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A New Type of Excited-State Intramolecular Proton Transfer: Proton Transfer from Phenol OH to a Carbon Atom of an Aromatic Ring Observed for 2-Phenylphenol[1]

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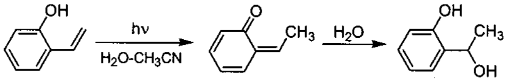
Abstract: The photochemical deuterium incorporation at the 2′- and 4′-positions of 2-phenylphenol (**4**) and equivalent positions of related compounds has been studied in D_2O (CH_3OD)−CH_3CN solutions with varying D_2O (CH_3OD) content. Predominant exchange was observed at the 2′-position with an efficiency that is independent of D_2O (MeOD) content. Exchange at the 2′-position (but not at the 4′-position) was also observed when crystalline samples of **4**-OD were irradiated. Data are presented consistent with a mechanism of exchange that involves excited-state intramolecular proton transfer (ESIPT) from the phenol to the 2′-carbon position of the benzene ring not containing the phenol, to generate the corresponding keto tautomer (an *o*-quinone methide). This is the first explicit example of a new class of ESIPT in which an acidic phenolic proton is transferred to an sp^2-hybridized carbon of an aromatic ring. The complete lack of exchange observed for related substrates **6**−**9** and for planar 4-hydroxyfluorene (**10**) is consistent with a mechanism of ESIPT that requires an initial hydrogen bonding interaction between the phenol proton and the benzene π-system. Similar exchange was observed for 2,2′-biphenol (**5**), suggesting that this new type of ESIPT is a general reaction for unconstrained 2′-aryl-substituted phenols and other related hydroxyarenes.

Introduction

Excited-state intramolecular proton transfer (ESIPT) is a simple and fundamentally important photochemical process that has received considerable attention.[2,3] For aromatic organic compounds, ESIPT generally arises when both acidic and basic functionalities on the molecule experience simultaneous enhancement of the acidity and basicity of these groups upon electronic excitation. This enhancement is often sufficient for direct protonation of the basic site by the acidic group. In some cases, the mediation of a protic solvent is required if the distance between the two sites is too far for direct proton transfer. ESIPTs generally involve heteroatoms (as part of a heteroaromatic ring) serving as the basic site and OH or NH acids, either as a substituent on or part of an aromatic ring system. ESIPT in these systems is wholly reversible and in most cases extremely fast. Such "energy wasting" reactions have been exploited for use as photostabilizers and other applications.[4] The first example of an ESIPT between a phenol OH and a carbon atom (the β-carbon of an alkene moiety) was first reported by Yates and co-workers[5] while studying the photohydration reactions of styrenes and arylacetylenes (eq 1). Photolysis of *o*-hydroxystyrene (**1**) in aqueous CH_3CN gave the hydration product **3** via *o*-quinone methide **2**. The primary photochemical event from S_1 is believed to be ESIPT from the phenol to the β-carbon of the alkene moiety. Reverse proton transfer is not observed, and instead **2** is trapped quantitatively by water to give **3**.



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To our knowledge, there are no explicit examples of ESIPT to a carbon atom that is part of an aromatic ring. In related work on excited-state proton transfer (ESPT), Webb, Tolbert, and co-workers[6] have suggested that the geminate recombination process in the ESPT reaction of 1-naphthol could result in protonation at the C-5 and C-8 ring carbon positions, via solvent-

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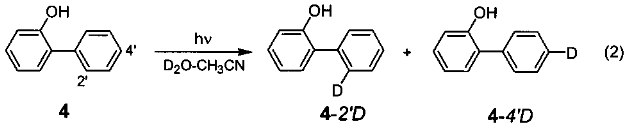
mediated ESIPT. This type of ESIPT would not be available in the absence of a suitable solvent to assist the initial deprotonation. In addition, reports of the photoprotonation (by aqueous acid) of the ring carbons of a variety of aromatic rings (usually containing an electron-donating group) are well known.[7] In particular, we have shown that hydroxy- and methoxy-substituted biphenyls are photoprotonated (in mild acid) exclusively on the benzene ring not containing the substituent.[7c] These results indicate that the aromatic ring carbons can be sufficiently basic on photoexcitation to undergo ESPT from moderately acidic aqueous acid. What is unknown is whether an explicit ESIPT (from phenol) to an aromatic ring carbon could operate in appropriately designed systems. We present results for the photochemical deuterium exchange in 2-phenylphenol (**4**) and related compounds that are entirely consistent with an explicit ESIPT from the phenol moiety to the ring carbon (position 2′) of the benzene ring not bearing the hydroxyl group, as first examples of a new type of ESIPT process between phenol and attached aromatic ring carbons.

Results and Discussion

Deuterium Exchange. Our studies of excited-state proton-transfer-initiated reactions of a wide variety of phenol derivatives[8] led us to consider the possibility of ESIPT from a phenol OH to an attached aromatic ring carbon, which led us to examine the photochemistry of 2-phenylphenol (**4**), it being the simplest compound that could undergo the reaction. This compound is effectively the "aromatic" analogue (replacement of alkene by phenyl) of *o*-hydroxystyrene (**1**), which was shown by Yates and co-workers[5] to undergo efficient ESIPT. Because **4** was not expected to give an isolable photohydration product, we sought to follow the anticipated proton transfer by deuterium exchange (in D_2O). Initial photolysis of **4** in 1:1 (v/v) D_2O-CH_3CN (argon purged) for 1 h yielded as photoproducts (after H_2O wash) starting material deuterated at the *ortho* (2′) (**4**-2′D)- and *para* (4′) (**4**-4′D)-positions (47 and 14% exchange, respectively) of the aromatic ring not containing the hydroxyl group (eq 2). The exchange was readily observable by ^{1}H NMR (360 MHz), although this method of analysis cannot differentiate between mono- or dideuteration of the two equivalent 2′-positions. The reduction in the area of the NMR signal assigned to the two protons of the 2′-position (δ 7.58, dd) (H_a) on photolysis (1 h) is accompanied by formation of a broad doublet (but no reduction in peak area) of the peak assigned to the neighboring *meta* (3′) proton (δ 7.38, dd) (H_b) due to coupling to deuterium that is incorporated at H_a (Figure 1). Protons at the 2 (H_g)- and 4′ (H_c)-positions were not resolvable and appear as a multiplet at δ 7.28. The area of this peak is also reduced on photolysis in D_2O although much less efficiently. Because the signal of H_f (neighboring proton of H_g) remains unchanged throughout the photolysis, we can reasonably conclude that the residual decrease in signal of the H_g/H_c signal is exclusively due to exchange of H_c (4′-proton). All other peaks remain unchanged, consistent with the absence of deuterium exchange at these positions on photolysis. Comparison of oxygen- and argon-bubbled runs showed similar exchange yields at low conversion (although significant photodecomposition was observed in high conversion oxygen-bubbled runs). Analysis of MS data confirms the extent of deuteration measured by NMR. No observable exchange took place in the dark under otherwise identical conditions.



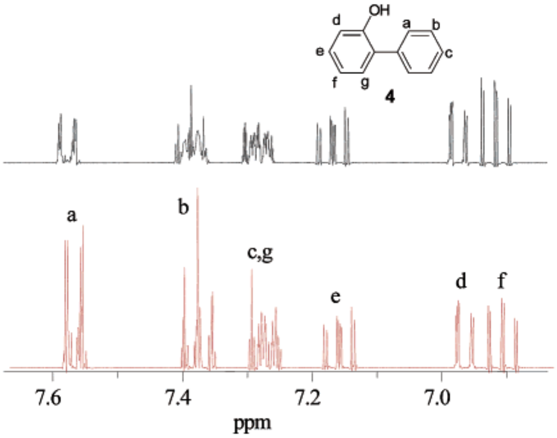
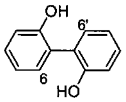


Figure 1. ^{1}H (360 MHz) NMR showing the spectrum (expanded aromatic region) of **4** before (bottom) and after (top) photolysis (1 h, 254 nm) in 1:1 D_2O-CH_3CN. NMR integration indicates 55% and 15% deuteration at the 2′ (H_a)- and 4′ (H_c)-positions, respectively.

The readily available 2,2′-biphenol (**5**) displayed similar photoexchange behavior. When photolyzed under similar conditions as **4**, deuterium exchange was observed at the 6- and 6′-positions to an extent of 35%, which is marginally lower than the exchange observed for the equivalent position of **4**. Exchange at the *para* (4,4′)-position of **5** was not detectable by ^{1}H NMR.

Irradiation of *m* and *p*-phenylphenols (**6** and **7**, respectively) in 1:1 (v/v) D_2O-CH_3CN gave no measurable deuterium incorporation (by NMR), even when extended photolysis times were employed. Methyl ether analogues **8** and **9** were also nonreactive. These analogues have no available acidic proton, or one that is not at the *ortho* position. Their lack of photoexchange is consistent with a mechanism of reaction of **4** and **5** that requires an *o*-phenyl-substituted phenol capable of undergoing ESIPT to the adjacent ring.



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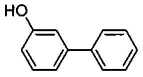

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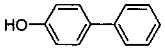

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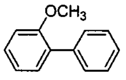

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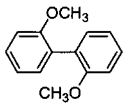

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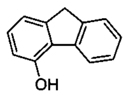

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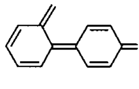

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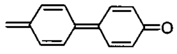

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To gain further insights into the exchange mechanism of **4** (and **5**), the extent of exchange (by NMR and MS) was

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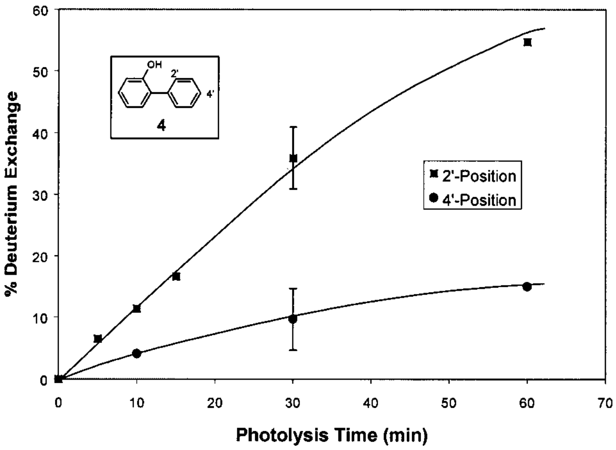

Figure 2. Plot of % deuterium exchange at the 2′ (■)- and 4′ (●)-positions of 2-phenylphenol (**4**) with photolysis time in 1:3 D_2O-CH_3CN (as determined by NMR). At lower conversions, exchange at the 2′-position is due to monodeuterium incorporation (by MS). Because significant exchange at the 4′-position is observed only at longer photolysis times, a combination of 4′-monodeuterated and 2′,4′-dideuterated (and higher) products is contributing.

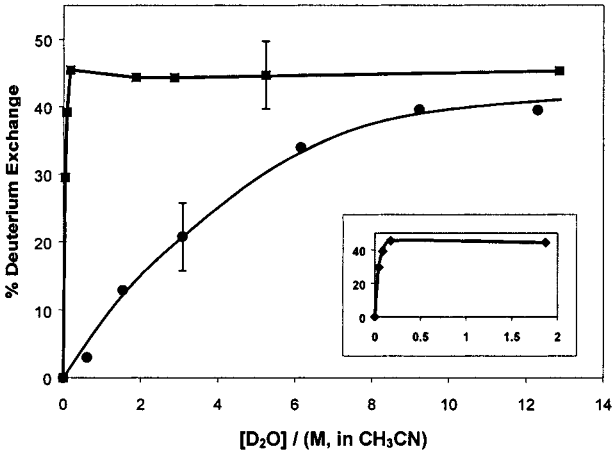

Figure 3. Plot of total % deuterium incorporation at the 2′ (■)- and 4′-positions (●) of **4** versus D_2O concentration (in CH_3CN), as measured by ^1H NMR. Because of the lower efficiency of exchange at the 4′-position, photolysis times were tripled for these experiments to increase conversion. Inset: expansion of data for exchange at the 2′-position at low D_2O concentration.

monitored as a function of photolysis time (Figure 2). The data show that exchange at the 2′-position is significantly more efficient than exchange at the 4′-position at all conversions. Higher conversion runs led to significant proportions of 2′,2′- and 2′,4′-dideuterated and small amounts of trideuterated products. Quantitative exchange of the 2′-positions can be achieved with extended photolysis (not shown in Figure 2).

It is well known[9] that bulk water is generally required for the efficient ESPT of phenols and other hydroxyarenes (to solvent). Thus, decreasing the water (D_2O) content of the solvent system should retard ESPT and water-assisted ESIPT processes. To explore the effect of water content on the deuterium incorporation reaction of **4** and **5**, exchange studies were carried out in which the D_2O concentration (in CH_3CN) was varied. The extent of exchange at the 2′- and 4′-positions of **4** as a function of D_2O content is shown in Figure 3. Decreasing the concentration of D_2O present in the solvent mixture led to no measurable decrease in exchange efficiency at the 2′-position until very low D_2O concentrations were reached. A nominal concentration of D_2O is necessary to exchange the phenolic protons of the starting material (i.e., convert **4** to **4**-OD), as well as the fact that the CH_3CN contains residual H_2O. We interpret the sharp rise (between 0 and 0.25 M D_2O) in exchange yield at the 2′-position observed at low D_2O concentrations as arising from the conversion of **4** to **4**-OD, and when **4** is fully converted to **4**-OD, the exchange efficiency is independent of D_2O concentration. The lack of a "bulk" solvent dependence was also observed when CH_3OD was used in place of D_2O. Again, the exchange efficiency did not change with CH_3OD concentration until very small concentrations were reached. The apparent lack of D_2O (CH_3OD) concentration dependence is consistent with exchange at the 2′-position arising from direct proton transfer from the phenol to the adjacent phenyl ring in the excited state. Similar "solvent-independent" behavior for exchange (at the 6,6′-positions) was observed for **5**.

A much different solvent dependence was observed for exchange occurring at the *para* (4′)-position of **4** (Figure 3). Although the efficiency of exchange at the 4′-position is considerably lower as compared to the exchange at the 2′-position (vide supra), the amount of exchange rises steadily as the concentration of D_2O is increased (data obtained from extended photolysis runs). Such behavior strongly indicates that the mechanism for exchange at this position differs markedly from that of the 2′-position. It is apparent that "bulk" D_2O is necessary for efficient exchange at the 4′-position. As the 4′-position is too far from the acidic phenol for direct protonation to take place, a proton transfer from the phenol to this position would have to be solvent mediated. In addition, no exchange was observed at the 4′-position when CH_3OD was used as the cosolvent (unlike the observed behavior at the 2′-position). These observations suggest that exchange at the 4′-position is due to reprotonation of the excited-state phenolate ion (at the 4′-position) by D_2O, because water is required for formation of the excited-state phenolate (vide infra).

Efficient deuterium exchange at the 2′-position of **4** was also observed when the photolyses were carried out in neat EtOD or cyclohexane (with **4**-OD) with no observed exchange at the 4′-position. Exchange efficiencies in water and alcohols were similar, whereas the exchange is considerably more efficient in cyclohexane (about 2-fold more efficient as compared to that in 1:1 (v/v) D_2O-CH_3CN). The latter observation suggests that the presence of water or other protic solvents hinders ESPT to the 2′-position. This is consistent with intrinsic ESIPT from the phenol to the 2′-position as responsible for the observed exchange. Additional evidence for this mechanism was the finding that photolysis of powdered crystals of **4**-OD resulted in exclusive deuterium incorporation at the 2′-position (~10%). Because crystalline samples of **4** grown in H_2O did not contain included solvent, the exchange observed in the solid state result is further evidence of an intrinsic ESIPT mechanism.

Molecular modeling (Chem 3D, AM1 optimization) and crystallographic data[10] show that the ground-state structure of **4** is twisted with a dihedral angle between the aromatic rings

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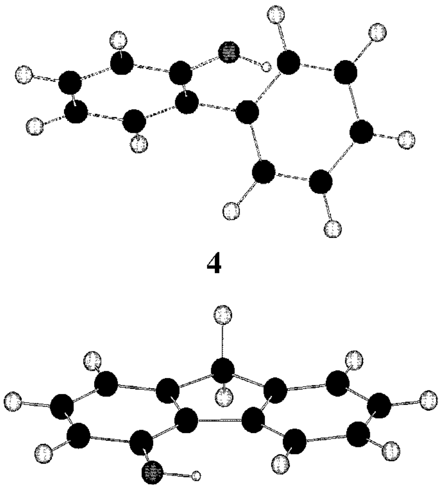

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Figure 4. Geometry optimized (Chem3D, AM1) structures of **4** and **10**. The dihedral angles between the aromatic rings (in the ground state) for **4** and **10** are 54° and 0°, respectively.

Table 1. Photophysical and Photochemical Parameters

compound	Φ_{ex}[a]	Φ_f[b]	τ[c] (ns)	pK^*[d]
4	0.041	0.32	1.9 (0.5)	1.15 ± 0.04
5	0.034	0.28	1.8	
6	<0.001[e]	0.35	4.5 (1.5)	1.36 ± 0.02
7	<0.001[e]	0.20	7.7 (1.2)	1.83 ± 0.04
10	<0.001[e]	0.65	3.5	

[a] Quantum yield for deuterium incorporation in 1:3 D_2O-CH_3CN at the 2′-position of **4** and 6-position of **5**. Estimated error ±10% of quoted value. Measured relative to the quantum yield for deuterium incorporation reported for dibenzosuberene.[13] [b] Fluorescence quantum yield in neat CH_3CN. Measured relative to the reported fluorescence quantum yield for fluorene ($\Phi_f = 0.68$).[14] Estimated error of ±10% of quoted value. [c] Fluorescence lifetime in neat CH_3CN measured by single photon counting. Values in brackets are the fluorescence lifetimes in water, from ref 15. Lifetimes measured in this way have an estimated error of ±0.2 ns. [d] pK_a for the excited singlet state, from ref 15. [e] No observable exchange by NMR under conditions employed.

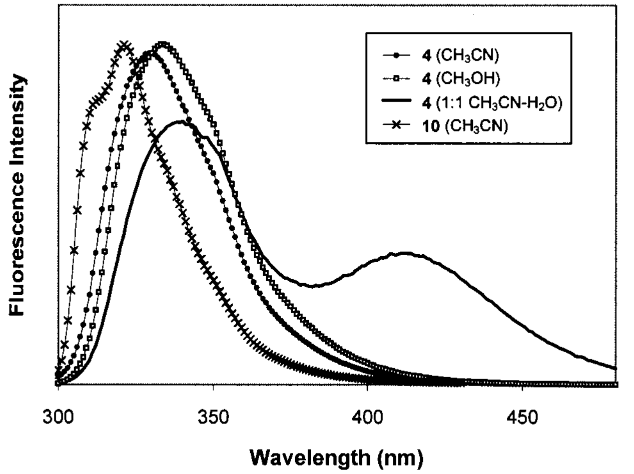

Figure 5. Fluorescence emission spectra of **4** and **10** in various solvents. The emission at 420 nm observed only in water is assigned to phenolate **13**.

of ~54° (Figure 4). In this conformation, the hydroxyl group can engage in significant interaction with the π-system of the other ring.[11] Indeed, there is considerable evidence that such an interaction exists for **4** and derivatives.[10,12] As a preliminary investigation into the geometric requirements of the ESIPT of **4** and **5**, 4-hydroxyfluorene (**10**) was synthesized and studied. Molecular modeling indicated that **10**, unlike **4**, is planar in the ground state, with the OH group lying within the plane of the ring with no possibility of interaction between the phenol OH and the aromatic π-system (Figure 4). Photolysis of **10** in 1:1 (v/v) D_2O-CH_3CN gave no detectable deuterium incorporation, even on prolonged irradiation, with quantitative recovery of substrate. This result was somewhat unexpected because **10** has all of the apparent structural requirements that **4** and **5** possess with the added bonus of a longer singlet lifetime due to the rigid fluorene backbone (Table 1). Its complete lack of reactivity supports the notion that ESIPT between the phenol OH and the 2′-position requires some degree of orbital overlap between the S-orbital of the acidic proton and the accepting π-system prior to excitation.

Quantum Yields of Deuterium Exchange. Quantum yields for deuterium incorporation (Φ_{ex}) for **4** and **5** were measured using the deuterium exchange reaction of dibenzosuberene as a secondary reference standard. Dibenzosuberene is known to undergo deuterium exchange of the benzylic C−H hydrogens when irradiated in 1:1 D_2O-CH_3CN ($\Phi = 0.030$).[13] Φ_{ex} at the 2′-position of **4** and the 6-position of **5** (measured in 1:3 D_2O-CH_3CN) were 0.041 ± 0.004 and 0.034 ± 0.004, respectively. For **4**, the quantum yield of exchange at the *para* position was much lower (less than 0.01) and hence not reliably measurable using this technique. The quantum yield for the actual photoprotonation step should be higher than the observed quantum yield of exchange because the intermediate obtained from ESIPT can also lose deuterium to regenerate nondeuterated starting material.

Fluorescence Measurements. We have recently shown[3g] that formal ESIPT (via S_1) from phenol to side-chain carbon atoms (of an alkene moiety) is mediated by water, where the use of steady-state and time-resolved fluorescence studies was essential for mechanistic characterization. In these systems,[3g] water is essential for reaction, acting as a bridge for the formal transfer of a phenol proton to the β-carbon of the alkene moiety; otherwise there is no ESIPT. The results obtained so far for deuterium exchange of **4** and **5** indicate that water is *not* essential for exchange at the 2′ (6)-positions, but is required for exchange at the 4′-position of **4**. Fluorescence measurements should provide additional insights into the requirement of water on reactivity. Strong fluorescence emission ($\lambda_{max} = 330$ nm; $\Phi_f = 0.32 \pm 0.03$) was observed for **4** in neat CH_3CN (Figure 5). The addition of ~10 M water caused minimal quenching of this band (about 10%). Above 10 M water, the intensity of this band was progressively reduced, along with concurrent growth of a second emission band ($\lambda_{max} = 420$ nm) which was assigned to the phenolate (by comparison with emission of authentic phenolate ion). The fluorescence emission is essentially unchanged in neat CH_3OH ($\lambda_{max} = 335$ nm, $\Phi_f = 0.32 \pm 0.03$) as compared to neat CH_3CN, with no observable phenolate

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(11) This type of aromatic π−H interaction (in the ground state) has been investigated in some detail, for example: Tarakeshwar, P.; Choi, H. S.; Kim, K. S. *J. Am. Chem. Soc.* **2001**, *123*, 3323.

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emission. The absence of phenolate emission in methanol indicates that this solvent is not sufficiently polar to mediate proton transfer from the phenol of **4** (to solvent). Therefore, the exchange observed exclusively at the 2′-position of **4** on photolysis in neat CH_3OD (vide supra) must arise from the protonated form of **4**, via ESIPT. A mechanism of exchange at the 4′-position of **4** involving protonation of the phenolate is supported by the fact that both the exchange at the 4′-position and the formation of phenolate require significant amounts of water.

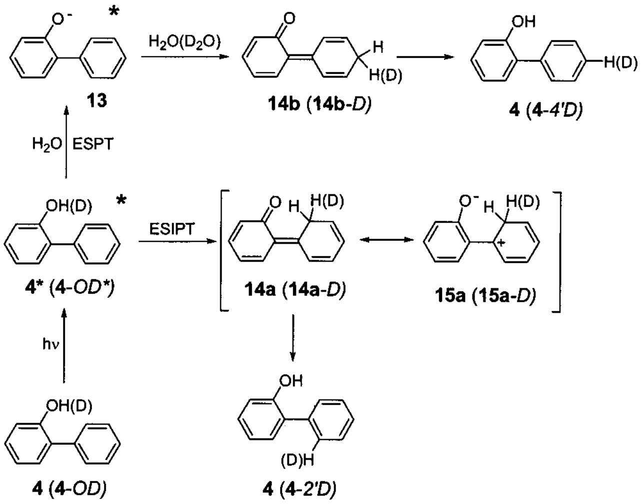
Biphenol analogue **5** exhibited fluorescence behavior similar to that observed for **4**. The emission at 348 nm (in neat CH_3CN) is reduced on addition of water with concomitant growth of the phenolate emission band at 397 nm. The strong fluorescence emission ($\lambda_{max} = 320$ nm, $\Phi_f = 0.65 \pm 0.07$) of **10** (in neat CH_3CN) was also reduced by the addition of water with observation of phenolate emission at 390 nm. The fluorescence quantum yields of **10** and for the parent fluorene ($\Phi_f = 0.68$)[14] are the same (within experimental error), indicating that the presence of a hydroxyl group to the 4-position apparently does not introduce any additional deactivational pathway, consistent with the lack of observable exchange.

Fluorescence lifetimes for **4**, **6**, and **7** were measured in neat CH_3CN (Table 1) and were found to be 1.9, 4.5, and 7.7 ns, respectively. Townsend and Schulman[15] observed that the fluorescence lifetime (in water) is shorter for **4** than for isomeric phenylphenols **6** and **7** (Table 1), and they attributed the difference to the higher efficiency of ESPT to water for **4** (more acidic in S_1). The much shorter lifetime observed for **4** as compared to isomers **6** and **7** in *neat* CH_3CN is not surprising given that only **4** undergoes ESIPT.

Laser Flash Photolysis (LFP). A wide range of quinone methide intermediates generated from phenol derivatives has been characterized[8] in our laboratory by nanosecond LFP, including biphenyl quinone methides[7c] **11** ($\lambda_{max} = 570$ nm, $\tau = 400$ ns) and **12** ($\lambda_{max} = 525$ nm, $\tau = 67$ μs) in aqueous CH_3CN. Exchange of **4** at the 2′-position via ESIPT (of **4**-OD) would give *o*-quinone methide **14a** (or **14a**-D). Similarly, exchange at the 4′-position via initial ESPT to solvent H_2O, followed by reprotonation, would lead to the isomeric *o*-quinone methide **14b** (or **14b**-D) (Scheme 1). Both **14a** and **14b** are structurally similar to **11** and **12**, and hence we anticipated that they will have visible bands in the 500−600 nm region, as was observed for **11** and **12**. The range in lifetimes (in water) for quinone methides studied to date vary from stable (>minutes) to subnanosecond (undetectable using nanosecond LFP). The point to be addressed in the next section is whether **14a** or **14b** is detectable by LFP.

LFP (266 nm) of **4**, **6**, and **7** (N_2 purged) in neat CH_3CN, 1:1 H_2O-CH_3CN, or cyclohexane gave a strongly absorbing transient ($\lambda_{max} \approx 350$ nm, $\tau \approx 1$ μs) whose lifetime was significantly reduced in the presence of oxygen. This transient is most likely the triplet state of these phenols, although radical intermediates (probably derived from two-photon processes) cannot be excluded. The triplet state of 3-cyanophenol has been reported at $\lambda_{max} \approx 325$ nm in EtOH.[16] In neat cyclohexane or neat CH_3CN (oxygen purged), a broad short-lived transient ($\lambda_{max} = 520$ nm, $\tau \approx 50$ ns) was observed for **4**. However, transients of similar intensity, λ_{max}, and lifetime were also observed for "unreactive" analogues **7** and **8**. Quinone methides **14a** and **14b** would be expected to absorb in the 500−600 nm region with anticipated lifetimes that are significantly shorter than those observed for related analogues **11** and **12**. This is because of the fact that both **14a** and **14b** can readily tautomerize, noting that resonance forms such as **15a** would expedite such a mechanism, whereas **11** and **12** can only undergo nucleophilic capture by water. The weakness of the transient as well as observation of residual signals in the same region from both **7** and **8** leads us to conclude that it is premature to assign the observed broad 520 nm transient as due to quinone methide **14a** or **14b** at this time.

Scheme 1



Mechanisms of Deuterium Incorporation. The proposed mechanisms for the deuterium incorporation at the 2′ and 4′-positions of **4** are outlined in Scheme 1. Singlet state reactivity is inferred from the correlation of fluorescence data with observed exchange, the lack of oxygen quenching of exchange, and the known enhanced excited singlet state acidity of phenylphenols, although residual triplet state reactivity cannot be excluded. ESIPT cannot be readily distinguished from an equivalent hydrogen transfer process, although this is a moot point, especially in those systems where the reverse transfer is very fast, and where no net deuterium incorporation is possible (such as between heteroatoms). We argue that the ESIPT observed in this work is best described as being true proton transfer on the basis of the following points: (i) the phenolic proton of phenylphenols is known to be quite acidic in S_1 ($pK^* < 2$) (Table 1); (ii) hydroxy- and methoxy-substituted biphenyls are photoprotonated (in mild acid) exclusively on the benzene ring not containing the substituent;[7c] (iii) examination of HOMO and LUMO coefficients of phenylphenols using simple Hückel-type calculations predicts that the benzene ring not containing the hydroxy substituent becomes more basic on excitation; (iv) the exchange reaction is observed only for those *o*-phenylphenols that are twisted in the ground state (i.e, **4** and **5** but not for **10**) which allows for significant OH−π hydrogen bonding, further polarizing the O−H bond.

In the proposed mechanism for deuterium exchange (Scheme 1), singlet excited **4**-OD (**4**-OD*) undergoes ESIPT to the 2′-position of the other aromatic ring to form *o*-quinone methide **14a**-D. This intermediate can then undergo reverse proton

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[14] Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed.; Marcel Dekker: New York, 1993.

[15] Townsend, R.; Schulman, S. *Chim. Oggi* **1992**, *10*, 49.

[16] Bonnichon, F.; Richard, C. *J. Photochem. Photobiol., A* **1998**, *119*, 25.

transfer to generate **4**-2′D. The reverse reaction could also be viewed as a [1,5]-hydrogen shift, although if one considers that the resonance form **15a** should be a strong contributor to the overall *o*-quinone methide structure, the reverse reaction may be best viewed simply as a proton transfer. Studies involving photolyses in solvents of varying D_2O content in CH_3CN and in CH_3OH, in neat cyclohexane, and in the solid state indicate that the initial proton transfer to the 2′-position does not require water.

ESPT to solvent from **4*** (or **4**-OD*) to generate **13** becomes increasingly efficient as the water content of the solvent system is increased, as evident from fluorescence studies (Figure 5; observation of increasing phenolate ion emission). Protonation of **13** by H_2O (D_2O) at the 4′-position will lead to formation of quinone methide intermediate **14b** (**14b**-D) which would result in deuterium incorporation at the 4′-position on deprotonation (to give **4**-4′D). While protonation of **13** at the 2′-position might also be occurring to some extent in solvent systems containing significant amounts of H_2O (D_2O), it is not possible to determine the contribution of this mechanism to the overall exchange observed at the 2′-position at high water content.

Proper relative geometric orientation of the phenol group and the accepting ring carbon is an important requirement for ESIPT in **4**. Ground-state hydrogen bond interactions between the donor and acceptor groups are generally required for systems to undergo efficient direct ESIPT reactions.[2] For unreactive analogue **10**, the phenolic proton is constrained within the nodal plane of the π-system resulting in no net overlap with the π-system of the adjacent benzene ring. It appears that ESIPT to the adjacent ring cannot occur unless the s-orbital of the phenolic proton can sufficiently overlap with the basic π-orbitals prior to proton transfer. The twisted ground-state geometries of **4** and **5** allow for such an interaction and hence are both able to undergo the observed ESIPT.

This work has revealed that a significant photochemical pathway for **4** (and **5**, and possibly many related compounds) is ESIPT from the phenol proton to the 2′-carbon of the adjacent benzene ring. This new type of ESIPT might be a general photochemical pathway for many unconstrained *o*-aryl phenols and *o*-aryl hydroxyarenes. As such functionalities are ubiquitous in organic chemistry, the identification of this new pathway will provide new insights into the photochemical behavior of many other related systems providing topics for continued studies in this area.

Experimental Section

General. ^1H NMR spectra were recorded on Bruker AC 300 (300 MHz) and AM 360 (360 MHz) instruments. MS were recorded on a Kratos Concept H spectrometer using the LSIMS ionization method using *m*-nitrobenzyl alcohol. CH_3CN was dried over CaH_2 and distilled prior to use. Other solvents were spectral grade from Aldrich and used as received.

Materials. Phenylphenols **4**−**7** were purchased from Aldrich and recrystallized before use. 4-Hydroxyfluorene (**10**) was synthesized from commercially available 4-aminofluorenone (Aldrich). Methyl ethers **8** and **9** were prepared from **4** and **5**, respectively, via Williamson ether synthesis.

4-Hydroxyfluorene (10). 4-Aminofluorenone (500 mg, 2.5 mmol) was suspended in 15 mL of water (ice bath) to which ∼20 mL of concentrated H_2SO_4 was added, at which point all of the solid dissolved. A solution of $NaNO_2$ (0.22 g, 3.2 mmol) in 10 mL of water was added dropwise over 2 min with stirring. The color of the solution turned from a bright orange to an olive green. Stirring was continued for a further 90 min, at which time the olive color disappeared leaving a deep orange solution. This solution was added dropwise (over 25 min) to a boiling solution of 1:1 (v/v) concentrated $H_2SO_4-H_2O$ (80 mL). After addition, the mixture was boiled for a further 15 min and then allowed to cool. The solution was extracted with 3 × 50 mL of CH_2Cl_2, and the combined organic layers were extracted with 5 × 150 mL of 0.1 M NaOH. The crude 4-hydroxyfluorenone was precipitated by acidification (10% HCl) of the aqueous extract, and filtered and air-dried (260 mg, 52%). The crude 4-hydroxyfluorenone (0.25 g, 1.3 mmol) was dissolved in 20 mL of EtOH to which was added 75 mg of Pd/C. The solution was stirred for 24 h under 35 atm of H_2. Filtration followed by evaporation of the solvent gave a yellow-orange solid, which was recrystallized from 95% EtOH, to give pure **10** (200 mg, 45% overall yield), mp 105−106 (lit. 108−109).[17] ^1H NMR ($CDCl_3$): δ 3.91 (2H, s), 5.25 (broad s, exchangeable in D_2O), 6.73 (1H, m), 7.13 (2H, m), 7.27 (1H, t, $J = 7.4$ Hz), 7.37 (1H, dd, $J = 7.4, 7.4$ Hz), 7.51 (1H, d, $J = 7.4$ Hz), 8.10 (1H, d, $J = 7.4$ Hz). ^{13}C NMR ($CDCl_3$): δ 37.3, 113.7, 117.6, 123.5, 124.4, 125.9, 126.8, 127.5, 128.6, 140.6, 142.5, 145.7, 151.5.

2-Methoxybiphenyl (8). To a solution of **4** (5.1 g, 30 mmol) in DMSO (50 mL) was added KOH (6.7 g, 120 mmol) and CH_3I (6.5 g, 45 mmol). The mixture was stirred at room temperature for 5 h, at which time the reaction was quenched by the addition of water (100 mL). This mixture was extracted with 2 × 50 mL of CH_2Cl_2 which was subsequently washed with 4 × 100 mL of water. The organic layer was dried ($MgSO_4$), and the solvent was removed under vacuum. The crude product (yellowish oil) was purified by bulb-to-bulb distillation, to give a colorless oil (4.3 g, 78%). ^1H NMR ($CDCl_3$): δ 3.83 (3H, s), 7.04 (2H, m), 7.35 (3H, m), 7.44 (2H, dd, $J = 7.4, 7.4$ Hz), 7.57 (2H, d, $J = 7.4$ Hz). ^{13}C NMR ($CDCl_3$): δ 55.6, 111.3, 120.9, 127.0, 128.0, 128.7, 129.6, 130.8, 138.6, 156.5.

2,2′-Dimethoxybiphenyl (9). In a similar procedure as above starting from **5**, **9** was isolated in 85% yield (5.46 g). ^1H NMR ($CDCl_3$): δ 3.77 (6H, s), 6.98 (4H, m), 7.24 (2H, d, $J = 7.3$ Hz), 7.32 (2H, dd, $J = 7.3, 7.3$ Hz). ^{13}C NMR ($CDCl_3$): δ 55.7, 111.1, 120.3, 127.8, 128.6, 131.5, 157.0.

Product Studies. Solutions were prepared in a quartz vessel and purged with argon (or O_2) gas for 10 min prior to and continuously during irradiation in a Rayonet RPR 100 photochemical reactor using 254 nm lamps. Cooling was achieved with a coldfinger (∼15 °C). Following photolysis, the solution was extracted with CH_2Cl_2, washed with water, and dried over $MgSO_4$.

Photolysis of 4. A 15 mg sample of **4** was irradiated for 60 min in 1:3 D_2O-CH_3CN (40 mL), which cleanly gave **4** with 55% deuterium incorporation at the 2′-position and 15% deuterium incorporation at the 4′-position (42% overall exchange of all possible 2′- and 4′-positions (3 in total)) (by 360 MHz ^1H NMR). MS (after ^{13}C correction) also indicates an overall exchange of 42%, arising from a product distribution of **4** (20%), **4**-D (42%), **4**-D_2 (32%), and **4**-D_3 (6%). A second 15 mg sample of **4** was irradiated for 5 min in 1:3 D_2O-CH_3CN (40 mL) and cleanly gave **4** with 7% deuterium incorporation at the 2′-position and 4% deuterium incorporation at the 4′-position (5.8% overall exchange) (by 360 MHz ^1H NMR). MS (after ^{13}C correction) indicates an overall exchange of 5.0%, arising from a product distribution of **4** (86%), **4**-D (13%).

Photolysis of 5. Irradiation of a 15 mg sample of **5** dissolved in 1:1 D_2O-CH_3CN (40 mL) for 60 min cleanly gave **5** with deuterium incorporated at the 6-position to an extent of 35% (by NMR).

Photolysis of 6−10. Solutions of each of **6**−**10** were prepared (1:1 D_2O-CH_3CN), and each was irradiated for 60 min. No deuterium incorporation could be observed by ^1H NMR (360 MHz) for any derivative.

Laser Flash Photolysis (LFP). All transient spectra and lifetimes were obtained using a Nd:YAG laser (Spectra Physics Quanta-Ray,

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(17) Pan, H.; Fletcher, T. L. *J. Org. Chem.* **1960**, *25*, 1106.

GCR, <30 mJ) with a pulse width of 10 ns and excitation wavelength of 266 nm. Flow cells (7 mm path length) were used, and solutions were purged with either nitrogen or oxygen for 10 min prior to excitation. 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 for 5 min before analysis. Steady-state fluorescence spectra were obtained using a Photon Technology International A-1010 (PTI) QuantaMaster luminescence spectrometer. Fluorescence quantum yields were determined by comparing the integrated emission bands with that of fluorene ($\Phi_f = 0.68$).[14] Fluorescence lifetimes were measured on a PTI LS-1 instrument using the time-correlated single-photon-counting technique, and all decays were first order.

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