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Excited-State Proton Transfer in Chiral Environments: Photoracemization of BINOLs¹

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Abstract

We have studied excited-state proton transfer (ESPT) from chiral proton donors to chiral and achiral acceptors. The key role of the exergonicity of the reaction and the transition-state position along the reaction coordinate for the existence of an enantiomeric effect was established. This effect was observed for “super” photoacids ($\Delta G \ll 0$) and vanished for endergonic reactions ($\Delta G > 0$) where a “late” transition state similar to planar achiral binaphtholate anion occurs. As a result, photoracemization was observed, as confirmed by circular dichroism spectroscopy. The photoracemization effects were studied for several chiral photoacids (BINOLs and their ethers) and proton acceptors (amines, aminoalcohols, and water) using UV-vis, steady-state fluorescence, and time-resolved fluorescence spectroscopies. The nature of the solvent and the proton acceptor, as well as the chemical structure of the BINOL, played a pivotal role in the photochemical reactivity of the system. Two proposed pathways competed for photoracemization: excited-state inter- and intra-molecular proton transfer, the former being more effective. Irradiation of the dimethoxy BINOL derivative, which lacks an acidic proton and cannot undergo ESPT, produced no appreciable reaction or racemization.

INTRODUCTION

One of the most dramatic aspects of biological systems involving proton transfer is their high stereoselectivity. Most biologically active molecules are chiral, including sugars and naturally occurring amino acids. In search of a stereospecificity in the excited-state proton transfer (ESPT) in model compounds we have studied the intermolecular ESPT from/to chiral proton donors and acceptors. We have discovered pronounced differences in ESPT rates from the “super” photoacid 5,8-dicyano-2-naphthol (DCN2) to optical isomers of 2-butanol.² Protolytic photodissociation was 2.6 times faster in the enantiopure solvent than in its racemic form. This phenomenon was explained in terms of long-range order and stability of homo- vs. heterodimers of this chiral alcohol, therefore adding a unique dynamic approach to the wide field of chiral recognition using optical tools.³ In a continuation of this research we have

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extended the range of chiral donor–acceptor pairs and studied ESPT from one of the simplest chiral photoacids known, 1,1'-bis-2-naphthol (BINOL) and its methyl ether. This compound and its derivatives have been extensively utilized as templates for chiral recognition.^{3a,4} Other 1,1'-bisnaphthol derivatives developed by R. Noyori (2001 Nobel Prize in Chemistry for chiral catalysis) are widely used in industry as catalysts for asymmetric reactions.⁵ However, in contrast to the DCN2/2-butanol pair, no significant ESPT enantioselectivity was observed between a given chiral BINOL and the optical isomers of the proton acceptors such as amines and aminoalcohols. At the same time we have discovered that, in the presence of proton acceptors, solutions of such chiral photoacids efficiently photoracemize.

The purpose of the present research is to establish a relationship between the exergonicity of the ESPT reaction and the mechanisms of photoracemization, thus shedding light on these very weak enantioselective effects. This includes further study of the solvent effects on these photoinduced processes, as well as the structure of the binaphthols and the nature of the proton acceptor.

BACKGROUND

In their comprehensive study⁶ Iwanek and Mattay examined the chirality effect on the BINOL *neutral band emission quenching* by various optically active amines in different solvents. In most cases very small or no enantioselectivity was detected, the maximum ratio of Stern–Volmer constants for *S*-(–)- and *R*-(+)-BINOL fluorescence quenching by chiral amines was 1.15 for the systems BINOL/1-cyclohexylethylamine and BINOL/*N,N*-dimethylphenylethylamine in acetonitrile. A significant BINOLate emission with an unusually large Stokes shift was observed in a wide array of organic solvents in the presence of strong proton acceptors (amines), while emission from the neutral form was quenched.⁶

An abnormal Stokes shift was also reported by Shi and Wan⁷ for 2-hydroxy-2'-methyl-1,1'-binaphthyl in CH₃CN/H₂O 1/1 vol mixture upon ground-state deprotonation. They proposed twisting of the excited-state anionic chromophore leading to a more planar structure, therefore enhancing the conjugation between the two naphthyl rings. In a later publication, Flegel et al.⁸ proposed a detailed resonance scheme for the excited BINOLate planarization that is identical to the one reported by us earlier.¹ However, no direct experimental evidence (including emission spectra) for this phenomenon was reported. Flegel et al.⁸ studied in detail the photoracemization of BINOL in methanol and D₂O-CH₃CN. However, they proposed that *intramolecular* ESPT was the driving force for racemization. In contrast to Flegel et al.,⁸ in the present work we demonstrate that *intermolecular* ESPT is the dominating factor for the photoracemization of BINOLs in the presence of strong proton acceptors by examining various BINOL derivatives as a function of proton acceptor and solvent.

The photochemistry of BINOL in methanol, acetonitrile, and its mixtures with water was studied in detail by Flegel et al.⁸ and Zandomeneghi and coworkers.⁹ No ESPT product was observed in the emission spectra, and the photolysis led to formation of photoproducts A⁸ or B⁹ (see Scheme 1). The mechanism of formation of A was supposed to include formal intramolecular ESPT leading to planar quinine methide, ultimately resulting in photoracemization. The mechanism of B formation was considered an intramolecular addition of a phenolic OH group to a C–C double bond.

EXPERIMENTAL

R-(+)- and *S*-(–)-1,1'-bis-2-naphthol (BINOL), 2-hydroxy-2'-methoxy-1,1'-bi-2-naphthyl (MeBINOL), and 2,2'-dimethoxy-1,1'-bi-2-naphthyl (Me₂BINOL) were obtained from Aldrich, SynChem, and ACROS, respectively, in 99% purity. Dry toluene, acetonitrile, and methanol (<30 ppm, 10 ppm, and 50 ppm H₂O, respectively) were obtained from ACROS.

R-(−)- and *S*-(+)-(1-cyclohexyl)ethylamine and *R*-(−)- and *S*-(+)-*sec*-butylamines, 98% purity, were obtained from Aldrich. Photochemical reactions (non-deoxygenated) were performed in Pyrex glass (cutoff < 300 nm) vials in a PRP-3000A Rayonet Reactor equipped with 300-nm lamps (emission spectrum centered at 300 nm with 100 nm full width) with a total intensity of 336 watts. Absorbance, fluorescence, and circular dichroism (CD) spectra were recorded on Perkin Elmer Lambda 19, Spex Fluorolog 2, and Jasco J17 spectrometers, respectively.

Samples were prepared from optically pure BINOLs and a measured amount of amine was added with a microsyringe. The samples were irradiated for up to twenty minutes, and aliquots of solution were removed from the photoreactor at fixed time intervals.

The circularly polarized luminescence (CPL) spectra were recorded as described previously, operating in a differential photon-counting mode.¹⁰ The light source for excitation was a continuous wave 450 W xenon arc lamp from a Spex Fluorolog-2 spectrofluorimeter, equipped with excitation and emission monochromators with dispersion of 4 nm/mm (SPEX, 1681B). To prevent artifacts associated with the presence of linear polarization in the emission,¹¹ a high-quality linear polarizer was placed in the sample compartment, and aligned so that the excitation beam was linearly polarized in the direction of emission detection (*z*-axis). The key feature of this geometry is that it ensures that the molecules that have been excited and that are subsequently emitting are isotropically distributed in the plane (*x,y*) perpendicular to the direction of emission detection.^{12,13} It is common to report the degree of CPL in terms of the luminescence dissymmetry factor, $g_{\text{lum}}(\lambda)$, which is defined as follows: $g_{\text{lum}}(\lambda) = 2\Delta I/I = 2(I_L - I_R)/(I_L + I_R)$, where I_L and I_R refer, respectively, to the intensity of left and right circularly polarized emissions. A value of 0 for g_{lum} corresponds to no circular polarization, while the absolute maximum value is 2. All the g_{lum} values reported in this study have been measured with a standard deviation of ± 0.0004 .

RESULTS

Quick Screening of Various Chiral and Achiral Proton Acceptors

In methanol/water 1/1 vol solutions, both *R*- and *S*-BINOLs demonstrated dual emission, with the dominant peak at 369 nm belonging to neutral species and the weak emission at 550 nm from the ESPT product (Fig. 1), consistent with the weak photoacidity of BINOLs.¹⁴ Even weaker BINOLate emission was observed in saturated aqueous solutions of α -D-methylglucoside, a known chirality-inducing medium.¹⁵ In the present work we have chosen a straightforward criterion for ESPT efficiency. The latter can be estimated from the steady-state emission data, since the apparent ESPT rate constant k_{PT} is directly proportional to the ratio of fluorescence quantum yields of neutral Φ and deprotonated Φ' forms:¹⁶

$$k_{\text{PT}} = (\Phi'/\Phi)(k_f/k_f')/\tau'_0 \quad (1)$$

where k_f/k_f' is the radiative rate constant ratio for the neutral and deprotonated forms, and τ'_0 is the fluorescence lifetime of the deprotonated form. Each curve in Fig. 1 demonstrates only one combination of proton donor–acceptor enantiomers, but in all systems studied the ratio Φ'/Φ was independent of chirality for any proton donor–acceptor pair. Assuming k_f/k_f' independence and experimentally determined invariance of τ'_0 on the optical activity of BINOLs, these data demonstrate an absence of enantiomeric effects on ESPT from BINOLs to both chiral and achiral proton acceptors. The fluorescence lifetimes of BINOLs in acetonitrile and toluene measured at the neutral emission band did not change upon addition of amines, indicating predominantly static character of the quenching.

While we found no enantioselectivity for ESPT from BINOLs to chiral amines, we note that the Stokes shift for binaphthols upon excited-state deprotonation is significantly larger as compared to that for the widely studied 2-naphthol.¹⁶ We attribute the 550 nm emission observed in our experiments to the planar resonance structure (only one resonant structure⁸ is shown) depicted by Scheme 1. Since this transient achiral structure has an equal probability to relax to either enantiomer, racemization of the starting BINOL occurs.

General Features of Spectra Upon Photolysis

Steady-state absorption and emission spectra of BINOL in various solvents in the presence of amines have been reported previously⁶ and will not be discussed in detail. The addition of amine to the BINOL solution in organic solvents resulted in a small bathochromic shift of the absorption band, presumably due to the formation of a hydrogen-bonded complex. The stability constant of the ground-state BINOL–amine complex has complex solvent behavior,⁶ but generally, the magnitude of the former is larger for non-polar non-basic solvents. As a result, the Φ'/Φ ratio was larger for non-polar solvents at the same amine concentration. The efficiency of the ground-state hydrogen-bonded complex formation and the ESPT was much lower for MeBINOL than for BINOL (Fig. 2). Clearly, the nature of the proton acceptor affects the photochemistry of BINOLs. For BINOL and MeBINOL, the Φ'/Φ ratios for 2-butylamine (0.795, 0.153, respectively)¹⁷ are much larger than for 1-cyclohexylethylamine (0.280, 0.046, respectively), indicating that 2-butylamine results in more efficient ESPT. This is most likely due to the structures of the compounds where 1-cyclohexylethylamine contains a bulky six-carbon ring causing steric hindrance. For fully methylated Me2BINOL no ground- or excited-state prototropic behavior was observed.

The results of typical photolysis experiments for BINOL, MeBINOL, and Me2BINOL in organic solvents in the presence of proton acceptors are shown in Fig. 2. Upon irradiation with 300–350-nm light in the presence of an amine in toluene, the absorption spectrum of BINOL showed considerable degradation, complete loss of the characteristic absorption band at 337 nm, and appearance of the red-shifted absorbing structureless shoulder. At the same time, the initially strong CD signal totally disappeared after 8 min of irradiation. The emission spectra demonstrated complex behavior upon photolysis. A new emission with a prominent vibronic structure starting from 450 nm grew dramatically. MeBINOL demonstrated much weaker photodegradation, and no new “vibronic” product was observed in the emission spectra. However, MeBINOL lost optical activity at the same rate as BINOL. No photoreactions were detected for Me2BINOL. The same photostability of Me2BINOL was observed⁶ in organic solvents and their mixtures with water. A control series of experiments was also taken in pure toluene without amine. In the absence of proton acceptor, MeBINOL was photochemically inert, and a much slower photoreactivity of BINOL was observed; the photolysis products in the latter case were the same as in the presence of amine. Similar results were observed in acetonitrile with 1-cyclohexylethylamine and 2-butylamine. Both enantiomers of BINOL and MeBINOL behaved similarly upon irradiation, losing their optical activity at the same rate. In contrast to previous work⁸ that reported the photostability of BINOL in pure acetonitrile, we observed very slow photochemical reactions of BINOL, perhaps due to the presence of residual water (10 ppm). Additional deoxygenation and dehydration by the freeze–pump–thaw technique of freshly prepared samples in anaerobic conditions slowed down the decomposition rate even further.

Upon photolysis in the polar solvent methanol, both compounds produced an absorption maximum at 355 nm as well as a long wavelength band from 365 to 400 nm. In contrast, in toluene, a shoulder appeared over a broader range of 350–400 nm. It is interesting to note that the emission spectrum of BINOL in phosphate buffer at pH 6.9 reported by Xu and

McCaroll^{4e} exhibited an identical characteristic “vibronic” tail starting at 450 nm, probably due to the photoreaction described previously.

In this paper we will not analyze in detail the structure and mechanism of formation of photoproducts because in all cases the ESPT-assisted photoracemization was much faster than the accumulation of the latter. Nevertheless, we have attempted an HPLC separation of the products of 35 minutes of BINOL photolysis in methanol. Only one product was found using UV-absorbance detector. Its absorption spectrum with a maximum around 355 nm was identical to that reported earlier,^{8,9} and the fluorescence spectrum resembled the parent BINOL, but the quantum yield was at least an order of magnitude lower. ¹H NMR spectrum was identical to that of the photoproduct A reported in ref 8.

Circularly Polarized Luminescence Studies

CPL spectroscopy, the emission analogue to CD spectroscopy, was used to further investigate the effect of added chiral amines to BINOL derivative solutions in toluene. Of special importance with the CPL experiments is to confirm that the loss of chiroptical activity of the chiral BINOL systems after addition of chiral amines is the consequence of an efficient ESPT, as suggested by CD spectroscopy. It is thought that the ESPT in the systems of interest occurs through a planar transition state that leads to an effective photoracemization. Thus, one would expect that the solutions of neutral chiral BINOL derivatives would exhibit an active CPL signal, whereas these same solutions in the presence of chiral amines would result in a loss of the CPL activity. It should be noted that all luminescent organic molecules that are chiral will result in the observation of a CPL signal, but the extent of circular polarization is almost always less than 1×10^{-2} .¹³ For this reason most of the CPL studies have been conducted on lanthanide (III)-based systems for which g_{lum} values as high as 1.38 were observed.¹⁰

As expected, the magnitude of the g_{lum} values for the two BINOL enantiomers, *R*-(+)- and *S*-(-)-BINOL, are small (−0.0011 and +0.0009 at approximately 375 nm, respectively). However, these results confirm that the neutral BINOL solutions in toluene or acetonitrile exhibit an active CPL signal and also that the emitted light is polarized in opposite directions for the two enantiomeric forms of BINOL. In contrast, we were not able to detect a CPL signal for the racemic BINOL solution, as one would expect. It should be noted that the observation of a photochemical degradation occurring upon extended UV exposure prevented us from recording any CPL spectra for the various BINOL derivative-based systems studied. For this reason we have only measured the g_{lum} values of these sample solutions at the maximum of the emission spectra over a short UV exposure period.

Unlike the CD measurements, the CPL experiments performed on the BINOL derivative solutions after addition of chiral amines were not conclusive. Since a considerable change in the intensity of the emission signals was observed after addition of a chiral amine (i.e., chiral cyclohexylethyl amine) to a *R*-(+)-MeBINOL solution (significant decrease of the emission band around 375 nm and appearance of a weak emission band in the 500–550 nm region), the required time for each g_{lum} value determined at the maximum of the emission bands corresponding to the neutral and deprotonated forms of *R*-(+)-MeBINOL (around 375 nm and in the 500–550 nm region, respectively) was several hours of photon collection. As a result, no CPL signals were detected. These results suggest that in the presence of proton acceptors the BINOLs photoracemize and/or photochemically degrade faster than CPL signal accumulation. This was confirmed by recording CD spectra immediately before and after the CPL measurements were done. It was observed that the CD signal around 322 nm of the *R*-(+)-MeBINOL solution in the presence of the chiral cyclohexylethyl amine completely disappeared during the long UV exposure required for the CPL measurements. Indeed, a much longer signal accumulation (hours vs. minutes) and a more powerful xenon lamp (450 W vs. 150 W) were used for CPL compared to CD, respectively.

DISCUSSION

We will start the discussion with the “cleanest” case, the photoracemization of MeBINOL in a toluene/amine system (Fig. 2). The loss of optical activity is almost complete after only 4 min of exposure; however, the absorbance and emission of the new photoproducts are still very weak. Since no photochemical transformation of MeBINOL was observed in pure toluene, this suggests that *intermolecular* ESPT to amine via the formation of the planar structure (Scheme 1) is primarily responsible for the racemization. The yield of the irreversible photoproduct was much lower than that of photoracemization. The formation of the photoproducts in BINOL under the same conditions was more effective. It is hard to estimate relative contributions of the *intermolecular* ESPT and photoproduct formation, which may include *intramolecular* ESPT,⁸ to the apparent photoracemization. However, taking into account almost identical photoracemization rates for BINOL and MeBINOL and much slower photoracemization in the absence of amine, we conclude that the *intermolecular* ESPT is the major factor for BINOL racemization in toluene/amine solvents (Scheme 1). The photoracemization of atropisomeric diaryls is a known phenomenon and several mechanisms have been suggested¹⁸ in addition to those discussed in the present paper. However, an analysis of the published data evidences that the *intermolecular* ESPT-induced photoracemization is the most efficient mechanism for this process.

Very weak fluorescence of the isolated product of BINOL photolysis and the similarity of the absorbance spectra for BINOL and MeBINOL photolysis products led us to assume that product A is formed preferentially (Scheme 1), since product B would have more red-shifted optical spectra due to extended conjugation. The absence of formation of product B in the case of MeBINOL suggests that both protons must be involved in its formation. We suggest an alternate *intramolecular* ESPT may give rise to intermediate C, which upon hemiketal formation and proton shift could result in the observed product (see Scheme 2). Such an IESPT has been reported by Wan and coworkers for similar structures.⁸

Clearly, time-resolved methods¹⁹ should be utilized to detect the proposed transient structure shown in Scheme 1. We are now utilizing fs time-resolved UV-pump IR probe spectroscopy to detect and possibly identify intermediate that must have a distinct IR spectrum. Recent time-resolved CD measurements of Niezborala and Hache²⁰ demonstrated a 20–30° decrease of the dihedral angle in ethanolic BINOL solution. It is interesting that without an appropriate proton acceptor, full planarization is not achieved. This confirms our observation that the photoracemization in pure alcohols is slow.

We can now explain the lack of enantiomeric effects on the ESPT in the BINOL/proton acceptor system. Endoergonic ESPT from the weak photoacids has a late transition state that should be similar to the product: planar *achiral* binaphtholate. Thus the geometry of BINOLs in the ESPT transition state is close to planar (*achiral*) and *no enantiomeric effects are observed*. Planarization of the transition state leads to photoracemization in the case of efficient ESPT. In contrast, we assume that the chirality of the transition state is preserved in the ESPT from much stronger photoacid DCN2 to 2-butanols, and the enantiomeric effects are not extinguished.²

CONCLUSIONS

Diastereotopic ESPT is an elusive phenomenon. The exergonicity of this reaction and the transition-state position along the reaction coordinate plays the key role for the existence of the enantiomeric effects. This effect was observed for “super” photoacids ($\Delta G \ll 0$) and vanishes for endergonic reactions ($\Delta G > 0$) where a “late” transition state similar to planar *achiral* binaphtholate anion occurs. As a result, a photoracemization was observed, as

confirmed by circular dichroism spectroscopy, and no diastereoselectivity was observed in a wide array of systems studied. Our studies may shed further light on the dynamic stereochemistry of chiral compounds.^{3,21}

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Fig. 1. Emission spectra of S-(-)-BINOL in the presence of chiral and achiral proton acceptors, $\lambda_{\text{ex}} = 320$ nm. (A) In MeOH/H₂O 1/1 vol solutions. (B) In saturated aqueous solutions of α -D-methylglucoside. (C) in 0.11 M solution of S-(+)-2-aminobutanol in CH₃CN. (D) In 0.47 M solution of S-(+)-2-butylamine in CH₃CN.

Fig. 2. Photolysis of S-(-)-BINOL and its ethers in toluene in the presence of 0.04 M 2-butylamine monitored by absorption, CD, and fluorescence spectroscopies. Color coding is the same for all graphs. For fluorescence spectra $\lambda_{\text{ex}} = 337$ nm. (Color visible online.)

Scheme 1.
Photochemical processes in BINOL and MeBINOL. S is a proton acceptor.

Scheme 2.
Mechanism of photocyclization.