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Solid state and solution phase photocyclization of a 2-(2′-hydroxyphenyl)benzyl alcohol: twisting motion to planarity occurs efficiently in the crystal

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Abstract

The photocyclization of α,α-diphenyl-2-(2′-hydroxphenyl)benzyl alcohol (**5**), a highly twisted biphenylmethanol from the X-ray crystal structure (dihedral angle between of the biphenyl ring system ≈ 80°), photocyclizes efficiently in CH_3CN solution as well as in the crystalline state, to give the much more planar α,α-diphenyldibenzo[b,f]pyran (**7**). The mechanism of reaction in neat CH_3CN solution is believed to involve initial excited state *intramolecular* proton transfer (from the phenol OH to the benzylic CPh_2OH) whereas the reaction in the crystal is proposed to involve excited state *intermolecular* proton transfer as the compound crystallizes as H-bonded dimers in a unit cell consisting of eight molecules (absence of included water) in which the phenol OH is H-bonded to the oxygen atom of the benzylic CPh_2OH group.

Keywords: Biphenyl quinone methide; Photocyclization; Solid state photochemistry; Excited state proton transfer

1. Introduction

Several years ago, we reported a new type of photocyclization reaction involving *o,o′*-disubstituted biphenyls, the parent reaction of which converted 2-(2′-hydroxyphenyl)benzyl alcohol (**1**) to 6*H*-dibenzo[b,d]pyran (**2**) (Scheme 1) in high chemical yield with quantum yields as large as 0.5 in basic aqueous CH_3CN solution [1]. The reaction was also observed in neat CH_3CN but with lower quantum efficiency ($\Phi = 0.12$). The X-ray crystal structure of **1** [1] shows a highly twisted biphenyl ring system (dihedral angle of 68°) where the two ortho benzene ring substituents (OH and CH_2OH) are in a syn-arrangement, most likely due to intramolecular H-bonding between the two ortho hydroxyl groups. Since product **2** is much more planar (dihedral angle of 24° from a molecular mechanics (Alchemy III) calculation), the overall photoreaction requires a significant twisting motion to planarity *along* with substantial charge redistribution in the excited singlet state to effect the cyclization (with overall loss of H_2O).

A mechanism of reaction was proposed [1] (Scheme 1) in aqueous CH_3CN solution which requires the phenol moiety to ionize (to solvent) in the excited singlet state, to give the electronically excited phenolate ion **3**. Twisting motion at this stage (or concerted with phenol ionization) allows conjugation of the two benzene rings which, due to the enhanced electron donating effect of the phenolate ion in the excited state, causes the hydroxide ion from the benzylic position to be ejected. This gives rise to a relatively planar *o*-biphenyl quinone methide **4** which undergoes electrocyclic ring closure to give the observed product **2**. The observation that the photocyclization also proceeds in neat CH_3CN prompted us to envisage mechanisms which involved intramolecular proton transfer, although the possibility that residual water in neat CH_3CN acting as the base could not be ruled out at the time. More recently, we have found that exploratory photolysis of crystalline samples of **1** also gave **2**.[1] This implies that a polar solvent is not required at all for the reaction although the efficiency may be enhanced when a polar solvent is used, presumably via a change in reaction mechanism. These initial results led us to explore in more detail the photocyclization of these types of compounds in the solid state, the first part of which is reported in this work.

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[1] C.-G. Huang, Y. Shi, P. Wan, unpublished results, 1994.

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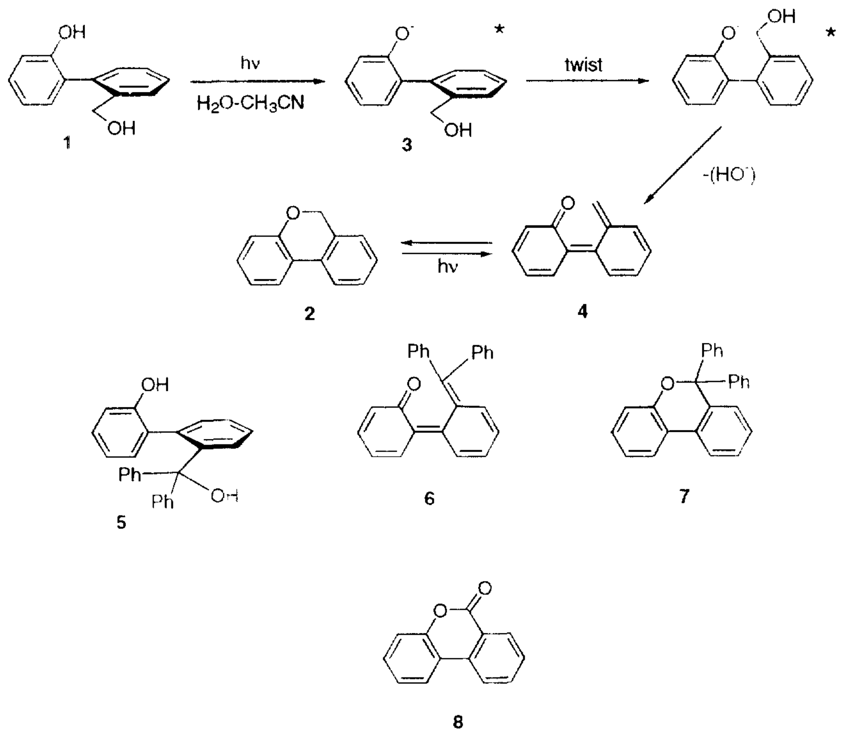

Scheme 1.

Photochemical reactions in the solid state have been of intense interest for many years [2–5]. More recently, organic photochemists have utilized such reactions for controlling stereoselectivity [6,7] and regioselectivity [8,9] with promising results, as well as exploring the mechanism of solid state photoreactions requiring large torsional motions [10] and photosolvolysis in the solid state (with co-crystallized solvent molecules) [11]. We have chosen to study the solid state photocyclization of the α,α-diphenyl-substituted biphenyl derivative **5** (α,α-diphenyl-2-(2′-hydroxyphenyl)benzyl alcohol) due to the ease in which crystals suitable for X-ray crystallography can be grown, the expected large dihedral angle of the biphenyl ring system, and the potential of using laser flash photolysis (in solution) to monitor for the formation of the corresponding *o*-biphenyl quinone methide **6**, which might be sufficiently long-lived for its detection due to the greater conjugation expected in the additional benzene rings at the α-position. We show that **5** photocyclizes efficiently in solution as well as in the solid state, to give the expected pyran **7**. Moreover, X-ray crystallography shows the absence of any included water in the unit cell of the crystal, with the OH protons exhibiting both intra and intermolecular hydrogen-bonding. Photocyclization mechanisms involving initial excited state intra and intermolecular proton transfer are presented and discussed.

2. Experimental details

2.1. General

^{1}H NMR spectra were taken on Bruker AC300 or AM360 spectrometers in $CDCl_3$ or acetone-d_6. Mass spectra were obtained on a Kratos Concept H (EI) instrument. UV–Vis spectra were measured on a Cary 5 instrument. Preparative photolyses were carried out using a Rayonet RPR 100 photochemical reactor using 254 or 300 nm lamps. Reaction mixtures for these photolyses were contained in 100 or 200 ml quartz tubes which were cooled to ≈ 15°C using a cold finger (tap water) and purged continuously during photolysis using a stream of argon via a stainless steel syringe needle.

2.2. Materials

Anhydrous CH_3CN used for fluorescence studies was distilled over CaH_2 and used immediately. Anhydrous THF was obtained by distillation from potassium metal. Preparative thin layer chromatography (TLC) was carried out on 20 cm × 20 cm silica gel GF Uniplates (Analtech). 2′-Hydroxybiphenyl-2-carboxylic acid lactone (**8**) required for the synthesis of **5** was prepared using a previously described method [1].

2.2.1. α,α-Diphenyl-2-(2′-hydroxyphenyl)benzyl alcohol (5)

To 5.0 g (25 mmol) of lactone **8** dissolved in 250 ml dry THF was added 160 ml of 1.8 M phenyl lithium with stirring over 2 h. The mixture was then refluxed for 4 h. After reaction, the solution was quenched with a mixture of ice and saturated NH_4OAc and extracted three times with CH_2Cl_2. A colourless oil was obtained after the solvent was removed. This crude oil was washed several times with hexanes after which it solidified on standing for several days. This solid was first recrystallized from toluene–hexanes and then from a mixture of hexanes, CH_2Cl_2, and CH_3COCH_3, to give good quality crystals (suitable for X-ray crystallography) of pure **5** (1.75 g, 20%), m.p. 103–105°C; ^{1}H NMR (360 MHz, $(CD_3)_2CO$) δ 5.25 (s, broad, D_2O exchangeable, ROH); δ 6.28 (dd, 1 H, J=7.6, 1.7 Hz), δ 6.41 (ddd, 1 H, J=7.4, 7.5, 1.2 Hz), δ 6.76 (dd, 1 H, J=8.0, 1.2 Hz), δ 6.87 (dd, 1 H, J=8.0, 1.4 Hz), δ 6.96 (ddd, 1 H, J=7.3, 7.3, 1.7 Hz), δ 7.05 (dd, 1 H, J=7.4, 1.5 Hz), δ 7.07–7.15 (m, 5H), 7.17–7.30 (m, 4 H), 7.33 (ddd, 1 H, J=7.4, 7.5, 1.4 Hz), δ 7.36–7.42 (m, 2 H); δ 8.40 (s, broad, D_2O exchangeable, ArOH); ^{13}C NMR ($(CD_3)_2CO$) δ 153.9, 148.3, 148.2, 147.1, 139.3, 134.1, 132.4, 131.3, 130.5, 129.1, 128.7, 128.3, 128.2, 128.0, 127.6, 127.4, 127.1, 119.9, 116.1, 83.0; MS (CI) m/z (relative intensity) 335 ((M+1) $-H_2O$) (100); chemical analysis, calculated for $C_{25}H_{20}O_2$, 85.20% C, 5.72% H; found 85.16 C, 5.71% H. Due to the efficient loss of water in the mass spectrometer, no attempts were made to obtain an exact mass. The X-ray crystal structure obtained below provided final proof of structure.

2.3. Product studies

2.3.1. Photolysis of 5 in 100% CH_3CN and 1:1 H_2O–CH_3CN

A solution of **5** (147 mg) in CH_3CN (200 ml) was photolyzed (254 nm) in a quartz tube for 30 min using the general procedure. The solvent was then removed by rotary evaporation. The residue (60% conversion to pyran **7** by ^{1}H NMR) was chromatographed on preparative thin layer chromatography (silica; 2:1 hexanes–CH_2Cl_2). The first band was collected to give a white solid, which was recrystallized from CH_3CN to give pure **7**, m.p. 137–139°C; ^{1}H NMR (300 MHz, $(CD_3)_2CO$) δ 6.73 (dd, 1 H, J=8, 1 Hz), δ 6.96 (ddd, 1 H, J=8, 8, 1 Hz), δ 7.07 (d, 1 H, J=8 Hz), δ 7.15–7.25 (m, 5 H), δ 7.25–7.36 (m, 7 H), δ 7.48 (ddd, 1 H, J=8, 8, 1 Hz), δ 7.78 (dd, 1 H, J=8, 1 Hz), δ 7.92 (dd, 1 H, J=8, 1 Hz); High resolution MS (EI), calculated for $C_{25}H_{18}O$, 334.1358, observed 334.1362; chemical analysis, calculated for $C_{25}H_{18}O$, 89.79% C, 5.43% H; found 88.89% C, 5.38% H.

When photolyzed in 1:1 H_2O–CH_3CN, the conversion to **7** was about 50% higher (by UV–Vis and ^{1}H NMR) indicating a more efficient reaction when water is present. In addition, at very high conversions, minor side products were observable in runs in 100% CH_3CN whereas they are absent in 1:1 H_2O–CH_3CN.

2.3.2. Photolysis of 7 in 1:1 H_2O–CH_3CN and 1:1 CH_3OH–CH_3CN

A solution of **7** (1.4×10^{-4} M, in 1:1 H_2O–CH_3CN or 1:1 CH_3OH–CH_3CN) was placed in a cuvette (3.0 ml) and irradiated at 254 or 300 nm. No changes were detected by UV–Vis spectrophotometry even on prolonged irradiation indicating the lack of any conversion to the ring-opened product (**5** in 1:1 H_2O–CH_3CN, and the corresponding methyl ether in 1:1 CH_3OH–CH_3CN). This was confirmed by ^{1}H NMR spectra of preparatory runs (more concentrated solutions; 60 min photolysis), which showed only **7**.

2.3.3. Photolysis of crystalline samples of 5

A sample of **5** (4 mg) was crushed into a fine powder with a mortar and then irradiated (in the mortar, opened to air) at 254 nm for 150 min. The sample was then dissolved in $(CD_3)_2CO$ and ^{1}H NMR showed 25% conversion to pyran **7**. No detectable side products were observed by NMR. In another experiment, 6 mg of powdered **5** was placed in a quartz cuvette and sealed under argon. The cell was then irradiated at 300 nm for 5 h. Analysis of the sample (^{1}H NMR) showed 10% conversion to **7**.

As an alternate method for studying the solid state photolysis, a solid film of **5** (4 mg) was cast between two quartz plates using CH_2Cl_2 and the solvent removed on a vacuum pump (residual 5–8% CH_2Cl_2 by NMR). This method allowed the progress of the photoreaction to be directly monitored by UV–Vis spectrophotometry, which showed clean conversion to **7** on photolysis, similar to that observed in runs in 1:1 H_2O–CH_3CN. In addition, the conversion could be taken higher compared to runs in which the powder was irradiated. However, the highest conversion achievable (^{1}H NMR analysis) was ca. 50%, even on prolonged photolysis, with the absence of detectable side products.

2.4. Laser flash photolysis

Laser flash photolysis (LFP) experiments were carried out at the University of Victoria LFP Facility at 20±2°C. A Spectra-Physics GCR 12 YAG laser at 266 nm (<30 mJ) was used for excitation and signals were digitized with a Tektronix TDS 520 recorder. Samples of OD $\approx$0.3 at 266 nm were prepared in quartz cells in a flow system to avoid photolysis of the photoproduct, which is formed efficiently. Purging was carried out using N_2 or O_2 prior to photolysis.

2.5. Quantum yields

Quantum yields for photocyclization of **5** to **7** were measured using UV–Vis spectrophotometry to follow the progress of the reaction. Experiments were carried out on an optical bench equipped with an Oriel 200 W Hg arc lamp and a monochromator set at 280 nm (slits = 10 nm). Generally, a quartz cuvette containing a 3.00 ml solution of the substrate was purged with argon for 5 min and then irradiated for a set time period on the optical bench. The extent of conversion to **7** was followed at λ_{max} = 308 nm (of the second absorption band of **7**), with ϵ = 6384 mol^{-1} L cm^{-1}. The light intensity was measured by potassium ferrioxalate actinometry [12]. The initial concentration of the substrate was adjusted such the absorbance at 280 nm was >2. The following quantum yields for photocyclization of **5** to **7** were measured: $\Phi=0.18\pm0.02$ (100% CH_3CN); 0.26 ± 0.03 (1:9 H_2O–CH_3CN); 0.27 ± 0.03 (1:1 H_2O–CH_3CN); 0.15 ± 0.02 (100% CH_3OH); 0.19 ± 0.02 (100% THF). No attempts were made to measure Φ for the solid state photolyses although qualitatively, the conversions were equally as efficient when compared to similar runs carried out in solution.

2.6. X-ray crystallography

The crystal (0.4×0.4×0.3 mm) of the compound (**5**) was mounted on a glass fibre and was cooled to 150 (2) K with a stream of dry N_2. The data was collected on a Siemens SMART CCD [13] diffractometer employing graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data were then reduced and integrated with the Siemens SAINT program [14]. The number of independent reflections was 3039 ($1.79 \leq \Theta \leq 25.53°$, $-13 \leq h \leq 27$, $-13 \leq k \leq 14$, $-14 \leq l \leq 14$). There was no absorption correction applied. The structure was solved by direct methods and Fourier difference synthesis, refinement on F^2 was by full-matrix least squares and anisotropic thermal parameters for all non-interacting atoms. The hydrogen atoms were found by Fourier difference synthesis and refined in the riding model with their temperature factor fixed at 1.2 times that of the parent atom. At convergence $R_1 = 0.0467$ (observed data) and w$R_2 = 0.1455$ (all data) for 305 parameters, goodness of fit = 1.207 and maximum and minimum residual electron density peaks 0.185, −0.201 Å e^{-3}. All crystallographic calculations were performed using SHELXTL-plus package [15] and the SHELXL-93 program [16]. The crystal structure data for **5** is given in Table 1.

Table 1
Crystallographic data for **5**

Formula	$C_{25}H_{20}O_2$
Molecular weight	352.41 g/mol
Crystal system	Monoclinic
Space group	$C2/c$
Cell dimensions: a (Å)	22.929(4)
b (Å)	13.038(2)
c (Å)	12.446(3)
α (°)	90
β (°)	93.3780 (10)
γ (°)	90
V (^{3})	3698(1)
$F(000)$	1488
Z	8
T (K)	150 (2)
λ (Å)	0.71073
ρ_{calc} (g ml^{-1})	1.266
μ (cm^{-1})	0.79
R_1	0.0491
wR_2 (all data)	0.1455

3. Results and discussion

3.1. Product studies in solution

UV–Vis traces of a sample of **5** (10^{-4} M) in 1:1 H_2O–CH_3CN photolyzed at 254 nm (Fig. 1) shows large changes consistent with transformation to the ring-closed product **7**, which is more intensely absorbing due to the improved conjugation of the biphenyl ring system (more planar structure in **7**). Conversions can be taken to essentially 100% since the final spectrum obtained is that of pure **7**. A similar trace taken in 100% CH_3CN is less clean as absorption >340 nm increases significantly at higher conversion. These results are confirmed by preparatory photolyses in which the yield of **7** is essentially quantitative when photolyzed in 1:1 H_2O–CH_3CN whereas in 100% CH_3CN, yields of 80–90% were observed.

In product studies of the parent system **1** [11], photolysis in 1:1 H_2O–CH_3CN gave a photostationary ratio of ca. 98% **2** and a residual 2% of **1** on exhaustive photolysis, implying that the photochemical reaction is reversible. This was confirmed [1] by the photolysis of **2** in 1:1 H_2O–CH_3CN, which gave a 2% yield of **1** on extended irradiation. That is, *o*-biphenyl quinone methide **4** undergoes electrocyclic ring closer to form **2** much faster than it is attacked by H_2O to form **1**. In the present case of **5**, it would appear that the corresponding *o*-quinone methide **6** is not attacked by H_2O but reacts only via electrocyclic ring closure. This is confirmed by photolysis of **7** in 1:1 H_2O–CH_3CN or 1:1 CH_3OH–CH_3CN, which resulted in no observable reaction (to give **5** or the corresponding methyl ether) even on extended photolysis. A reasonable explanation for the lack of any nucleophilic trapping products of **6** is the increased steric hindrance of the α-benzylic position (with two phenyl groups) which should retard nucleophilic attack at this site. In addition, *o*-biphenyl quinone methide **6** is less susceptible to nucleophilic attack than **4** based on electronic arguments as **6** has a more extended π-system (better delocalization of the residual positive charge at the benzylic carbon in the charge-separated resonance structure inherent in these quinone methides).

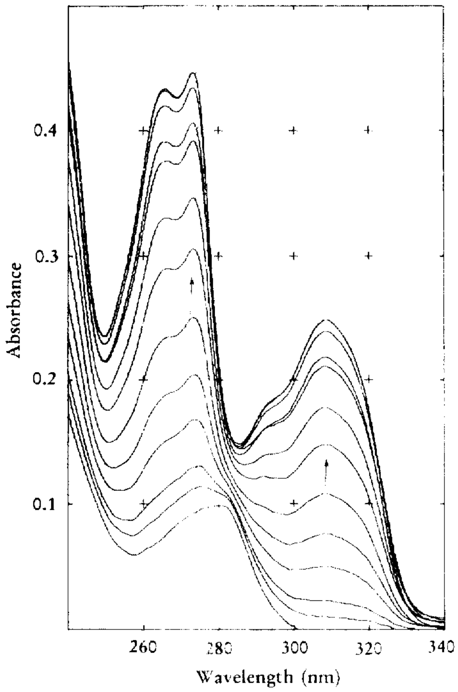

Fig. 1. The UV–Vis spectral traces observed on photolysis of **5** in 1:1 H_2O–CH_3CN at 254 nm. Each trace represents about 10 s photolysis.

In our study of the mechanism of photocyclization of **1** [1], we found that the photocyclization quantum yield was about twice as high in aqueous CH_3CN than in neat CH_3CN. This was rationalized as being due to the greater ability of water to solvate the phenolic proton, which is deprotonated on photoexcitation. A plot of quantum yield vs. pH (in aqueous solution) showed titration curves at pH ~ 1 and ~ 10, corresponding to the singlet excited state and ground state pK_as of the phenol moiety, respectively. These results support a mechanism in which the excited state phenolate ion is on the reaction pathway in the photocyclization mechanism in solution. Quantum yield measurements for photocyclization of **5** in a variety of solvents (vide supra) are consistent with this mechanism. Indeed, the quantum yields measured for **5** are very similar to those observed for **1** indicating that the presence of the two α-phenyl groups has very little effect on the photocyclization quantum yield. If anything, the photocyclization quantum yields for **5** are marginally higher (0.27 compared to 0.21 for **1** in 1:1 H_2O–CH_3CN and 0.18 compared to 0.12 for **1** in 100% CH_3CN) which might reflect the lack of nucleophilic trapping of **5** by H_2O, generated in situ or from the solvent (which leads back to starting material and hence reduce the observed quantum yield for photocyclization).

3.2. X-ray crystallography and product studies in the solid state

Compound **5** crystallizes in space group *C*2/c with eight molecules in the unit cell (Fig. 2). No included water molecules were found in the crystal. The eight molecules are arranged into four intermolecularly H-bonded dimers (Fig. 3) (phenol OH H-bonded with the benzylic O; O1–H2A/O1A–H2 distance is 1.86(3) Å, where atom X(A) is related to atom X by an inversion operation). Each dimer is also intramolecularly H-bonded (benzylic OH H-bonded with phenol O; O2–H1/O2A–H1A) distance is 1.88(3) Å). The dimer units are separated by normal van der Waals distances and the geometry of the monomer shows no exceptional or unusual features. A neutron diffraction analysis of this structure has confirmed the O–H positions and hence the H-bonding. These results will be published separately [17].

Shown in Fig. 4 is a view of **5** down the biphenyl axis (dihedral angle of the biphenyl ring system is 80°C) showing the *syn* arrangement of the two substituents on the biphenyl (the phenol OH and benzylic moiety), which is the optimal arrangement for photocyclization.

Crystals of **7** suitable for X-ray analysis were not available. We have used Alchemy III (Tripos) to generate an optimized geometry for **7** (Fig. 5) which shows a much more planar structure (of the dibenzopyran ring system, disregarding the α,α-diphenyl substituents) than for **5**, with a dihedral angle of 26°, which is only slightly more twisted than the parent pyran **2** (24° by Alchemy III). However, it is clear that a substantial twisting to planarity is required for **5** to give rise to **7** on photolysis.

Product studies of crystalline samples (of **5**) as well as samples cast as a solid film show an efficient and clean photoconversion to **7**. The crystal environment does not impart any substantial impediment to this photocyclization requiring

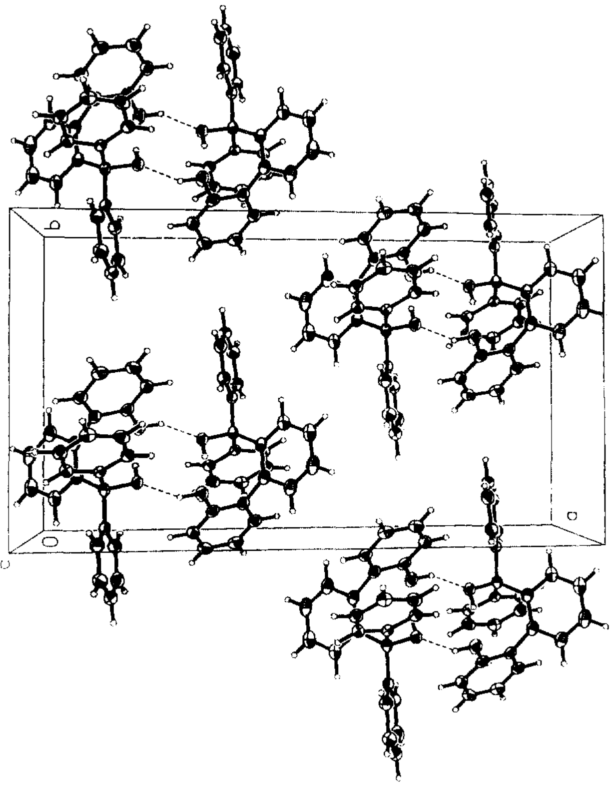

Fig. 2. The crystal structure (thermal ellipsoid plots with probability ellipsoids at 50%) view of the unit cell of 5.

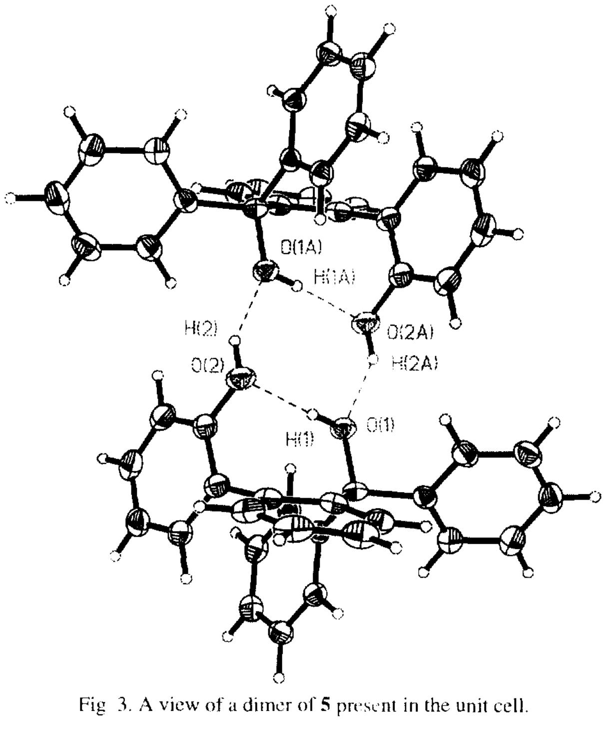

Fig 3. A view of a dimer of 5 present in the unit cell.

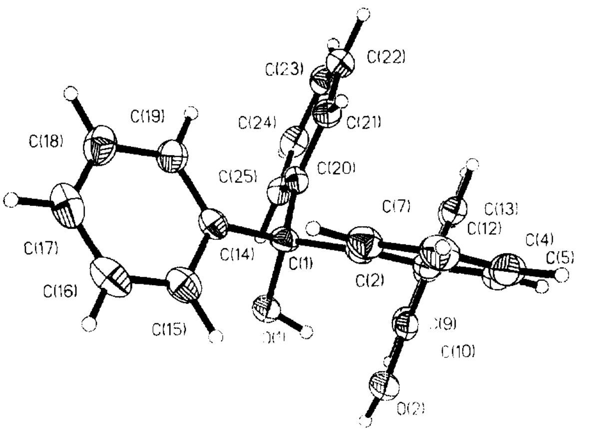

Fig. 4. A view of **5** showing large dihedral angle (≈ 80°C) of the biphenyl ring system and the *syn* arrangement of the substituents.

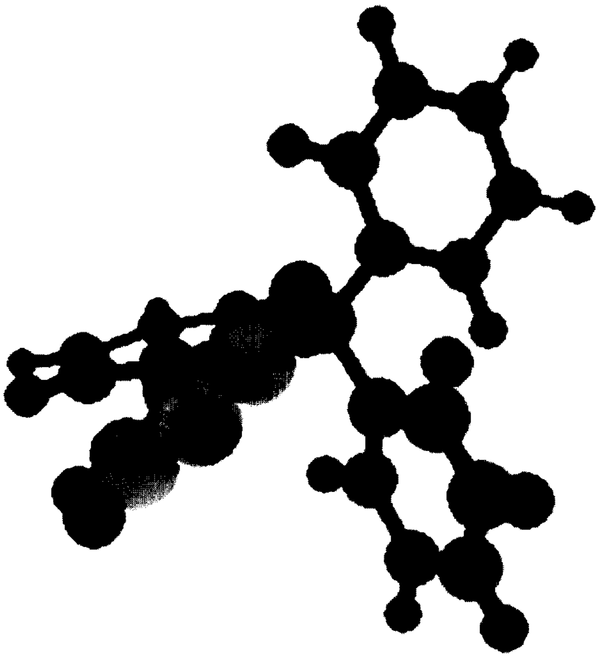

Fig. 5. The minimized geometry of **7** as calculated by the Alchemy III (Tripos) program.

substantial torsional motion. Since water is not included in the crystal lattice, the mechanism of photocyclization cannot involve water-assisted ionization of the phenol moiety, as proposed in aqueous solution.

We believe that the manner in which **5** crystallizes (as dimers) offers an intriguing mechanism for photocyclization in the solid state. We propose that the mechanism for photocyclization involves initial intermolecular proton transfer from the phenol OH to the oxygen of the benzyl moiety of the H-bonded partner $[\mathbf{5}]_2$ (Scheme 2), to generate a 'zwitterionic dimer' [13] (still electronically excited at the phenolate moiety) in which the charges are significantly stabilized by H-bonding network. Loss of hydroxide ion from [13] gives rise to **6** and presumably a molecule of **5** still H-bonded to hydroxide ion and a proton, which on proton reshuffling regenerates **5** and a water molecule. Electrocyclic ring closure of **6** gives the expected **7**. This mechanism implies that the maximum conversion of **7** is 50% which is consistent with experimental observations. We cannot at this time rule out an internal filter effect as the cause for the limiting 50% conversion of reaction in the solid state even though 100% conversion can be achieved in solution. Another possible explanation is due to the build-up of internal stress as reaction progresses, manifesting in kinetic arrest at 50%.[2] However, it is clear that excited state proton transfer (primary photochemical event) in $[\mathbf{5}]_2$ has to take place from the phenol moiety of one molecule to the benzyl alcohol moiety of the H-bonded partner (due to the nature of the crystal structure). The subsequent loss of hydroxide ion will necessarily be assisted by the partner as well. Therefore, the partner molecule can be envisaged as being a 'catalyst' for the photocyclization. This apparently cannot be accomplished with a single water molecule as **5** (monomeric form) does not react further. It should be noted that a single water molecule cannot act as a proton and hydroxide ion acceptor in the manner shown by **6** where the incipient charges are better delocalized.

3.3. Laser flash photolysis

LFP studies of **5** were carried out in an attempt to directly show the involvement of *o*-biphenyl quinone methide **6** in the reaction mechanism (in solution). We have recently shown [18] that photogenerated biphenyl quinone methides that cannot undergo electrocyclic ring closure are readily observable by LFP, with lifetimes in the 0.4–70 μs range in aqueous solution with long-wavelength maxima (500–575 nm). Although **6** does undergo electrocyclic ring closure, it was anticipated that the added phenyl groups might provide sufficient additional conjugation to decrease its reactivity. Previous nanosecond LFP studies of **1** gave no observable transients assignable to **4** supporting the notion that *o*-biphenyl quinone methides of the type **4** are very short lived.[3]

Laser flash photolysis of **5** in 1:1 CH_3CN–H_2O gave only a weak ($\Delta OD < 0.01$) transient in the 340–500 nm region ($\lambda_{max} = 420$ nm). This transient was not affected by added ethanolamine and O_2. This transient decays with a fast (6.7×10^5 s^{-1}) and a slow component (1.5×10^4 s^{-1}) which suggests there is more than one species. Because known biphenyl quinone methides absorb at much longer wavelength (500–575 nm) and are efficiently quenched by added ethanolamine, the transient observed for **5** is most likely due to a side reaction of **5**.[4] Thus it is clear that even **6** is too short lived for detection by nanosecond LFP. The possibility that **6** might be longer lived in the solid state and hence detectable using the present apparatus is a subject for further investigated.

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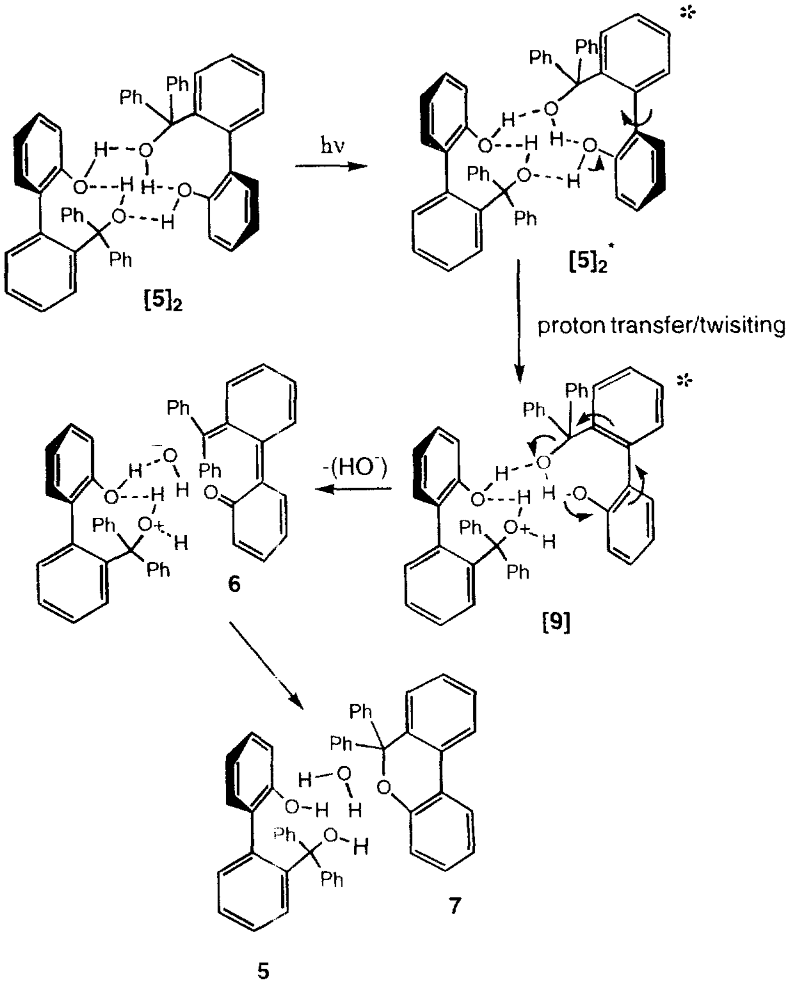
[2] We thank a referee for pointing out these alternative explanations for the kinetic arrest of the photocyclization at 50%.

[3] P. Wan, unpublished results, 1995.

[4] Y. Shi, P. Wan, unpublished results, 1997.



Scheme 2.

4. Summary

This study has shown that the photocyclization of α,α-diphenyl-2-(2′-hydroxphenyl)benzyl alcohol (**5**) to the corresponding pyran **7** is not inhibited in the solid state although the reaction requires significant torsional motion. It is believed the dimeric structure of **5** observed in the solid state ($[5]_2$, Scheme 2) offers a unique mechanism for the reaction involving both inter and intramolecular proton transfers and explains why the maximal yield in the solid state is ca. 50%. Additional studies are warranted to test the generality of this self-catalysis of photocyclization.

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References

[1] C.G. Huang, K.A. Beveridge, P. Wan, J. Am. Chem. Soc. 113 (1991) 7676.
[2] J.R. Scheffer, M. Garcia-Garibay, O. Nalamasu, Org. Photochem. 8 (1987) 249.
[3] M.D. Hollingsworth, J.M. McBride, Adv. Photochem. 15 (1990) 279.
[4] V. Ramamurthy, K. Venkatesan, Chem. Rev. 87 (1987) 433.
[5] J.R. Scheffer, P.R. Pokkuluri, in V. Ramamurthy (Ed.), Photochemistry in Organized and Constrained Media, VCH, New York, 1991.
[6] M. Leibovitch, G. Olovsson, J.R. Scheffer, J. Trotter, J. Am. Chem. Soc. 119 (1997) 1462.
[7] M. Sakamoto, M. Takahashi, S. Moriizumi, K. Yamaguchi, T. Fujita, S. Watanabe, J. Am. Chem. Soc. 118 (1996) 8138.
[8] S.H. Shin, A.E. Keating, M.A. Garcia-Garibay, J. Am. Chem. Soc. 118 (1996) 7626.
[9] A.E. Keating, S.H. Shin, K.N. Houk, M.A. Garcia-Garibay, J. Am. Chem. Soc. 119 (1997) 1474.
[10] G. Kaupp, M. Haak, Angew. Chem. Int. Ed. Engl. 35 (1996) 2774.
[11] N. Hayashi, Y. Mazaki, K. Kobayashi, Tetrahedron Lett. 35 (1994) 5883.
[12] S.L. Murov, I. Carmichael, G.L. Hug, Handbook of Photochemistry, 2nd edn., M. Dekker, New York, 1993.

[13] SMART Version 4.050, Siemens Analytical X-ray Instruments, Madison, USA, 1995.
[14] SAINT Version 4.050, Siemens Analytical X-ray Instruments, Madison, USA, 1995.
[15] G.M. Sheldrick, SHELXTL-Plus, Release 4.1, 1991, Siemens Analytical X-ray Instruments, Madison, USA.
[16] G.M. Sheldrick, SHELXL 93, Program for the Refinement of Crystal Structures, University of Gottingen, Germany, 1993.
[17] J.A.K. Howard, A. MacKinnon, C.C. Wilson, manuscript in preparation, 1997.
[18] Y. Shi, P. Wan, J. Chem. Soc., Chem. Commun., (1995) 1217.