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Excited state intramolecular proton transfer (ESIPT) in 2-phenylphenol: an example of proton transfer to a carbon of an aromatic ring

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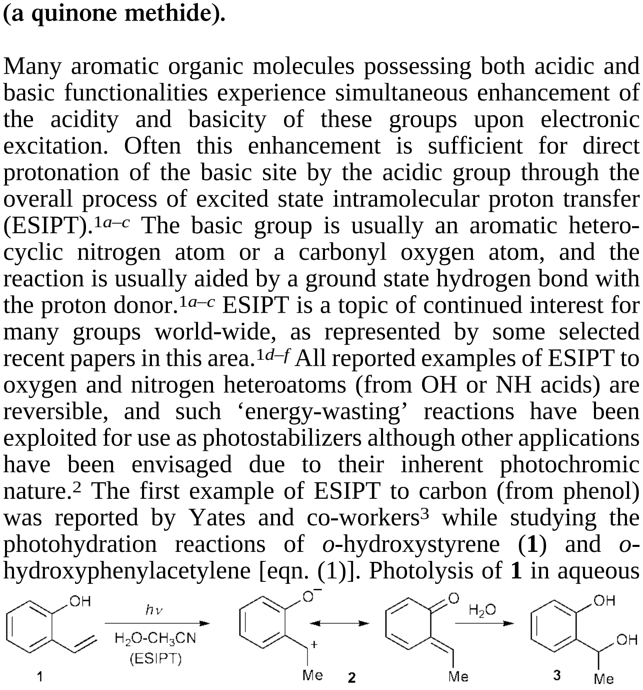
Received (in Corvallis, OR, USA) 19th January 2001, Accepted 13th April 2001
First published as an Advance Article on the web 15th May 2001

The title compound undergoes excited state intramolecular proton transfer (ESIPT) from the phenol moiety to the 2′-carbon position of the phenyl ring (not containing the phenol hydroxy group), to generate the corresponding keto isomer (a quinone methide).

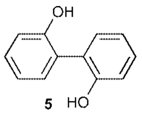
Many aromatic organic molecules possessing both acidic and basic functionalities experience simultaneous enhancement of the acidity and basicity of these groups upon electronic excitation. Often this enhancement is sufficient for direct protonation of the basic site by the acidic group through the overall process of excited state intramolecular proton transfer (ESIPT).[1a–c] The basic group is usually an aromatic heterocyclic nitrogen atom or a carbonyl oxygen atom, and the reaction is usually aided by a ground state hydrogen bond with the proton donor.[1a–c] ESIPT is a topic of continued interest for many groups world-wide, as represented by some selected recent papers in this area.[1d–f] All reported examples of ESIPT to oxygen and nitrogen heteroatoms (from OH or NH acids) are reversible, and such ‘energy-wasting’ reactions have been exploited for use as photostabilizers although other applications have been envisaged due to their inherent photochromic nature.[2] The first example of ESIPT to carbon (from phenol) was reported by Yates and co-workers[3] while studying the photohydration reactions of *o*-hydroxystyrene (**1**) and *o*-hydroxyphenylacetylene [eqn. (1)]. Photolysis of **1** in aqueous MeCN gave the hydration product **3** *via* *o*-quinone methide **2**. The primary photochemical step (from S_1) is ESIPT from the phenol to the β-carbon of the alkene moiety. Reverse proton transfer in **2** (from C–H to phenolate oxygen) is highly unfavourable and, instead, the intermediate is trapped completely by water to give **3**.[3,4]



(1)

To our knowledge, there are no explicit examples of ESIPT to a carbon atom that is part of an aromatic ring. However, Webb and coworkers[5] 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 carbons positions, *via* solvent-mediated ESIPT. In addition, reports of the photoprotonation (by aqueous acid) of the ring carbons of a variety of aromatic rings is well-known.[6] What is unknown is whether an explicit ESIPT to an aromatic ring carbon could operate in appropriately designed systems. Such systems would be unique as examples of a new type of ESIPT process. We present results for the photochemical deuterium exchange in 2-phenylphenol (**4**) that is entirely consistent with an explicit ESIPT from the phenol moiety to the ring carbon (position 2′) of the benzene ring not bearing the hydroxy group.

Exhaustive photolysis of **4** in 1 : 1 (v/v) D_2O–MeCN solution (Rayonet RPR-100 photochemical reactor; 254 nm lamps; 10^{-3} M; < 15 °C; argon-purged solutions; 1 h) yielded (after a H_2O-wash) **4** that is deuterated exclusively on the ring not bearing the hydroxy group. ^{1}H NMR (360 MHz) analysis of the sample showed that 70% of the 2′-(*ortho*) positions and 30% of the 4′-(*para*) positions were deuterated (not excluding dideuteration of the 2′-position since there are two such positions). These observations are consistent with an excited state where there is substantial charge transfer from the phenol ring to the benzene ring and would not be unusual based on photochemistry of some hydroxy-substituted biphenyls and biaryls already reported by our group.[6c,7] Similar results were observed for the photolysis of **5**† whereas photolysis of **6–8** gave no observable exchange.



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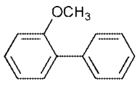

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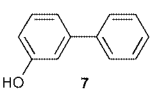

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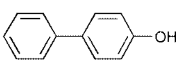

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For **4** and **5**, no exchange was observed in solutions that were not photolyzed. Clearly the hydroxy group is necessary for reactivity. The lack of reactivity for **7** and **8** suggest that the exchange observed for **4** and **5** may be due to an explicit ESIPT between the phenol OH and the 2′-position of the other benzene ring.

To investigate the possibility of an ESIPT mechanism for exchange, subsequent photolysis of **4** were carried out in MeCN solutions containing varying concentrations of D_2O and the extent of exchange analyzed by NMR. The results are plotted in Fig. 1. Under the conditions employed for these experiments, exchange at the *para* position was too low to be reliably measured (typically < 10% across the D_2O concentrations used). The plot shows that *ortho* exchange (which is significantly more efficient than exchange at the *para* position) is independent of D_2O concentration above 0.2 M D_2O. At lower concentrations, there is a rapid rise in the efficiency for exchange at the *ortho* position (see inset), reaching a plateau level at about 0.2 M D_2O. These observations strongly suggest that exchange at the *ortho* and *para* positions take place *via* different mechanisms. The rapid rise in yield of *ortho* exchange with increasing D_2O content at low concentrations essentially corresponds with the extent of exchange of the hydroxy proton of **4**; that is, once all of **4** has been deuterated at the hydroxy group (to give **4**-*OD*), the efficiency of photochemical deuteration at the *ortho* position is solvent independent. This is further corroborated by independent photolysis of a crushed crystalline sample of **4**-*OD*, which gave exclusive exchange (about 10%) at the *ortho* position, with no observable exchange at the *para* position. These results are consistent with a mechanism of *ortho* exchange involving ESIPT (Scheme 1). In this mechanism, photolysis of **4**-*OD* results in ESIPT to the 2′-carbon position, to generate the *o*-quinone methide intermediate **9**. Reverse transfer of a proton or water-assisted tautomerization gives **4**-*2′D* (after H_2O wash). A related ESIPT has been reported for compound **10** (and related systems) although in this case, the basic site is a nitrogen of an aromatic heterocyclic ring.[8] What we have shown in this work is that the *ortho* carbon atoms (on a simple

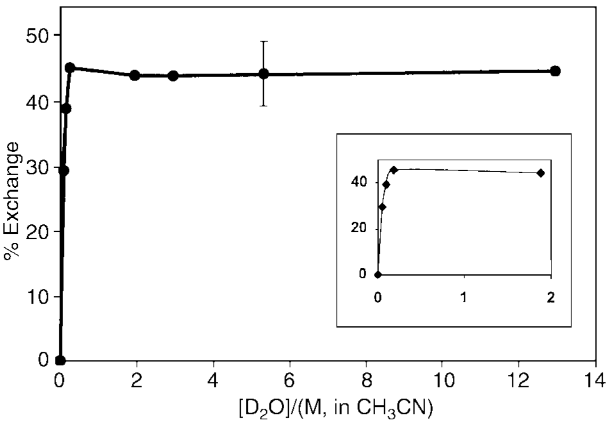
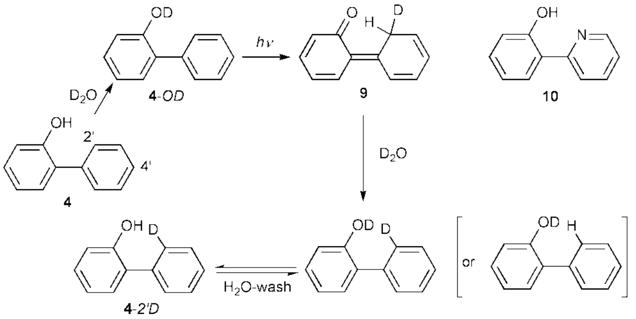


Fig. 1 Plot of % exchange at the *ortho* (2′) position observed for **4** *vs.* D_2O concentration (in MeCN). (Inset: expanded plot at low D_2O concentration).



Scheme 1

benzene ring) are sufficiently basic to accept the acidic proton in these systems.‡

The *para* (4′) carbon is too far away from the acidic hydroxy (phenol) proton to be directly protonated intramolecularly. Indeed, its exchange yield is much lower. These results imply that a different mechanism is operative for deuterium incorporation at the *para* position. This is further corroborated by the following experiments. Photolysis of **4** in 1:1 MeOD–MeCN resulted in deuterium incorporation exclusively at the *ortho* position and suggests that only the ESIPT mechanism operates in MeOH–MeCN. Fluorescence emission spectra of **4** in a number of solvents gave additional insights into the mechanism of exchange at the *para* position (Fig. 2). These spectra show that **4** does not undergo excited state dissociation of the phenolic proton in neat MeCN or MeOH whereas 1:1 H_2O–MeCN is sufficiently polar to allow the dissociation, and hence formation of the excited state phenolate ion at 415 nm. That water is generally required for adiabatic deprotonation of phenols is well-known and has been specifically studied for **4** in H_2O–MeOH solutions.[9] These results are consistent with a mechanism of deuterium incorporation at the *para* position involving protonation (at the 4′-carbon) of the excited or ground state phenolate ion, formed *via* deprotonation from S_1 that requires water. This is apparently not an efficient process as the carbon protonation step must compete with fluorescence of the excited state phenolate as well as reprotonation at the oxygen site. This mechanism of deuterium incorporation probably also contributes to the overall exchange observed at the *ortho* position in aqueous solution (the extent of which is unknown at present) although the evidence suggests that ESIPT is the only mode of reaction responsible for exchange in neat organic solvents and in the solid state.

In summary, the results observed are consistent with a new type of ESIPT in which the acidic proton from a phenol is

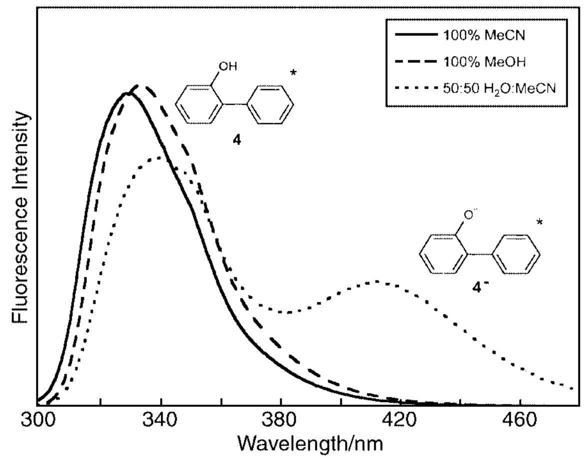


Fig. 2 Fluorescence emission spectra observed for **4** in 1:1 H_2O–MeCN, neat MeCN and neat MeOH (λ_{ex} = 285 nm; τ(neat H_2O) = 0.53 ns;[9] (1:1 H_2O–MeOH) = 1.25 ns;[9] estimated Φ_f (neat MeCN) ≈ 0.1).

directly transferred to a carbon atom of a benzene ring. The transfer is effectively reversible resulting in deuterium incorporation when carried out in D_2O. The dynamics and generality of this new type of ESIPT await further exploration.

We acknowledge the continued support of the Natural Sciences and Engineering Research Council (NSERC) of Canada and the University of Victoria. ML thanks NSERC for a post-graduate scholarship. Dr Y. Shi is acknowledged for preliminary studies.

Notes and references

† In this case, deuteration occurs on both rings since the system is symmetrically substituted.

‡ One would expect the ESIPT efficiency to be substantially lower when nitrogen is replaced by carbon. We have estimated the quantum yield for deuterium incorporation at the *ortho* (2)′-position in 1:1 D_2O–MeCN to be ≈ 0.02.

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