

Charge Polarization in Photoexcited Alkoxy-substituted Biphenyls: Formation of Biphenyl Quinone Methides

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Alkoxy-substituted biphenyls are highly polarized in S_1 , with the negative charge residing on the ring not possessing the alkoxy group, enabling the photogeneration of spectrophotometrically observable transient biphenyl quinone methides by laser flash photolysis.

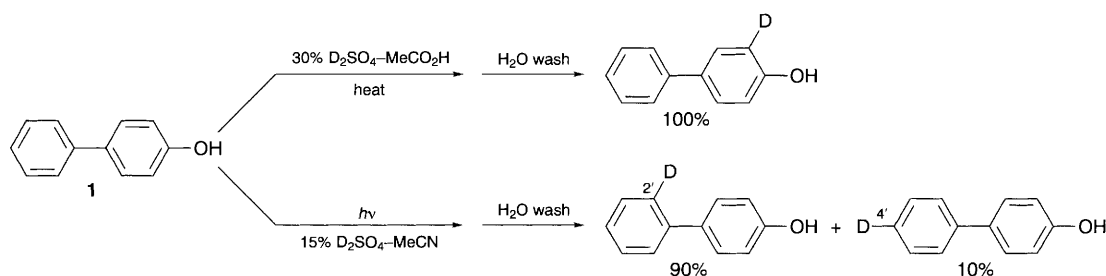
It is generally known that biphenyls and biaryls have twisted ground state structures with a tendency to become planar when electronically excited.¹ Dihedral angles in the ground state can be as large as *ca.* 80° (from crystal structures) for highly congested *ortho*-substituted systems.² Several photochemical reactions have been reported which utilize the inherent tendency for planarization of the biphenyl ring system in the excited state.³ It has also been shown^{3c,4} that substituted biphenyls are extensively polarized in S_1 , although the evidence presented were either indirect or encumbered with multi-substituents on the ring system. Here, we show unequivocally using product studies and laser flash photolysis that simple biphenyl derivatives have significant charge polarization in S_1 which can result in new photochemistry.

The two biphenyls initially chosen for study were 4-phenylphenol **1** and 4-methoxybiphenyl **2** since it is known that alkoxy groups are potentially good electron-donating groups (by resonance). As a chemical probe for charge transfer in these systems, we monitored for deuterium exchange of the aromatic protons in aqueous medium (D_2O or D_2SO_4 solutions) by 1H NMR (360 MHz). Electronic communication between the two benzene rings of biphenyls is minimal in the ground state. This was demonstrated by the observation that when **1** was refluxed in 2:1 (v/v) 20% (*m/m*) D_2SO_4 - $MeCO_2H$ (3 h), deuterium incorporation was observed exclusively at the 2-position of the phenol ring (Scheme 1). This would be as expected based on Hammett substituent effects for a hydroxy and a phenyl group on the same benzene ring. In addition, the requirement of moderately strong acid at reflux for observable exchange

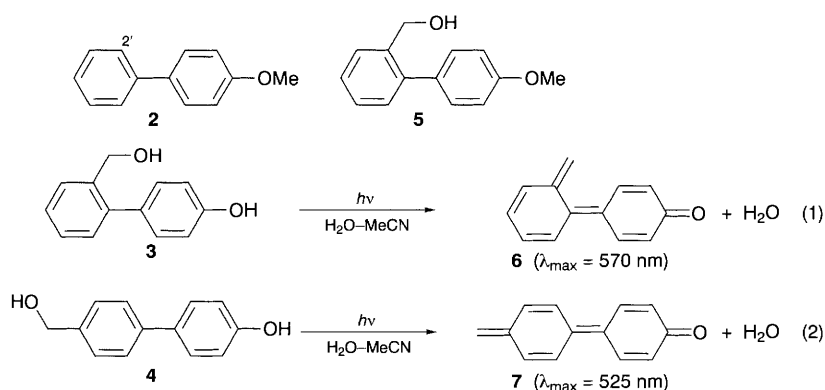
indicates that there is only moderate activation of the 2-position by the hydroxy group.

However, when both compounds **1** and **2** were irradiated in D_2SO_4 - $MeCN$ (1:2, 15%) (Rayonet photochemical reactor; *ca.* 15 °C; 4 h; no dark exchange was observed), deuterium exchange was observed *exclusively* on the ring *not* bearing the hydroxy or methoxy substituent. For compound **1**, exchange was observed mostly at the 2'-position and a minor amount at the 4'-position (Scheme 1) while compound **2** gave only observable exchange at the 2'-position. 4-Phenylphenol **1** also underwent deuterium exchange when irradiated in neutral solution (D_2O - $MeCN$ 1:2), with exchange taking place predominantly at the 4'-position (on the ring not bearing the substituent). Since phenols are stronger acids in the excited singlet state [$pK(S_1)$ *ca.* 1-3], the change in regiochemistry may be attributable to the fact that in neutral solution, the excited phenolate ion is the reactive form whereas in D_2SO_4 (15%), deprotonation in S_1 does not take place.

These results show that there is a high degree of polarization of simple methoxy or hydroxy-substituted biphenyls, with the negative charge residing primarily on the ring not bearing the substituent, which is then protonated by solvent protons, to generate a quinone-type species with the bond joining the two benzene rings having substantial double bond character. To test for the possibility that such an intermediate is on the reaction pathway, biphenyl alcohols **3** and **4** were synthesized. These systems allow for the loss of hydroxide ion from the corresponding benzylic positions and if there is indeed significant negative charge development at these positions, the



Scheme 1



resulting loss of hydroxide ion will give rise to biphenyl quinone methide intermediates which should be spectrophotometrically observable as these species are highly conjugated. Loss of hydroxide from benzylic positions is now a well known primary photochemical process.⁵

Laser flash photolysis (LFP; Nd:YAG laser; 266 nm; <30 mJ/pulse) of flowing solutions of compound **3** (H₂O–MeCN, 1:1) and compound **4** (H₂O, 100%) gave long wavelength transients centred at 570 and 525 nm, respectively (Fig. 1). Much stronger signals were observed when compound **3** was studied in H₂O (100%) making it difficult to see the transient from compound **4** when presented on the same figure. These transients were unaffected by oxygen but their lifetimes were shortened by the addition of ethanolamine (and water to H₂O–MeCN mixtures) as nucleophile. LFP in MeCN (100%) failed to give any significant signal but upon addition of water, the signals became much stronger, reaching a maximum in H₂O (100%). LFP of methoxy derivative **5** failed to give any signal indicating that the phenol hydroxy group is necessary.

Preparative photolysis (254 nm) of compounds **3** and **4** in MeOH–H₂O (1:1) gave the corresponding benzylic methyl ether products with quantum yields for methyl ether formation at the benzylic position (Φ) of 0.24 and 0.03 for compounds **3** and **4**, respectively, indicating that electrophilic species are photogenerated. The greater Φ observed for compound **3** is consistent with the stronger transient signal observed for this

compound. All of the above observations strongly implicate the formation of biphenyl quinone methides† **6** and **7**, respectively, from photolysis of compounds **3** and **4** [eqns. (1) and (2)]. As far as we are aware, this is the first report of their characterization as transient intermediates. Of particular interest is the broadness of the absorption of compound **6**. Decays monitored at several different wavelengths indicate that it is due to one transient.

In summary, we have demonstrated that hydroxy and methoxy groups are significantly electron donating to the other ring on a biphenyl system in the excited singlet state and are capable of displacing hydroxide ion from the benzylic position, giving rise to observable biphenyl quinone methides. These results invite investigations of the corresponding terphenyls and higher order systems, the results of which may be of significance in the fabrication of molecular devices.⁷

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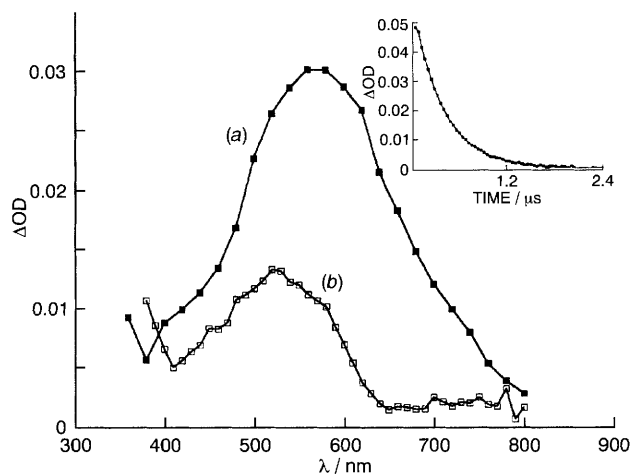


Fig. 1 Transient spectra observed on laser flash photolysis of compound **3** [spectrum (a) in H₂O–MeCN (1:1)] and compound **4** [spectrum (b) in H₂O (100%)]. Lifetimes were measured in H₂O (100%) and were 0.40 and 67 μs for compounds **6** and **7**, respectively. Inset: first order decay of transient compound **6** in H₂O (100%).

Footnote

† Simple *p*-quinone methides are generally much longer lived ($t_1 = 26$ s in water for the parent quinone methide with 2,6-dimethyl substituents)⁶ than the biphenyl quinone methides observed in this work and one possible reason is that the latter species can revert to a phenol possessing two aromatic rings instead of only one for simple quinone methides.

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