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Photochromism in 1,1′-Bi-2-naphthols

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For a long time the events following electronic excitation of naphthols have been studied;[1] excited-state proton transfer is a typical process in such cases.[1b] We report here on the photochemistry of both racemic and optically active 1,1′-bi-2-naphthol (**1**). A novel photochromic cycle involving the main photoproduct has been observed: the photoequilibrium was strongly dependent on both the wavelength of the irradiating light and the solvent. In addition, the photoreactions discovered were highly selective, stereospecific, and of synthetic value for compounds with complex structure and stereochemistry.

When 1,1′-bi-2-naphthol (5×10^{-4} M in methanol) was irradiated with an immersion medium-pressure Hg lamp (100 W), a sluggish decrease of the concentration of **1** was observed with concomitant formation of four aromatic products, which were detected by HPLC analysis. We were able to isolate the most relevant compound (**2**), which, however, was produced with an almost negligible quantum yield. The structure best fitting our experimental data (mass spectrometry data, ^{1}H and ^{13}C NMR, UV, CD, and IR spectroscopies)[2] is reported in Scheme 1.

In Figure 1a, the UV absorption spectra of **1** and **2** are displayed together for comparison. In Figure 1b, the CD spectra of (−)-**1** and of (−)-**2**, the compound obtained from irradiation of (−)-**1** (*vide infra*), are also reported.

Photoaddition of an OH group to a C−C double bond is a uncommon event reported, for example, in the intramolecular cyclization of *o*-allylphenol to give dihydrobenzofuran.[3]

The absence of phenolic OH function in **2** is confirmed by unreactivity of **2** with CH_2N_2 in diethyl ether solution, while, in identical experimental conditions, quantitative formation of the dimethoxy derivative of **1** is obtained. In contrast with the Hg lamp photochemical experiment, irradiation with the 334 nm emission of a CW Ar^+ laser (100 mW) of a methanol solution of **1** (5×10^{-4} M) resulted in the production of **2** with a reasonable quantum yield (ca. 0.038) and ca. 50% conversion (*vide infra*). However, **2** was not formed by the other UV Ar^+ laser emissions at 351 and 364 nm. In addition, photochemical reversion of **2** to **1** was observed with all three emissions of the Ar^+ laser. Scheme 1 shows the main features of the reactions involving **1** and **2**.

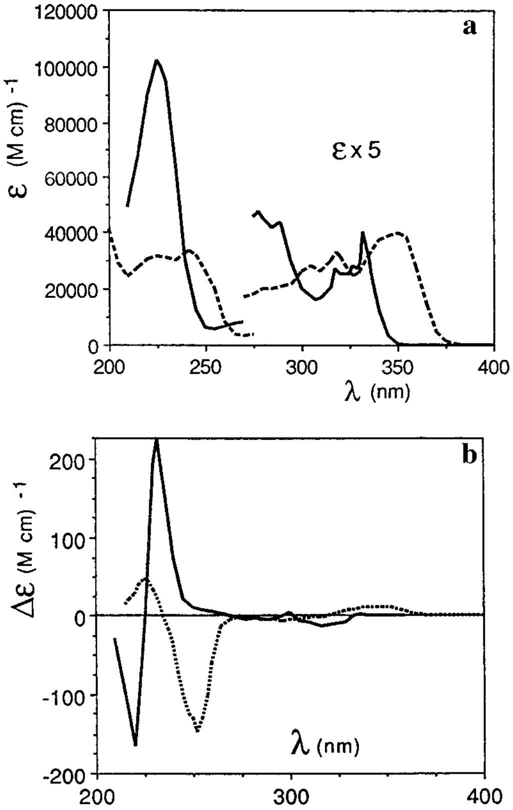
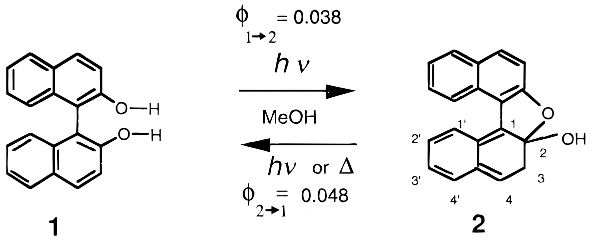


Figure 1. (a) UV spectra of **1** (continuous line) and **2** (dashed line) in MeOH. (b) Circular dichroism spectra of (−)-**1** (continuous line) and of (−)-**2** (dashed line) in *n*-hexane.

Scheme 1



From the UV spectra in Figure 1a, we see the strong absorption of **2** at $\lambda > 350$ nm, likely due to the *o*-xylylene moiety in **2**,[4] in contrast with the quasi-transparency of **1** in the same region. Thus, we can understand why **2** is not formed during irradiation of **1** at the other UV Ar^+ laser emissions of 351 and 365 nm. From Scheme 1 it is clear that irradiation must result in a photostationary state in which the [**2**]/[**1**] ratio depends on the extinction coefficients ϵ_1 and ϵ_2 and on the ratio of the quantum yields, $\phi_{1\to2}$ and $\phi_{2\to1}$, at the irradiation wavelength according to the formula:

$$[\mathbf{2}]/[\mathbf{1}] = \epsilon_1\phi_{1\to2}/\epsilon_2\phi_{2\to1}$$

The ratio [**2**]/[**1**], at $\lambda = 334$ nm, was calculated to be 0.8 (i.e., 45% **2** and 55% **1** in the photostationary mixture). The observed proportion of **2** and **1** was 49 and 51%, respectively,

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[2] ^{1}H NMR (C_6D_6) δ: 3.00 (2H, m, H-3), 4.87 (1H, br s, OH), 4.97 (1H, m, H-4), 5.85 (1H, dddd, $J_{3,4'} = 2.0$ and 2.68, $J_{4,4'} = 3.0$, $J_{3',4'} = 10.26$, H-4′), 6.25 (1H, dddd, $J_{3.3'} = 1.5$ and 2.36, $J_{4,3'} = 1.9$, $J_{3',4'} = 10.26$, H-3′), 6.86 and 7.00 (2H, AB system, $J = 8.3$, H-2′ and H-1′), 7.10−8.00 (series of d, naphthalene protons). ^{13}C NMR ($CDCl_3$) spectrum displays, in addition to the aromatic carbons, two signals at δ 29.1 (t) and 71.7 (d) ppm. These signals were unambiguously assigned to C-3 and C-4 by a HETCOR experiment. The IR spectrum presents a series of bands not present in the **1** spectrum. The new C−H out of plane bending vibrations occur at 639 (m), 701 (s), 791 (s), 859 (m) cm^{-1}.

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with ±1.5% experimental error. The difference between calculated and observed concentration ratios can be reasonably explained by a small amount of side reactions from **1** which were not included in Scheme 1, in addition to experimental errors in the quantum yields, evaluated at ca. 15% conversion of **1** and **2**, respectively. Also, the inefficient production of **2** observed with a standard medium-pressure Hg lamp can be explained. In fact, the photoequilibrium ratio was calculated to be 0.03 taking into account the energy distribution of the emissions of the 100 W medium-pressure Hg lamp used (essentially 366 and 334 nm), the pyrex transmittance, and the absorbance of **1** and **2** at these emissions. Probably, this small photoequilibrium ratio explains why **2**, obtained in a very small amount, was not detected and reported until now.

Subsequently, some stereochemical aspects of the **1** → **2** transformation have to be reported. It is noted that 334 nm irradiation of 99.5% optically pure (−)-**1** in MeOH gave **2** with (−)-**2** as the prevailing stereoisomer.[5] The optical purity of both **1** and **2** recovered from the irradiation mixtures was lower than that of the starting material; the optical purity decreased with the amount of the energy absorbed. When (−)-**1** (99.5% enantiomeric excess (ee)) in MeOH was photolyzed up to 15% photoconversion, (−)-**2** with 99% ee (analysis by chiral HPLC) was obtained. At 28% phototransformation, the ee_2 was found to have lowered to 98.5% ee_2, at 36% conversion 97.8% ee_2 was measured, and finally, at 44.2% conversion 95.3% ee_2 was observed. The corresponding enantiomeric excesses of **1** were 98.1, 97.3, 95.9, and 92.3%, respectively. Thus, $ee_1 < ee_2$; this fact could be the result of photoracemization of **1** or connected to the **2** → **1** phototransformation. The racemization of **1** through its direct electronic excitation is probable because such processes have been observed in other atropisomeric diaryls[6] and also in the photolysis of the (−)-**1** antipode complexed to bovine serum albumin.[7] In contrast with the above photoconversions starting from (−)-**1**, selective photolysis of chemically pure (−)-**2** resulted in the production of optically active (−)-**1**, whose ee was exactly equal to that of **2**. During the photolysis ee_2 remained constant. Selective photolysis of **2** was obtained by using the 364 nm laser emission (this line is not absorbed by formed **1**, cf., Figure 1a). Moreover, the constancy of ee_2 proved that excitation of **2** gave no racemization of **2**, taking into account that ca. 95% of absorbed 364 nm photons electronically excite **2** without converting it, as revealed by the quantum yield value 0.048 of the **2** → **1** conversion. Then, photoracemization of **1** explains the lowering of ee_1 and ee_2 as well as the result of $ee_1 < ee_2$ during the irradiations of optically active **1**. It seems very likely that inversion of the chirality during the **1** → **2** transformation, if any, is a minor occurrence with respect to the photoracemization of **1**.

We note that atropisomerism of **1** is converted into the more usual asymmetric carbon dependent chirality in **2**, which stereospecifically reverts to the original atropisomerism by the **2** → **1** photo(or thermal, *vide infra*)transformation. Thus, experimental findings show that the chirality in **2**, derived from a covalent structure, is more photostable than the chirality in **1**, derived from conformational barriers. Finally, the asymmetry of **2** *appears* higher than that of **1**, when the maximum values of the dissymmetry factor, the Kuhn *g*-factor,[8] in the 200−400 nm spectral region is considered; $g_{\max} = (\Delta\epsilon/\epsilon)_{\max} = 0.0067$ at 260 nm for **2**, compared to $g_{\max} = 0.0034$ of **1** at 240 nm.

The effect of the solvent in the **1** → **2** photorearrangement is particularly noteworthy. In fact, this reaction was strongly depressed in an aprotic solvent such as CH_3CN (a 20-fold reduction), compared with that in CH_3OH. The inverse **2** → **1** photoreaction was only lowered by half. Thus, the photoequilibrium [**2**]/[**1**] ratio in CH_3CN became almost zero at 334 nm: in practice it was difficult to observe any photoreaction of **1** in CH_3CN. Interestingly, in a 80:20 (v/v) CH_3CN/H_2O mixture, the photoreaction proceeded as well as when carried out in CH_3OH. Finally, we were unable to observe the **1** → **2** phototransformation when **1** was dissolved in *n*-hexane.

Let us now turn to the properties and structure of the novel molecule **2**. Observing the *o*-xylylene moiety present in **2** and remembering its intrinsic lability also in substituted xylylenes,[4] one is inclined to tribute some thermal instability to **2**. In reality, this fact, showing **2** as a valence isomer of **1**, was the first to be noticed. The thermal back reaction of **2** revealed some interesting features:

(1) It was strongly dependent on the solvent. At 85 °C we found no reaction in CH_3CN, but the monomolecular kinetic constants $k = 6.2 \times 10^{-6}$ s^{-1} and $k = 1.8 \times 10^{-5}$ s^{-1} were measured for the thermal back reaction in CH_3CN-H_2O (80:20, v/v) and in CH_3OH, respectively. In other words, CH_3CN protects **1** from phototransformation into **2** and protects **2** from thermal return to **1**.

(2) Thermal racemization in the conversion **2** → **1** was not detected at 85 °C in CH_3OH.

(3) An activation energy of 106 kJ/mol was measured in the temperature range of 65−85 °C in CH_3CN/H_2O solutions (80:20, v/v). The activation energy relates to the thermal reversion in other photochromic systems being of the same order of magnitude (e.g., for cis-/trans-azobenzene and azonaphthalene it is ca. 96 kJ/mol).[9]

Finally, an extension of the above findings to other binaphthols was attempted. We found formation of the methyl ether derivative of **2** starting from the monomethyl ether of **1**. The UV and CD absorption properties of this compound were very similar to those of **2**. On the contrary, no phototransformation of the dimethyl ether of **1** was found. Clearly, the presence of acidic hydrogen(s) is required by the photoreaction described.

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[5] For the pure (−)-**2** antipode, obtained by semipreparative chiral HPLC, [α] = −571, −615, and −871 at 578, 546, and 446 nm, respectively, in CH_3OH and 0.135 g/100 mL. Chiral HPLC: $t_R = 35$ and 41 min for the (+)-**2** and (−)-**2** antipodes, respectively; 0.5 mL/min flux; mobile phase *n*-hexane/isopropyl alcohol 85:15 (v/v); Chiralcel OJ.

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