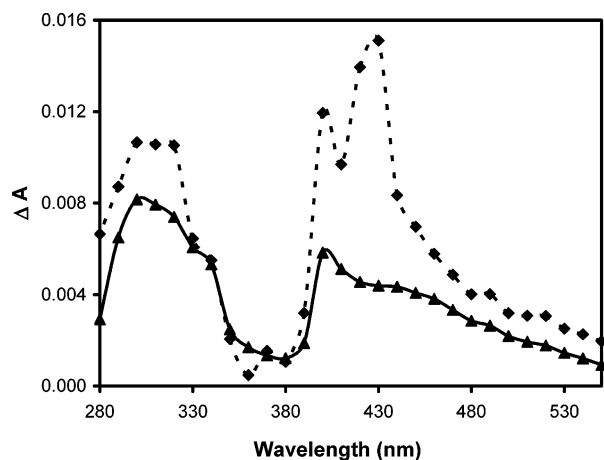
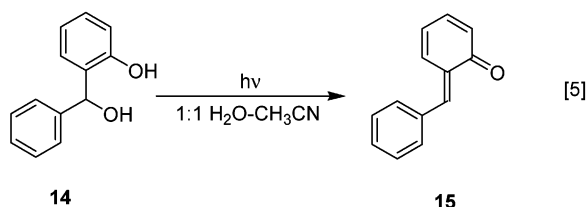


Figure 5. Transient absorption spectra recorded by LFP of **6** in 5 M H₂O (in CH₃CN) taken 0.3 (dashed line) and 15 μs (solid line) after laser flash ($\lambda_{\text{ex}} = 266$ nm). Data between 330 and 390 nm are obscured due to bleaching of the substrate.

methide **15** that is formed by net photodehydration (eq 5).¹³



The transient showed a strong absorption band at 350 nm and a weaker and broader band at 450 nm, with both bands decaying to baseline with a lifetime of 5–10 s. The quinone methide intermediate **8** formed by formal ESIPT reaction of **6** in this study bears a structural resemblance to quinone methide **15** and is therefore expected to possess similar absorption characteristics. The steric demands on **8** (vide infra) are more severe than those for **15**, so we were expecting the former to decay faster.

LFP of **6** in 1:9 H₂O–CH₃CN under nitrogen-purged conditions gave rise to a transient absorption between 280 and 550 nm (Figure 5). Absorption between 330 and 390 nm could not be reliably measured due to bleaching of the absorption of the substrate **6** in this region by the laser flash. Two transients were readily identifiable. A short-lived species ($\tau = 250$ ns) was detected that showed an absorption maximum at 430 nm and absorbed across the entire spectral range measured, as shown in Figure 5. Saturating the solution with oxygen reduced the lifetime of this species to 50 ns. This transient is assigned to the triplet state of **6** on the basis of its sensitivity to oxygen and its spectral similarity to the known T–T absorption of **13** ($\lambda_{\text{max}} = 428$ nm).¹⁴ The second transient that was detected is too long-lived for the decay rate to be reliably measured by the available experimental setup, indicating that the lifetime is on the order of milliseconds or greater. Attempts to detect this intermediate by conventional UV–vis techniques failed, indicating that the lifetime is shorter than several seconds. Thus, we estimate that the lifetime of **8** is between 10 ms and 1 s, which is in line with expectations for this quinone methide. While an

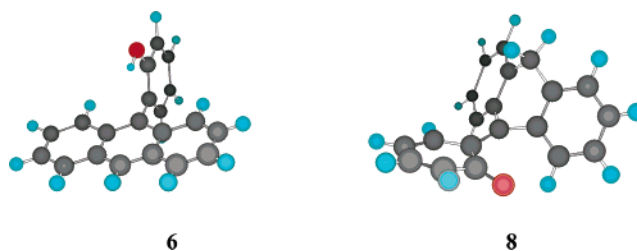


Figure 6. Chem 3D (MOPAC; AM1) minimized ground state structures of substrate **6** and proposed quinone methide intermediate **8**. The dihedral angle between the phenol and the anthracene ring of **6** is about 90°. The distance between the phenol OH and the anthracene 10-position (site of protonation) of **6** is 4.203 Å, which is too far for a simple direct proton transfer.

important spectral region was obscured by substrate bleaching, the region that is visible shows absorption characteristics expected for **8**: absorption between 280 and 550 nm and a maximum (or shoulder) at 440–450 nm. Thus we are confident in assigning this transient absorption to that of **8** based on its similarity to the known absorbance and lifetime characteristics of the related quinone methide **15**.

Mechanism of Reaction. Our data are fully consistent with formation of the critical quinone methide intermediate **8** on photolysis of **6** in aqueous CH₃CN or water–alcohol solutions. It is informative to consider the changes in molecular geometry that are required in this transformation. Chem 3D (MOPAC, AM1) minimized ground state structures are shown in Figure 6 for **6** and **8**. The two aromatic rings of the starting compound **6** are essentially orthogonal to each other (dihedral angle $\sim 90^\circ$). The distance between the phenolic OH and the carbon-10 on the anthracene ring (position of protonation) is 4.203 Å, which is too far for a simple direct proton transfer from the phenol. Thus, unlike the ESIPT reported for **1**,³ compound **6** does not react without the mediation of a hydroxylic solvent. Moreover, reaction of **6** involves substantial molecular distortions: (i) the originally orthogonal phenol ring twists by about 90° such that it becomes somewhat coplanar with the central ring of the “anthracene”; (ii) the anthracene ring puckers out of planarity as the 10-position is protonated. Another important consideration in the discussion of mechanism is the sequence of events that results in the *formal* proton transfer that occurs when **6** forms **8** (these two are tautomeric structures, as would be required in an ESIPT process, formal or otherwise). We have so far designated this as a *formal* ESIPT, but a discussion of how this actually occurs would be important in any mechanistic discussion.

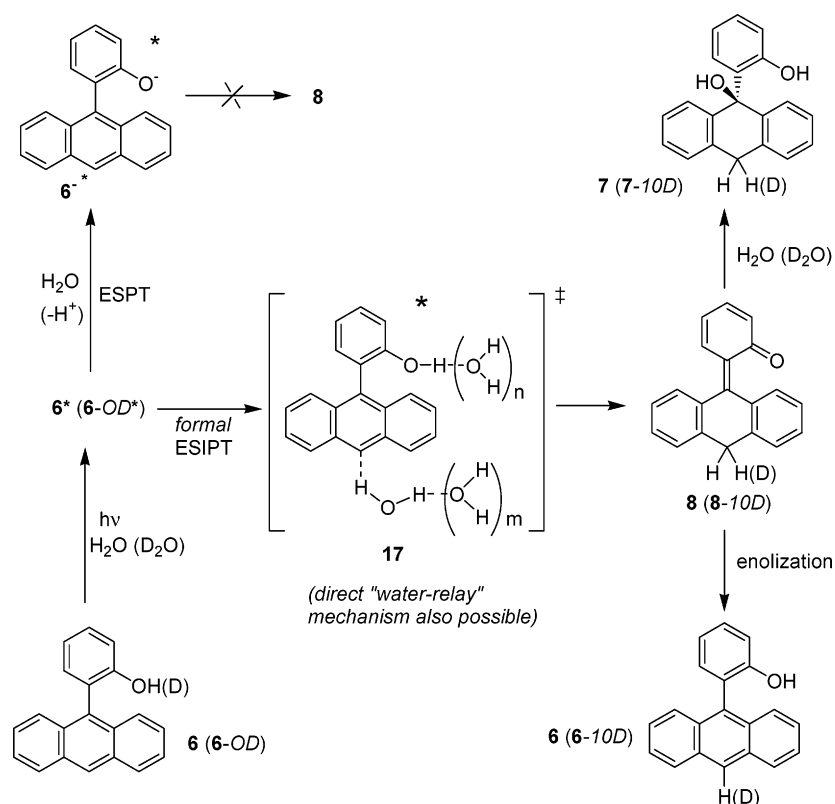
The timing of the events discussed above are probably very fast (picosecond or faster time scale), and a detailed analysis of all the steps would be beyond the scope of this work. Indeed, our LFP studies (nanosecond time resolution) were only able to discern the “instantaneous” formations of triplet–triplet absorption and a long-lived transient assignable to quinone methide **8**. However, these results coupled with fluorescence quenching studies clearly point to the singlet state of **6** as the reactive state. This is in accord with a number of other photoreactions of phenols in aqueous solution reported by our group.^{6,13}

A provisional mechanism that is consistent with all current experimental data for the observed photochemistry of **6** is presented in Scheme 1. Once formed, quinone methide **8** is transformed to **7** (hydration product) or returns to **6** via

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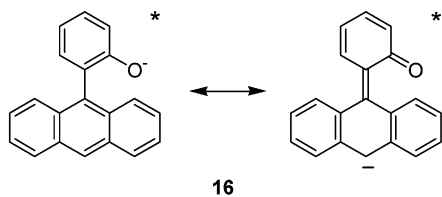
Scheme 1



enolization. These two reaction pathways from **8** are really not surprising apart from the isolation of the stable anthracene hydrates and alcohol adducts.

In order for **6** to proceed to **8**, the following must occur: (i) a formal proton transfer from the phenol OH to the carbon atom at the 10-position of the anthracene moiety, the latter resulting in a puckering of the anthracene ring geometry, and (ii) twisting about the biaryl bond to (or toward) planarity. These two events may be coupled (i.e., concerted) or stepwise. Fluorescence results indicate that in neat CH₃CN, a solvent that is unable to mediate the proton transfer and where there is no photochemistry, the excited state geometry remains highly twisted, as only emission from the anthracene chromophore was observed, with essentially no Stokes shift. Charge transfer from the phenol ring to the anthracene ring in the excited state is thought to be the driving force for the ESIPT, but this cannot occur if the two rings are in a perpendicular arrangement. The situation is changed when water (or alcohol) is present in the solvent mixture. Now the formal ESIPT reaction proceeds readily, as determined by the product studies and fluorescence quenching results.

One simple pathway for the overall reaction is as follows. The added water mediates the ionization of the phenol, to give rise to an electronically excited phenolate, which then twists to a more planar form **16**. The more planar form can then protonate



at the carbon 10-position to give **8**. The whole process could be concerted, via **17**. This simple mechanism is consistent with most of the experimental data. One interesting point is that the reaction is observed at very low water content (maximal efficiency at about 5 M H₂O, in CH₃CN, Figures 2 and 4). It is known that the excited state dissociation of *simple* phenols to bulk water requires water concentrations in excess of 10 M for appreciable ionization, whereas the much more acidic cyano naphthols (in S₁) can dissociate at much lower water content or even in alcohols.^{6,15} Therefore, the inference here is that the anthracenyl phenol **6** is a strong photoacid, although we have no direct measurement of its excited state pK_a. It is interesting to note that direct photolysis of an authentic sample of phenolate ion of **6** (generated at pH 12, a pH in which **8** is known to be stable if formed) gave no observable loss of the anthracene absorption band which is indicative of lack of photohydration; only broadening of the absorption was observed, suggesting photodecomposition of the phenol moiety only. This implies that excited state phenolate from **17** (after deprotonation of the phenol moiety) is not identical to that obtained by simple direct excitation of the ground state phenolate. For example, they differ in the nature of their counterions (hydronium ion vs alkali metal ion) and medium acidity and therefore would be expected to have different reactivities. A more speculative mechanism for formation of **8** involves a *concerted* deprotonation of the phenol with twisting motion of the phenol ring, coupled with proton transfer at the anthracene 10-position, mediated by water (structure **17** but with the mediating water molecules coupled in a "wire", in a "water-relay" mechanism). However, definitive proof of this "water-relay" pathway would require additional

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studies along the lines presented by Leutwyler and co-workers¹⁶ for their demonstration of operation of an “ammonium wire” for conducting ESIPT in 7-hydroxyquinoline.

The identification of a *formal* ESIPT process for **6** shows that the generality of ESIPT from phenol to aromatic ring carbons can be extended to anthracenyl substituents and provides an impetus for studying other aromatic systems. The photohydration reaction of the anthracenyl moiety is the first example of the photohydration of an aromatic system via ESIPT. Although a similar type of photohydration is available via the ESIPT processes reported for **1**³ and **3**,⁴ the resulting hydrates would be much less stable and expected to revert to substrate quickly. Addition of hydroxylic solvents to alkenes and alkynes is a reaction of enormous importance in conventional organic chemistry, but addition to aromatic moieties is not commonly encountered. Aromatic hydrates generally cannot survive the harsh conditions necessary for their generation via thermal methods. This work demonstrates that addition of hydroxylic solvents to aromatic ring systems can indeed be achieved photochemically under mild conditions (low temperatures, neutral pH) to give isolable products. The observation that only the derivative with the acidic phenol OH group (**6**, but not **12**) is reactive demonstrates the unique ability of phenols to bring about the phototransformation of attached aromatic rings (via ESIPT). Of additional interest in this system is the apparently unique role of water in mediating the ESIPT reaction. While the ESIPT was also observed in CH₃OH and 2-PrOH, the highest efficiencies were observed when water was present in solution, presumably because of its superior ability to mediate the proton transfer.

Experimental Section

General. ¹H NMR spectra were recorded on Bruker AC300 (300 MHz) and AVANCE 500 (500 MHz) instruments. MS were recorded on a Kratos Concept H spectrometer (EI). UV-vis spectra were recorded on a Varian Cary 50 instrument. CH₃CN was dried over CaH₂ and distilled prior to use. Other solvents were reagent grade and used as received.

Materials. 9-Bromoanthracene, 2-methoxyphenylboronic acid, Pd(PPh₃)₄, and BBr₃ (1.0 M solution in CH₂Cl₂) were purchased from Aldrich.

9-(2'-Methoxyphenyl)anthracene (12). A solution of 9-bromoanthracene (7.01 g, 27.3 mmol) and Pd(PPh₃)₄ (0.32 g, 0.28 mmol) in 90 mL of toluene was added to a solution of 2-methoxyphenylboronic acid (4.97 g, 32.7 mmol) in 80 mL of ethanol, followed by addition of K₂CO₃ (8.30 g, 60.0 mmol). The mixture was stirred and heated to reflux for 20 h under N₂ and allowed to cool to room temperature. To the reaction mixture was added 0.5 M NaOH solution (200 mL), and the mixture was extracted with 2 × 100 mL of CH₂Cl₂. The organic phases were combined, dried over MgSO₄, and filtered, and the solvent was removed under reduced pressure to yield **12** as an off-white solid (6.97 g, 90%); mp 181–182 °C (ref 17, 177–179 °C). Purification was achieved by recrystallization from a mixture of toluene and ligroin. ¹H NMR (300 MHz, acetone-*d*₆) δ 3.96 (s, 3H), 7.16–7.64 (m, 10H), 8.10 (d, 2H), 8.58 (s, 1H); HRMS calculated for C₂₁H₁₆O 284.1201; observed 284.1202.

9-(2'-Hydroxyphenyl)anthracene (6). A solution of BBr₃ (1.0 M in CH₂Cl₂) (18 mL, 18 mmol) was added dropwise over a period of 20 min to a stirring solution of **12** (1.05 g, 3.68 mmol) dissolved in 50 mL of CH₂Cl₂ under N₂ and cooled in an ice bath. Once the addition

was complete, the mixture was removed from the ice bath and stirred for an additional 1 h at room temperature. The reaction was quenched with 100 mL of H₂O, and the mixture was extracted with 2 × 50 mL of CH₂Cl₂. The combined organic phases were dried over MgSO₄ and filtered, and the solvent was removed under reduced pressure to give **6** as an off-white solid (0.89 g, 90%). Yellow crystals were obtained on recrystallization from hot toluene, mp = 186–188 °C (ref 18, 178–180 °C). ¹H NMR (500 MHz, acetone-*d*₆) δ 7.09 (ddd, 1H, *J* = 7.0, 7.0, 1.0 Hz), 7.15 (dd, 1H, *J* = 8.0, 1.0 Hz), 7.19 (dd, 1H, *J* = 7.5, 2.0 Hz), 7.39 (ddd, 2H, *J* = 7.5 Hz, 7.5 Hz, 1.0 Hz), 7.44 (ddd, 1H, *J* = 7.5, 7.5, 1.5 Hz), 7.48 (ddd, 2H, *J* = 7.5, 7.5, 2.0 Hz), 7.64 (dd, 2H, *J* = 9.0, 1.0 Hz), 7.88 (s, 1H, exchanges with D₂O), 8.10 (d, 2H, *J* = 8.5 Hz), 8.59 (s, 1H). ¹³C NMR (acetone-*d*₆) δ 116.9, 120.5, 125.7, 125.9, 126.2, 127.4, 127.5, 129.2, 130.3, 131.5, 132.6, 133.3, 134.2, 156.5; HRMS, calculated for C₂₀H₁₄O 270.1045; observed 270.1050.

UV-Vis Studies. Solutions (10⁻⁶–10⁻⁵ M) of **6** in the appropriate solvent system were prepared in 1.0 cm quartz cuvettes (3.0 mL) and deoxygenated by bubbling with a stream of argon gas (syringe needle) for 5 min, and irradiated in a RPR 100 photochemical reactor containing 16 lamps (350 nm). A merry-go-round apparatus was employed. Cooling was achieved with a fan. The irradiation was stopped at regular time intervals and UV-vis traces were recorded.

Product Studies. Solutions (~10⁻³ M) were prepared in a 100 mL quartz tube and purged with argon 10 min prior to and continuously during irradiation in a RPR 100 photochemical reactor containing 16 lamps (350 nm). Cooling was achieved with an internal coldfinger (~15 °C). To the photolysate was added 100 mL of H₂O, and the resulting mixture was extracted with CH₂Cl₂ and dried over MgSO₄; the solvent was removed under reduced pressure.

Photolysis of 6 in 1:9 H₂O-CH₃CN. A solution of 53 mg of **6** in 80 mL of 1:9 H₂O-CH₃CN was irradiated for 1.5 h (350 nm), and the photoproducts were analyzed by ¹H NMR which showed a mixture of **7** and **6** in a 60:40 ratio. Compound **7** was isolated chromatographically on silica gel (1:9 ethyl acetate-hexanes). ¹H NMR (500 MHz, acetone-*d*₆) δ 4.15 (dd, 2H, *J* = 26, 20 Hz), 6.39 (s, 1H, exchanges in D₂O), 6.56 (m, 2H), 6.74 (d, *J* = 8 Hz), 6.99 (ddd, 1H, 9 Hz, 6 Hz, 3 Hz), 7.25 (m, 4H), 7.34 (m, 2H), 7.75 (m, 2H), 9.85 (s, exchanges in D₂O). ¹³C NMR (acetone-*d*₆): δ 34.7, 78.2, 117.8, 119.4, 127.1, 127.6, 127.7, 127.9, 128.5, 128.7, 131.6, 134.6, 142.7, 155.9. IR (film), 3515 (m), 3305 (s, br), 3064 (m), 1583 (s), 1486 (s), 1451 (s) 1233 (s). MS (*m/z*), 270 (M⁺ - H₂O). The compound dehydrates to **6** on heating; thus no melting point was recorded.

Photolysis of 6 in 1:9 D₂O-CH₃CN. A solution of 7 mg of **6** in 60 mL of 1:9 D₂O-CH₃CN was irradiated for 10 min, and the photoproducts were analyzed by ¹H NMR which showed a mixture of **7**-10D and **6** in a 65:35 ratio. The area of the peak corresponding to the 10-position of **6** (δ 8.59) was reduced by 70%, indicating a 30:70 ratio of **6** and **6**-10D present in the sample, giving an overall product ratio of 65:10:25 of **7**-10D:**6**:**6**-10D. Runs at different D₂O concentrations were performed in the same way. Results from these runs appear in Figure 2.

Photolysis of 6 in 1:2:5 CH₃OH:H₂O:CH₃CN. A solution of 32 mg of **6** was dissolved in 80 mL of a 1:2:5 CH₃OH:H₂O:CH₃CN solution and irradiated for 45 min. ¹H NMR analysis showed quantitative conversion to **9**. ¹H NMR (500 MHz, acetone-*d*₆) δ 2.86 (s, 3H), 4.24 (d, 1H, *J* = 21 Hz), 4.32 (d, 1H, *J* = 21 Hz), 6.65 (ddd, 1H, *J* = 7.5, 7.5, 1.5 Hz), 6.70 (dd, 1H, *J* = 8.5, 1.0 Hz), 6.98 (d, 1H, *J* = 7.5 Hz), 6.99 (ddd, 1H, *J* = 7.0, 7.0, 1.5 Hz), 7.24 (dd, 2H, *J* = 8, 8 Hz), 7.28 (ddd, 2H, *J* = 7.0, 7.0, 1.5 Hz), 7.37 (dd, 2H, *J* = 7.5, 1 Hz), 7.47 (dd, 2H, *J* = 7.5 Hz, 1.5 Hz), 9.17 (s, 1H, exchanges in D₂O). Compound gives **6** on heating.

Photolysis of 6 in 1:2:5 2-Propanol-H₂O-CH₃CN. A solution of 35 mg of **6** in a solution of 1:2:5 2-PrOH-H₂O-CH₃CN was irradiated for 45 min to give **10** in near quantitative yield. ¹H NMR

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(300 MHz, acetone- d_6) δ 7.50 (d, 6H, $J = 7$ Hz), 3.30 (dt, 1H, $J = 7$, 7 Hz), 4.35 (s, 2H), 6.55 (m, 1H), 6.75 (m, 1H), 7.00 (dd, 1H, $J = 7$, 7 Hz), 7.10–7.50 (m, 9 H), 9.85 (s, 1H, exchanges in D_2O). Warming a sealed NMR tube to 80 °C for 2 h led to 35% conversion back to **6**, concomitant with release of 2-propanol.

Photolysis of 6 in the Presence of $NaBH_4$. A solution of 32 mg of **6** and 1.0 g of $NaBH_4$ in 80 mL of 1:3 H_2O-CH_3CN was irradiated for 1 h. The reaction was quenched with 100 mL of 10% HCl solution to decompose excess $NaBH_4$ prior to standard workup. 1H NMR analysis indicated ~60% conversion to **11**, along with minor amounts of other unidentified products. Product **11** (oil) was isolated from the product mixture on silica gel (10% ethyl acetate–hexanes). 1H NMR (500 MHz, acetone- d_6) δ 4.03 (d, 1H, 19 Hz), 4.30 (d, 1H, 19 Hz), 5.81 (s, 1H), 6.65 (ddd, 1H, $J = 7.5$, 7.5, 1.5 Hz), 6.72 (dd, 1H, $J = 7.5$, 1.5 Hz), 6.90 (dd, 1H, $J = 8.0$, 1.0 Hz), 6.97 (ddd, 1H, $J = 8.0$, 7.5, 2 Hz), 7.14 (ddd, 2H, $J = 7.5$, 7.5, 2 Hz), 7.18 (ddd, 2H, $J = 7.0$, 7.0, 1.5 Hz), 7.34 (dd, 2H, $J = 7.5$, 1 Hz), 7.38 (dd, 2H, $J = 7.0$, 1.5 Hz), 8.64 (s, 1H, exchanges in D_2O). IR (film) 3500 (m), 3427 (m, br), 1588 (m), 1485 (s), 1451 (s). HRMS, calculated for $C_{20}H_{16}O$ 272.1201; observed 272.1203.

Laser Flash Photolysis (LFP). All LFP studies were conducted at the University of Victoria LFP facility employing a Spectra Physics Quanta-Ray YAG laser, model GCR-11, with a pulse width of 10 ns

and excitation wavelength of 266 nm. Pulse power was adjusted to 20 mJ. Flow cells (7 mm path length) were used and solutions were bubbled with either nitrogen or oxygen for 10 min prior to excitation. Optical densities (ODs) at 266 nm were ~0.3.

Steady-State and Time-Resolved Fluorescence Measurements. All solutions (OD = 0.1 at excitation wavelength) were purged with argon or nitrogen for 5 min prior to analysis. Steady-state fluorescence spectra were obtained on a Photon Technology International (PTI) A-1010 Quanta-Master luminescence spectrometer. Fluorescence quantum yields were determined by comparison of the integrated emission bands with that of quinine bisulfate ($\Phi_f = 0.55$ in 0.1 M H_2SO_4),⁹ followed by correction for differences in index of refraction. Measurements were made at three different concentrations to exclude possible aggregation affects. Fluorescence lifetimes were measured on a PTI LS-1 instrument using the time-correlated single-photon-counting method with 10 000 counts.

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