764 *J. Phys. Chem. A* **1997,** *101,* 764−767

DMSO Solvent Induced Photochemistry in Highly Photostable Compounds. The Role of Intermolecular Hydrogen Bonding

Peter F. McGarry, Steffen Jockusch, Yoshihisa Fujiwara, Nikolas A. Kaprinidis, and Nicholas J. Turro*

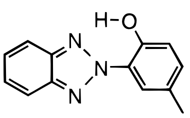
Department of Chemistry, Columbia University, New York, New York 10027

Received: May 14, 1996; In Final Form: November 1, 1996⊗

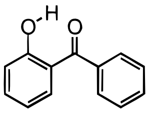
2-(2′-Hydroxy-5′-methylphenyl)benzotriazole, **1**, Tinuvin P, and *o*-hydroxybenzophenone, **2**, are thought to achieve exceptional photostability through highly reversible deactivation associated with their intramolecular hydrogen bonds. Excimer laser excitation (10 mJ, 20 ns at 308 nm) of these molecules in argon-bubbled hexane solution at room temperature affords no discernible transient signals (absorption or emission) between 320 and 800 nm. In DMSO solution under the same conditions, however, strong transient absorptions in the visible (λ_{max} 410 and 425 nm for **1** and **2**, respectively) are observed. The transients responsible for the absorptions are quenched by oxygen and acid, and the spectra match well with the ground state difference spectra generated from the corresponding phenolate ions. When a bulky group is incorporated ortho to the hydroxyl function such as in 2-(2′-hydroxy-3′-cumyl-5′-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, **3**, Tinuvin 928, no appreciable transient absorption is observed even in DMSO solution. These results are consistent with the disruption of the intramolecular hydrogen bond of **1** and **2** (but not **3**) as the result of intermolecular hydrogen bond formation with DMSO. The "dramatic" ortho effect implies that the bulky group adjacent to the hydroxyl function sterically shields the intramolecular hydrogen bond from disruption by polar basic environments.

Introduction

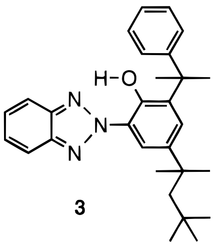
There are several classes of molecules which undergo efficient excited state intramolecular proton transfer followed by rapid internal conversion to the ground state starting material with dissipation of the absorbed energy as benign heat. Among these are the 2-(2′-hydroxy-5′-methylphenyl)benzotriazole, **1**, and the *o*-hydroxybenzophenone, **2**, and their derivatives.[1,2] For example, molecules such as **1** and **2** and their derivatives have been used to great effect as ultraviolet light absorbing polymer stabilizers.[1−3] Their photochemistry is negligible by most chemists' standards as they frequently exhibit quantum yields of disappearance on the order of, or less than, 10^{-6}.[4,5] From an applications' point of view, however, their loss and degradation over years of exposure to sunlight is real and limiting in their practical use.[5−8] Because of the complex environment in which they are employed as well as the length of time required to achieve significant loss of these materials, the study of their photochemistry resulting from direct excitation (as opposed to mechanical loss or autoxidation) has been very difficult to characterize.[5−14] Thus many studies have been carried out under more controlled and simplified conditions, including some excellent recent studies in solution by Gerlock and co-workers.[7,8]



1



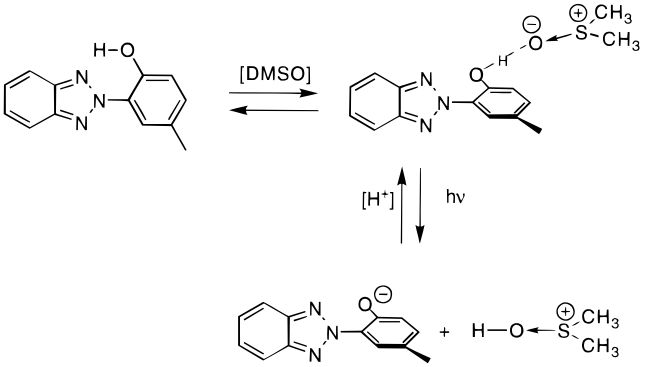
2



3

Known Polar Effects. It has been known for some time that the intramolecular hydrogen bond in benzotriazole-based stabilizers, such as **1**, can be disrupted in polar solvents. This has been demonstrated by various methods including FT-IR,[15,16] UV−vis,[15,17−19] fluorescence,[15,17,18,20−22] and H-NMR.[21,23] For example FT-IR provides compelling evidence for the equilibrium shown in Scheme 1 in DMSO solution.[16] It occurred to us that this disruption of the intramolecular hydrogen bond should have as a result the removal of the source of photostability of **1** and **2**.[24] Therefore, we decided to investigate the flash photolysis of **1** and **2** in DMSO.

SCHEME 1



A dramatic ortho effect was observed previously in benzotriazole-based stabilizers.[21] Substitution of the hydroxyphenyl ring at the 3′-position with a sterically bulky group was reported to protect the intramolecular hydrogen bond from polar basic environments. Thus we chose to investigate the bulky *o*-cumyl group in **3** to see whether or not it would exhibit photostability in DMSO solution.

It is known that **1** shows a weak fluorescence in DMSO assigned to the "open" form with an intermolecular hydrogen bond.[17] Under the same excitation condition, the fluorescence spectrum of **3** in DMSO differs substantially in intensity (Figure 1), with almost no emission being detected. On the basis of earlier reports,[21] this low fluorescence intensity of **3** can be

---

⊗ Abstract published in *Advance ACS Abstracts,* January 1, 1997.

S1089-5639(96)01382-5 CCC: $14.00

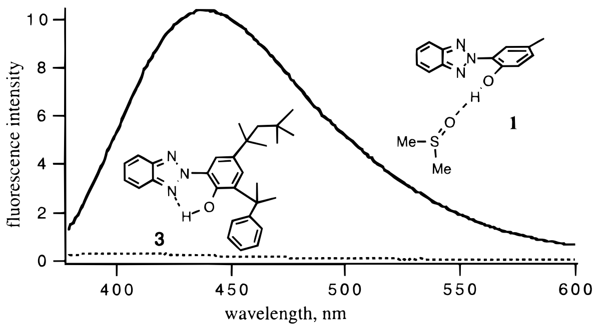


Figure 1. Fluorescence spectra of **1** (solid line) and **3** (dashed line) in DMSO ($\lambda_{exc} = 330$ nm).

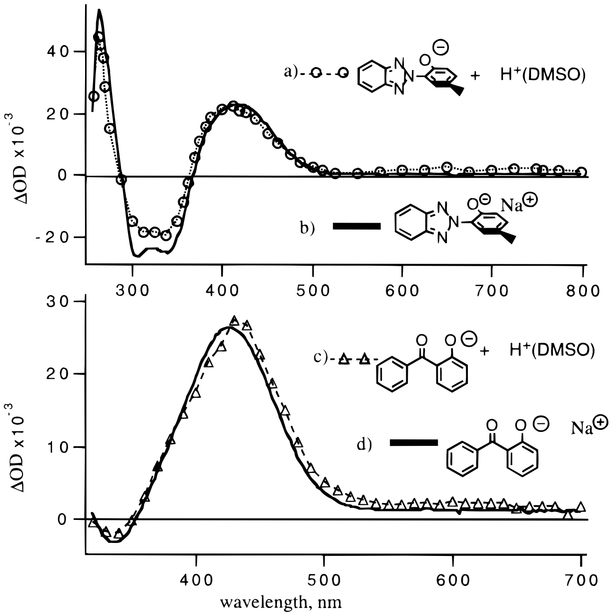


Figure 2. (a) Irradiation of **1** in argon-saturated DMSO ($\lambda_{exc} = 308$ nm). Spectrum recorded 500 ns following the flash with a 10 μs time window. (b) The steady-state difference spectrum generated from subtracting a spectrum of **1** in aqueous DMSO from a spectrum of the same sample except for the addition of two drops of 2 N NaOH. (c) Transient absorption spectrum for *o*-hydroxybenzophenone, **2**, (measured as in (a)). (d) Difference spectrum of the phenolate ion of **2**, (measured as in (b)).

explained in terms of the shielding effect of the bulky *o*-cumyl group. The intermolecular hydrogen bond to DMSO probably becomes weakened, favoring the conformers where the intramolecular hydrogen bond is intact, suggesting that **3** exhibits a higher photostability in DMSO solutions than **1**.

We report herein the first examples of nanosecond transient absorption signals from photostabilizers **1**, **2**, and **3** in argon-purged DMSO solution at room temperature following nanosecond excimer laser excitation. The transients for **1** and **2** are assigned to the respective phenolate ions based on their spectra and reactivity. Compound **3** shows little or no transient absorption under similar conditions in the time-resolved experiments, implying a heightened photostability in DMSO solution brought about by the bulky ortho substituent! The results are discussed in terms of their possible relevance to the long-term photostability of the stabilizer molecules in polar and nonpolar environments.

Results

Spectra. The transient absorption spectra shown in Figure 2 are composed of absorbances recorded 500 ns after the laser pulse and averaged over a 10 μs time window as a function of wavelength. Superimposed upon these spectra in Figure 2 are the normalized difference spectra generated by subtracting a steady state UV−vis spectrum of **1** and **2** respectively in DMSO from the spectra of identical samples except for the addition of a few drops of 2 N NaOH. The similarity between these difference spectra is striking. The negative absorption centered at 330 nm for spectra a and b in Figure 2 is due in each case to a decrease in the concentration of **1,** and the enhanced absorption centered at 410 nm is due to the phenolate ion, presumably formed by photodeprotonation in the case of the transient spectrum and formed by action of the strong base in the case of the steady state UV spectrum. Very similar results are shown in spectra c and d for **2**. Compound **3** showed an extremely weak transient absorption in DMSO. The spectrum obtained showed no discernible absorption maximum and did not compare well with the steady state UV−vis spectrum of its phenolate ion.[25]

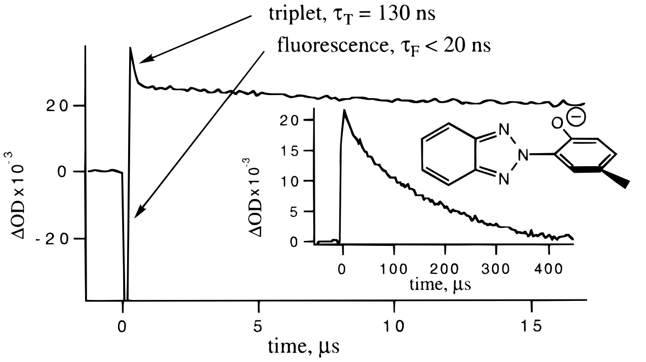


Figure 3. Prompt transient fluorescence, followed by prompt incomplete decay, and a long-lived transient absorption monitored at 420 nm following laser flash photolysis with a 308 nm, 20 ns, 10 mJ excimer laser pulse in argon-bubbled DMSO at room temperature. The inset shows the full decay to baseline on a longer time scale for the phenolate ion of **1** which has a lifetime of ~80 μs in argon-purged DMSO.

Kinetics. Dilute solutions of **1** or **2** in argon-bubbled DMSO at room temperature were subjected to a 20 ns, 308 nm XeCl excimer laser pulse, and subsequently the transient absorption kinetics at various wavelengths were monitored as described previously.[26] In both cases substantial transient signals were obtained and, on the basis of the spectra described above and kinetic evidence to be discussed below, attributed to anion generation via excited state proton transfer to the DMSO solvent. Figure 3 shows a typical trace for **1** monitored at 420 nm. The negative signal at short times within the laser pulse is due to fluorescence which has been reported previously for these conditions.[18] At short times (0−200 ns) there is fast decay ($t \cong 130$ ns) which is strongest at 390 nm. The kinetics of this species is strongly dependent on oxygen concentration and is tentatively assigned to the triplet state, T_1, of **1**.[27] Further, we have found that no signals either absorptive or emissive are observed for **1** (nor are they observed for **2** or **3**) on the nanosecond time scale in nonpolar solvents such as hexane. The reactivity of the long-lived transients toward acid and oxygen were consistent with the assignment above.

Reaction with O_2 and H^+. In laser flash photolysis experiments the observed decay rate constant of the long-lived transient formed in the photolysis of **1** increased in oxygen-saturated DMSO solution compared to that in the argon-saturated solution. This faster decay in the presence of oxygen is caused by oxidation of the phenolate ion by singlet oxygen. The singlet oxygen is produced by triplet−triplet annihilation involving triplets of oxygen and **1**.[28] It has been shown that the phenolate ion is easily oxidized by singlet oxygen.[29] Consistent with our assignment for **1** is the fact that the maximum change in optical

TABLE 1: Bimolecular Rate Constants for the Reaction of 1 and 2 with Acid in DMSO Solution at Room Temperature[a]

stabilizer	$k_q(H_2SO_4)$, 10^9 M^{-1} s^{-1}	$k_q(H_3CCOOH)$, 10^7 M^{-1} s^{-1}
1	3.8 ± 0.6	4.9 ± 0.5
2	4.0 ± 0.7	2.7 ± 1.1

[a] The error is reported as $\pm 2\sigma$.

density of the transient is not diminished by the presence of oxygen, consistent with the transient being derived from the singlet excited state, S_1. (It has long been known that the acid dissociation constant for the excited singlets of phenols is larger by a factor of 10^6-10^7 than the corresponding ground state values; see refs 30 and 31.) In the case of **2**, almost no change in signal intensity and kinetics of the long-lived transient was observed in oxygen-saturated solution compared to deoxygenated solutions. This is consistent with the rapid intersystem crossing in benzophenone in general[32] and with the known acidity of the so-called "charge-transfer" triplet of 4-hydroxybenzophenone which undergoes facile deprotonation in alcohol.[33] The triplet is too short-lived (1.5 ns in alcohol)[34] to be quenched by oxygen.

In the presence of strong and weak acids, the observed decay rates of the long-lived visible transients increased rapidly as a function of decreasing pH. A plot of the observed decay rate constant for the anion of **1** in DMSO against the sulfuric acid concentration yields the bimolecular rate constant for protonation from the slope of the least-squares best line fit to the data of $(3.8 \pm 0.6) \times 10^9$ M^{-1} s^{-1}. Other rate constants are summarized in Table 1.

We summarize the logic in the assignment of the transient absorptions observed in DMSO as follows: (i) they have spectra identical to those of the respective phenolate ions of **1** or **2** generated in basic solution; (ii) the transient decay kinetics increase in low pH solutions, consistent with reprotonation to regenerate **1** or **2** as shown in Scheme 1; (iii) the likely source of the transient is the singlet state, not the triplet (for **1**), due to the lack of dependence of the signal on oxygen concentration (see above). One could argue that a zwitterion formed via excited state intramolecular proton transfer could possibly exhibit the behavior of the observed transients. We infer from the lack of observed transients when a polar but less basic solvent is employed (acetonitrile)[35] and from FT-IR data which clearly indicate a solute−solvent intermolecular hydrogen bond in DMSO[16] that a zwitterion is not a likely candidate in either case. There is a very recent report of excited state proton transfer to solvent in a similar system involving 2-(2′-hydroxyphenyl)benzimidazole in aqueous and ethanolic solutions.[36]

Discussion

Clearly the equilibrium between planar and nonplanar forms of **1** or **2** in DMSO has been disturbed from that found in apolar solvents. The stabilizer molecules which no longer possess an intramolecular hydrogen bond exhibit new pathways for energy dissipation from the first excited singlet state, S_1. These pathways include fluorescence, intersystem crossing, and excited state intermolecular proton transfer to the solvent. Gerlock and co-workers reported product studies of the photolysis of several (hydroxyphenyl)benzotriazoles and drew the conclusion that an excited state in polar solutions must be the species reactive toward radicals and which eventually leads to products.[8] Our results suggest a modification of their conclusions, since no long-lived excited states are observed under these conditions. A phenolate ion is a more probable source of irreversible chemistry,[37] e.g., the phenolate ion of **1** has been shown to be easily oxidized by singlet oxygen.[29]

Nevertheless it is important to note that the equilibrium (Scheme 1) found in DMSO likely exists in nonpolar solvents but consists of a much greater amount of planar intramolecularly hydrogen-bonded conformer. (For example, ^{1}H-NMR shows that the benzotriazole protons are equivalent, implying rotation about the carbon−nitrogen bond linking the benzotriazole and hydroxyphenyl rings is faster than the NMR time scale).[35] Since the anion is easily oxidized[29] and is a moderately long-lived species, its photogeneration may be a good candidate for a significant degradation pathway of UV stabilizers in polymer films, lacquers, paints, and coatings, especially where polar environments exist or where metals are present. This conclusion is also supported in a study by Dux and co-workers who found evidence based on fluorescence studies in a polymer blend which indicates benzotriazoles that lack an intramolecular hydrogen bond are more photoreactive than those with an intramolecular hydrogen bond intact.[24] Alternatively, if the benzotriazole-based stabilizer incorporates a bulky ortho group such as that found in **3**, the photostability of the molecule should remain largely intact in a polar environment, based on our results.

In a very interesting paper by Catalan and others,[21a] the role of the ESIPT mechanism in the photophysics of **1** was questioned. ESIPT, it was argued, could not be taking place, since the keto tautomer produced by such a mechanism should exhibit the characteristic Stokes-shifted fluorescence at room temperature, whereas none is observed. Shortly thereafter Wiechmann et al.[19] demonstrated that the Stokes-shifted fluorescence is present in solution at room temperature, albeit extremely weakly (quantum yield $< 10^{-5}$), with a subpicosecond emission lifetime. A more recent study appears to demonstrate another contradictory case in which the keto fluorescence is observed at room temperature.[24] It was also demonstrated in the same study that the keto fluorescence had a temperature dependence typical of a process involving quantum mechanical tunneling and was consistent with the involvement of a light particle such as a proton. We believe, since the hydrogen bond appears to be stronger intramolecularly in **1** than the intermolecular one to DMSO and since excited state proton transfer is facile in the latter case, that ESIPT is most likely and definitely energetically feasible in **1**. If the proton transfer does not occur in the excited state of **1**, then it would have to result from kinetic reasons rather than energetic reasons. Catalan's mechanism now appears unlikely.

For **2** it seems quite likely that the ESIPT mechanism and *not a hydrogen atom transfer mechanism* takes place in the triplet manifold since our results clearly show proton transfer to the solvent. The triplet of **2** has been directly observed in alcohol to be very short-lived (ca. 1.5 ns)[34] and indicates a highly efficient pathway for radiationless decay analogous to that in the singlet state. Thus **2** is dominated by its phenolic character. The radical-like nature of the n,π* triplet of **2**, normally associated with benzophenones, appears to be completely suppressed.

Conclusion

DMSO shifts the hydrogen bond equilibrium between intramolecular and solvent bonding by virtue of its strong hydrogen bond accepting character. The resulting intermolecular hydrogen bond of **1** and **2** in DMSO solvent leads to different photophysical *and photochemical* behavior. Photoinduced intermolecular proton transfer yields a reactive phenolate ion that is easily oxidized and which is readily characterized by laser flash photolysis experiments. Although nonpolar environments favor the photostable intramolecularly hydrogen-bonded forms of the photostabilizers, a finite amount of the intermolecularly hydrogen-bonded, photoreactive, nonplanar form should still exist. The latter species represents a possible source of long-term degradation of the stabilizers, particularly in polar polymer environments. Compound **3**, on the other hand, seems to be impervious to the DMSO effect. The bulky group ortho to the hydroxyl function in **3** suppresses the effect of a polar environment. In this case the photostability should remain intact even in polar environments. Further work providing a more detailed characterization of the triplets and fluorescence observed and focusing on the relative yields of the phenolate ion and triplet as a function of stabilizer structure will be reported elsewhere.

Experimental Section

Materials and Solvents. 2-(2′-Hydroxy-5′-methylphenyl)-benzotriazole (**1**) (Ciba-Geigy) was recrystallized from ethanol and then from hexane. 2-(2′-Hydroxy-3′-cumyl-5′-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole (**3**) (Ciba-Geigy) and *o*-hydroxybenzophenone (**2**) (Aldrich, 99+%) were used as received. DMSO (Aldrich Sure Seal), hexane (Fisher HPLC), and acetonitrile (Aldrich spectrophotometric grade) were used as received.

Measurements. UV−vis absorption spectra were recorded on an HP8452A UV spectrometer. Fluorescence spectra were measured with a Spex FluoroMax-2 spectrometer using a 1 × 1 cm quartz cell and concentrations of **1** and **3** such that the optical density was 0.32 at the excitation wavelength (330 nm). Laser flash photolysis experiments employed the pulses from a Lambda Physik Lextra 50 excimer laser (308 nm, ca. <20 mJ/pulse, 20 ns) and a computer-controlled system described elsewhere.[26] Solutions of **1** or **2** were prepared at concentrations such that the optical density was ca. 0.3 at the excitation wavelength employed. Transient absorption spectra were recorded employing a Suprasil quartz flow cell (1 × 1 cm) to ensure that a fresh volume of sample was irradiated by each laser pulse. Quenching rate constants for reaction of **1** and **2** with acid were measured in aerated DMSO.

Acknowledgment. We thank the Ciba-Geigy Additives Division of Tarrytown, NY, for their generous support and for donation of the benzotriazole UVAs. In addition the authors thank Drs. R. Seltzer, R. Ravichandran, J.-P. Wolf, A. D. De Bellis, and J. Suhadolnik for helpful discussions and comments on the manuscript. S.J. thanks the German Academic Exchange Service for a postdoctoral fellowship.

References and Notes

(1) Dexter, M. In *Encyclopedia of Polymers Science and Technology*; Interscience: New York, 1980; Vol. 23; pp 615.

(2) Rabek, J. F. *Photostabilisation of Polymers - Principles and Applications*; Elsevier Applied Science: Barking, U.K., 1990.

(3) Heller, H. J.; Blattmann, H. R. *Pure Appl. Chem.* **1973**, *36*, 141.

(4) Otterstedt, J. E. A. *J. Chem. Phys.* **1973**, *58*, 5716.

(5) Pickett, J. E.; Moore, J. E. in Sixteenth Annual International Conference on Advances in the Stabilization and Degradation of Polymers, Luzern, Switzerland, 1994; pp 253−269.

(6) Pickett, J. E.; Moore, J. E. *Polym. Prepr.* **1993**, *34*, 153.

(7) Dearth, M. A.; Korniski, T. J.; Gerlock, J. L. *Polym. Degrad. Stab.* **1995**, *48*, 111.

(8) Gerlock, J. L.; Tang, W.; Dearth, M. A.; Korniski, T. J. *Polym. Degrad. Stab.* **1995**, *48*, 121.

(9) Pickett, J. E.; Moore, J. E. *Polym. Degrad. Stab.* **1993**, *42*, 231.

(10) Decker, C.; Zahouily, K. *Polym. Mater. Sci. Eng.* **1993**, *68*, 70.

(11) Hodgeman, D. K. C. *J. Polym. Sci.* **1978**, *16*, 161.

(12) Hodgeman, D. K. C. *J. Macromol. Sci., Chem.* **1980**, *A14*, 173.

(13) Kurumada, T.; Ohsawa, H.; Yamazaki, T. *Polym. Degrad. Stab.* **1987**, *19*, 263.

(14) Gugumus, F. *Polym. Degrad. Stab.* **1993**, *39*, 117.

(15) Reiker, J.; Lemmert-Schmitt, E.; Goeller, G.; Roessler, M.; Steuber, G. J.; Schettler, H.; Kramer, H. E. A.; Stezowski, J. J.; Hoier, H.; Henkel, S.; Schmidt, A.; Port, H.; Weichmann, M.; Rody, J.; Rytz, G.; Slongo, M.; Birbaum, J.-L. *J. Phys. Chem.* **1992**, *96*, 10225.

(16) Unpublished results: We find two IR active OH stretching bands are observed in a 1:1 CCl_4/DMSO solvent mixture containing **1**. Both bands are broadened and shifted to lower frequencies (from free OH frequencies ∼3600 cm^{-1}) typical of hydrogen bonding. Both the absorption at 3480 cm^{-1} and that centered at 3210 cm^{-1} are dependent on DMSO concentration. With increasing DMSO concentration the absorbance of the 3480 cm^{-1} band increases while that of the band at 3210 cm^{-1} decreases in intensity. The latter band is the only one present in neat CCl_4. Thus the first band must arise from **1** having an intermolecular hydrogen bond to DMSO. Similar results are obtained for **2**.

(17) Woessner, G.; Goeller, G.; Rieker, J.; Hoier, H.; Stezowski, J. J.; Daltrozzo, E.; Neureiter, M.; Kramer, H. E. A. *J. Phys. Chem.* **1985**, *89*, 3629.

(18) Catalán, J.; Pérez, P.; Fabero, F.; Wilshire, J. F. K.; Claramunt, R. M.; Elguero, J. *J. Am. Chem. Soc.* **1992**, *114*, 964.

(19) Wiechmann, M.; Port, H.; Frey, W.; Lärmer, F.; Elsässer, T. *J. Phys. Chem.* **1991**, *95*, 1918.

(20) Ghiggino, K. P.; Scully, A. D.; Leaver, I. H. *J. Phys. Chem.* **1986**, *90*, 5089.

(21) (a) Catalán, J.; Fabero, F.; Guijarro, M. S.; Claramunt, R. M.; Maria, M. D. S.; Foces-Foces, M. C.; Cano, F. H.; Elguero, J.; Sastre, R. *J. Am. Chem. Soc.* **1990**, *112*, 747. (b) De Bellis, A. D.; Rodebaugh, R. K.; Suhadolnik, J.; Hendricks-Guy, C. *J. Phys. Org. Chem.* **1997**, *10*, in press.

(22) Huston, A. L.; Scott, G. W. *J. Phys. Chem.* **1987**, *91*, 1408.

(23) The intramolecular hydrogen bond has been thoroughly characterized via NMR and FT-IR and will be the subject of an upcoming paper.

(24) Dux, R.; Ghiggino, K. P.; Vogl, O. *Aust. J. Chem.* **1994**, *47*, 1461.

(25) On the basis of the extinction coefficients of the phenolate ions and benzophenone triplet based transient absorption actinometry, an upper limit estimate of photoionization yield is $^1/_{25}$ of that formed by compound **1**. Further work detailing the actinometry experiments and others will be reported elsewhere.

(26) McGarry, P. F.; Cheh, J.; Ruiz-Silva, B.; Hu, S.; Wang, J.; Nakanishi, K.; Turro, N. J. *J. Phys. Chem.* **1996**, *100*, 646.

(27) Werner, T. *J. Phys. Chem.* **1979**, *83*, 320.

(28) This mechanism is supported by the fact that the observed decay rate constant of the phenolate ion increases with increasing laser intensity in oxygen-saturated solutions. The observed decay rate constants of the phenolate ions should depend on the concentration of singlet oxygen, and the singlet oxygen concentration produced by sensibilization with triplets of **1** depends on the laser intensity.

(29) Catalán, J.; Valle, J. C. D.; Fabero, F.; Garcia, N. A. *Photochem. Photobiol.* **1995**, *61*, 118.

(30) Klöpffer, W. *Adv. Photochem.* **1977**, *10*, 350.

(31) Bartok, W.; Lucchesi, P. J.; Snider, N. S. *J. Am. Chem. Soc.* **1962**, *84*, 1842.

(32) McGarry, P. F.; Doubleday, J. C. E.; Wu, C.-H.; Staab, H. A.; Turro, N. J. *J. Photochem. Photobiol., A* **1994**, *77*, 109.

(33) Porter, G.; Suppan, P. *Trans. Faraday Soc.* **1965**, *61*, 1664.

(34) Hou, S.-Y.; Hetherington, W. M., III; Korenowski, G. M.; Eisenthal, K. B. *Chem. Phys. Lett.* **1979**, *68*, 282.

(35) Unpublished results.

(36) Mosquera, M.; Penedo, J. C.; Rodriguez, M. C. R.; Rodriguez-Prieto, F. *J. Phys. Chem.* **1996**, *100*, 5398.

(37) The lifetime of the ion, while quite long, is short enough to make the encounter between it and a radical species in solution unlikely.