Photocyclization of a 1,1′-bisnaphthalene: planarization of a highly twisted biaryl system after excited state ArOH dissociation

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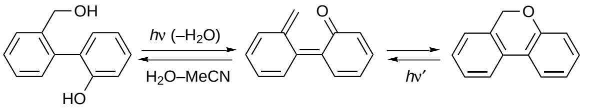
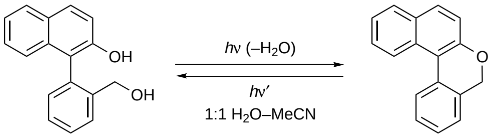
Photolysis of the highly twisted 1,1′-bisnaphthalene 6 gives the much more planar dinaphthopyran 10 with high quantum yield (Φ = 0.17) in aqueous MeCN, demonstrating that the expected enhanced electronic communication between the connected aromatic rings of biaryls in S_1 is sufficient to drive thermally unfavourable reactions requiring initial planarization of these biaryl systems.

Twisted ground state structures of biphenyls and biaryls in general become much more planar when electronically excited.[1] However, this phenomenon has been utilized only on a limited basis to design or induce new photochemistry.[2] We demonstrated several years ago that photolysis of twisted (dihedral angle of 72°) 2-(2′-hydroxyphenyl)benzyl alcohol **1** in aqueous solution or in 100% MeCN gave the essentially planar 5*H*-dibenzo[*b,d*]pyran **3** *via* the proposed *o,o*′-biphenyl quinone methide **2** with high quantum efficiency (Φ up to 0.5) [eqn. (1)].[2c,d] We wondered whether the reaction could be extended to binaphthyls and related compounds since large biaryls are of interest in a variety of areas including supramolecular chemistry where photoflexible systems are useful as photoswitches,[3] and as ligands in catalysis design.[4] Since 1,1′-binaphthyls are more twisted than biphenyls in general due to the additional steric interactions from introduction of two additional benzene rings, the notion that electronically excited binaphthyls can undergo extensive twisting to a more planar form even under these additional constraints would be relevant chemical information for use in supramolecular chemistry where large torsional motions are of intrinsic value in molecular switching.

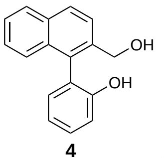


1 **2** **3** (1)

Biarylmethyl alcohols **4–6** were made *via* LAH reduction of the corresponding lactones **7–9**, which were synthesized according to method of Bringmann *et al.*[5] All of **4–6** were smoothly converted to their corresponding pyrans on photolysis in MeCN or aqueous MeCN at 254 nm [*e.g.* eqn. (2)].† Shown in Fig. 1 is the UV–VIS spectra for conversion of **6** to pyran **10** in 1 : 1 H_2O–MeCN at 254 nm showing the clean conversion to almost 100% **7**, with Φ = 0.17. Photolysis of the pyran **10** at > 350 nm resulted in > 50% conversion back to **6** illustrating the reversibility of the photoreaction. Although reaction of **5** was clean and reversible, the quantum yield for cyclization ($\Phi \approx 0.04$) was substantially lower than observed for **4** and **6** (*vide infra*). Molecular mechanics calculations of **5** and **6** and an X-ray crystal structure‡ of **4** showed that these biaryls are highly twisted with dihedral angles approaching 90°. However, the corresponding pyran products are much more planar. For example, the dihedral angle for **10** (the most non-planar of the pyrans products) is 37° from X-ray crystallography.‡ Thus, these photocyclizations involve a very substantial twisting motion to planarity on the excited state surface. Moreover, the photoreversibility of the reaction shows that there is an equally substantial twisting motion out of planarity in the ring opening reaction, which formally requires conrotatory motion of the orbitals involved (a photochemically induced electrocyclic ring opening). Indeed, the degree of twisting motion displayed in these systems on photolysis approach those observed for *cis–trans* photoisomerization of alkenes.



6 **10** (2)



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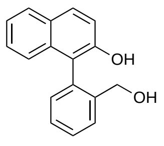

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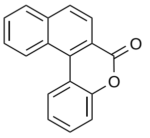

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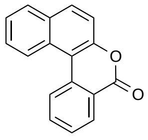

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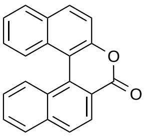

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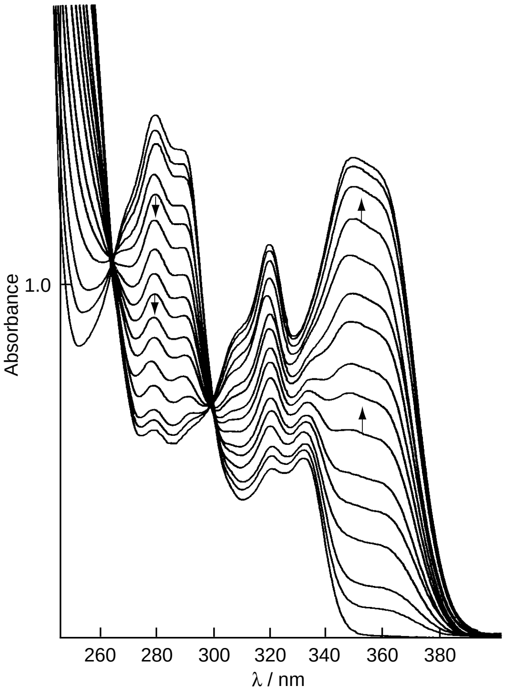
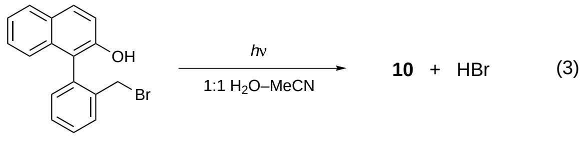


Fig. 1 UV–VIS traces of conversion of **6** to **10** on photolysis of at 254 nm in 1 : 1 H_2O–MeCN. Each trace taken after about 5–20 s irradiation in a UV cuvette.

Bromide derivative **11** was photolyzed in 1 : 1 H_2O–MeCN and gave **10** in > 90% yield ($\Phi \approx 0.35$) along with a dramatic decrease in the pH of the aqueous solution (from pH 7 to 2.6) indicating that these binaphthyl systems can also photo release strong acid concurrent with geometric change [eqn. (3)]. The additional fact that **11** was found to be thermally stable to 125 °C makes these systems potentially useful for the photodeprotection of esters and related functional groups by making the required naphthylmethyl derivatives from bromide **11**.



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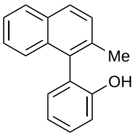
The twisting motion of biaryls towards planarity on the excited state surface has been generally rationalized[2a,6] by noting that the coefficients of the two carbons joining the two aryl rings in the LUMO have the same sign whereas they have opposite sign in the HOMO. Thus population of the LUMO on electronic excitation causes an increase in the π-bond strength joining the two aryl groups; hence a twisting motion to a more planar structure.

However, simple twisting of the two aryl rings to a more planar geometry on electronic excitation does not completely explain why these compounds cyclize and lose water. Additional chemical steps are required, *viz.* dissociation of the hydroxynaphthalene (or phenol) proton and loss of hydroxide ion from the arylmethyl (benzylic) position to form the corresponding biaryl naphthoquinone methide. In our first report of this type of reaction[2c] [eqn. (1)], we were not able to address whether twisting took place before proton dissociation from the phenol or *vice versa*, or that they took place together, although it was clear that the phenolate ion in the excited state was the reactive species. We now report that a better understanding is available for **4**–**6**. We have studied the fluorescence behaviour of model compounds **12** and **13** (for **4** and **6**, whose fluorescence were too weak for proper study due to their high photoreactivity for cyclization) and **5** (which is sufficiently fluorescent), and found that there is a correlation between the amount of observed Stokes shift (a useful measure of the degree of change in geometry between the Franck–Condon and the fluorescent states)[1] and the quantum efficiency of cyclization.



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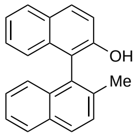

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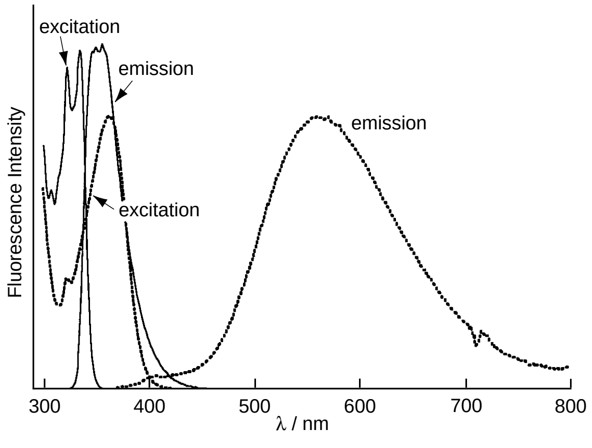

Fig. 2 Fluorescence excitation and corrected emission spectra of **13** in 100% MeCN (solid lines) and in 1 : 1 MeCN–0.01 mol dm^{-3} NaOH (dashed lines). The measured Stokes shifts are 1700 and 7500 cm^{-1} for the protonated (ArOH) and naphthoate (ArO^-) forms of **13**, respectively.

All of **5**, **12** and **13** display only a modest Stokes shift in 100% MeCN (*ca.* 1700 cm^{-1}, Fig. 2) where the fluorescence is from the protonated form. This implies that the degree of twisting of the excited protonated phenol or naphthol is insignificant. However, when their fluorescence spectra were taken in pH 12 (excitation of the phenolate or naphthoate forms), the Stokes shifts of the emission from the deprotonated forms were substantial for **12** and **13** (*ca.* 7500–8000 cm^{-1}) (Fig. 2) but much less for **5** (*ca.* 3000 cm^{-1}). We can conclude that these systems twist to become more planar only after (adiabatic) excited state deprotonation. That is, the mechanism for cyclization must involve initial adiabatic deprotonation from the twisted (Franck–Condon) structure followed by twisting to a more planar form, which then loses hydroxide ion from the arylmethyl position to generate the required (naphtho)quinone methide intermediate. The much lower quantum yield of cyclization observed for **5** is most likely due to the lesser degree in which this system is capable of twisting (to the more planar form) after deprotonation although the exact reasons for this is unknown at this time. A possible explanation we are currently investigating is that there is a dependence of the degree of twisting and the amount of available electron density to the $ArCH_2OH$ moiety from the electronically excited ArO^- ring. We believe the above new results and improved understanding of the reaction mechanism will help us design supramolecular systems which can incorporate these chromophores for use as photoactivatable systems.

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Footnotes

† Oxygen had no measurable effect on these photocyclizations. The fluorescence results reported here and previously[2c,d] indicate that these are most likely reactions from the singlet excited state. Although we have not been able to directly observe the proposed *o,o′*-biaryl quinone methides by nanosecond laser flash photolysis (presumably due to their very short lifetimes), we have observed[2d] similar quinone methides when they cannot cyclize to the corresponding pyrans. This argues in favour of a photocyclization mechanism *via* such intermediates rather than, for example, simple displacement of the hydroxide of the methylene carbon by the phenol oxygen.

‡ Details of the X-ray crystal structure analyses will be published in due course.

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