Excited-State Dynamics and Photophysical Properties of *para*-Aminobenzophenone

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The photophysical properties of the singlet (S_1) and triplet (T_1) excited states of *p*-aminobenzophenone (*p*-ABP) have been investigated in various organic solvents using steady-state as well as transient absorption spectroscopy with picosecond and subpicosecond time resolution. *p*-ABP is weakly fluorescent in benzene as well as in polar aprotic solvents, acetonitrile, DMSO, and DMF, but nearly nonfluorescent in cyclohexane and methanol. In cyclohexane, the S_1 state has the $n\pi^*$ configuration and is short-lived [$\tau(S_1) \sim 12$ ps]. In methanol, a polar and protic solvent, the S_1 state is much shorter-lived [τ (S_1) < 1ps, and hence, we have not been able to detect any transient, even in subpicosecond time scale] because of the formation of an intermolecular hydrogen-bonded complex with the solvent. In all other solvents, the S_1 state has a $\pi\pi^*$ or CT configuration and, hence, is much longer-lived (>100 ps). The triplet yield is much higher in nonpolar solvents than in polar solvents but the lifetime shows the reverse trend. In nonpolar solvents, the T_1 state is an equilibrium mixture of the states having $n\pi^*$ and $\pi\pi^*$ configurations because of their close proximity in energy, and it is photochemically reactive toward hydrogen-atom-abstraction reactions. In polar solvents, the T_1 state is unreactive because of its $\pi\pi^*$ or CT character. A comparison has also been made among the photophysical properties of benzophenone (BP), *p*-hydroxybenzophenone (*p*-HOBP), and *p*-ABP.

Introduction

In aromatic carbonyl compounds, the energy gap between the lowest excited singlet and triplet states is small, and these electronic states are strongly coupled via spin−orbit interaction. Hence, the intersystem-crossing (ISC) process producing the triplet state can compete kinetically with the other processes, such as internal conversion (IC) and fluorescence emission, originating from the singlet excited state. This results in a large triplet yield because of the efficient and ultrafast ISC process for aromatic carbonyl compounds in solution.[1,2] In the case of benzophenone (BP), the parent of the aromatic carbonyl compounds, the quantum yield for the T_1 state is close to unity; hence, this state not only participates in the major relaxation pathway of the excited molecule to the ground state, but also is responsible for all of the major photochemical reactions of BP.[3−6]

One of the most important and widely studied photochemical reactions undergone by aromatic carbonyl compounds is photoreduction by hydrogen-atom donors. The rate, efficiency, and mechanism of this reaction have been shown to depend on two main factors—the electronic configuration of the T_1 state and the identity of the hydrogen-atom donors.[3−7] In these compounds, three types of excited states having different electronic configurations, namely, $n\pi^*$, $\pi\pi^*$ and charge transfer (CT), both in the singlet and in the triplet manifold, have been identified as being responsible for differences in their photophysical and photochemical behaviors.[8] The S_1 and T_1 states of BP have been shown to have an $n\pi^*$ configuration in almost all kinds of solvents, including nonpolar and polar, as well as hydrogen-bonding.[9] However, after the substitution of electron-donating groups, such as OH, OCH_3, and NH_2, onto the aromatic rings of benzophenone, the relative positions of the $n\pi^*$ and $\pi\pi^*$ states in either the singlet or the triplet manifold are largely affected by the solvent polarity, and hence, the reactivities of these substituted benzophenones vary greatly in different kinds of solvents.[8−11] The triplet states of benzophenone and many of its derivatives are capable of abstracting a hydrogen atom from a variety of substrate molecules, including hydrocarbons, alcohols, and amines, with about unit efficiency.[12] However, its amino derivative, *p*-aminobenzophenone (*p*-ABP), is completely unreactive toward alcohols and even less reactive toward any other kind of solvents and molecules.[12] Such a low photoreactivity of *p*-ABP has been correlated to the $\pi\pi^*$ or CT character of the T_1 state.[9,10,13,14]

In our earlier studies on the spectroscopic properties of hydroxy-substituted benzophenones, we reported that the excited triplet states of *p*-hydroxybenzophenone (*p*-HOBP) in nonpolar solvents, having the $n\pi^*$ configuration, is capable of abstracting a phenolic hydrogen atom from another parent molecule, forming ketyl- and phenoxy-type radicals.[11] In polar but non-hydrogen-bond-forming solvents, such as acetonitrile (ACN), the energy level of the high-lying $\pi\pi^*$ triplet state comes closer to that of the $n\pi^*$ state, and hence, they remain in thermal equilibrium during their lifetime. Because of the presence of the $n\pi^*$ state, the hydrogen-atom-abstraction reaction has also been observed in this solvent. The $n\pi^*$ triplet excited state of this ketone is capable of abstracting the phenolic proton from another molecule in the ground state. However, the triplet state is short-lived in hydrogen-bond-forming solvents, such as alcohols, because of the strong association between the ketone and the solvent via the formation of a hydrogen-bonded complex, and hence, it is nonreactive toward abstraction of either an alkyl hydrogen atom from the solvent or a phenolic hydrogen atom from another molecule in the ground state. Probably, in

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alcohols and other hydrogen-bond-forming solvents, e.g., dimethyl sulfoxide (DMSO) and *N*,*N*-dimethylformamide (DMF), the energy level of the $\pi\pi^*$ triplet state of *p*-HOBP, which has an unsymmetrical charge distribution because of the electron-donating properties of the OH group and has been assigned by Porter et al.[9] as the CT state, is well below that of the $n\pi^*$ triplet state. Also, the triplet yields in this class of solvents have been found to be very low (in methanol, $\phi_T \sim 0.2$), as compared to that in nonpolar solvents (e.g., in cyclohexane $\phi_T = 0.9$) because of the efficient radiationless relaxation process taking place from the singlet excited state via the O−H stretching vibrations in the intermolecular hydrogen bond. Also, the quenching of the singlet excited CT state via the proton-transfer reaction to the solvent, which leads to the formation of the phenolate ion, might be another reason for the low triplet yields.

In the case of *p*-HOBP, the substituent group, OH, may not be a sufficiently strong donor to ensure complete charge transfer from the phenolic moiety to the carbonyl group to form a pure CT state. However, the substitution of amino or substituted-amino groups onto the aromatic rings of benzophenone possibly ensures the complete charge transfer from the aniline moiety to the carbonyl group, providing perfect CT character to the $\pi\pi^*$ state. Porter and Suppan, in fact, predicted the transfer of about 0.8*e* charge from the substituent NH_2 group to the carbonyl group in *p*-ABP.[9a] However, they provided no quantitative evidence in favor of this prediction. The photochemical reactivity of *p*-ABP in different polar and nonpolar solvents has been reported earlier by Suppan and co-workers.[13,14] According to their report, although the yield of the triplet state, which has an $n\pi^*$ configuration in cyclohexane, is about 0.8, the quantum yield of hydrogen abstraction from the solvent molecule is only about 0.2.[14] This fact indicates the very low photoreactivity of the triplet state of *p*-ABP as compared to that of BP. The photoreactivity of the triplet state of BP in cyclohexane toward H-atom abstraction is about unity.[8,9.] However, no reasonable explanation has been provided for the low reactivity of the triplet state of *p*-ABP. Also, to the best of our knowledge, there has been no report on the detailed spectroscopic properties and lifetimes of the S_1 and T_1 states of *p*-ABP, except for the very preliminary reports mentioned earlier.[13,14] However, recently, Borisevich et al. reported the results of their studies on the twisted intramolecular charge-transfer (TICT) dynamics in the singlet excited state of *p*-*N*,*N*-dimethylaminobenzophenone.[15] In the present paper, we report the detailed photophysical properties of both the singlet and the triplet excited states of *p*-ABP using steady-state fluorescence, as well as ultrafast transient absorption, spectroscopic techniques. This will help us to understand the excited-state relaxation dynamics and the photochemical behavior of *p*-ABP, which has been a textbook example for its inability to take part in hydrogen-abstraction reactions in alcohols despite the fact that it is an aromatic ketone.[16]

Experimental Section

p-ABP, (about 98% pure), obtained from Aldrich (Milwaukee, WI) was purified by recrystallization from aqueous ethanol. All of the solvents used were of spectroscopic grade (Spectrochem, Hyderabad, India) and used as received without further purification. High-purity-grade nitrogen gas (Indian Oxygen, Calcutta, India, purity >99.9%) was used to deaerate the samples. All the experiments were carried out at room temperature (296 ± 1 K) unless specified otherwise. Steady-state absorption spectra were recorded on a Shimadzu model UV-160A spectrophotometer. Steady-state phosphorescence spectra were recorded in ethanol and methylcyclohexane (MCH) glasses at 77 K using a Hitachi model F-4010 fluorescence spectrometer equipped with a phosphorescence accessory. ^{13}C and ^{1}H NMR spectra were recorded at room temperature using a Bruker Avance 300 FT NMR machine.

The picosecond transient absorption spectrometer has been described in detail elsewhere.[11] Steady-state fluorescence spectra were recorded with this same setup by blocking the probe light, and the fluorescence yields were determined by comparing the areas under the fluorescence curves with that of a standard, pentaphenylfullerene-2-ol (PPF), under the same experimental conditions. The fluorescence quantum yield for PPF in benzene solution has been reported to be 0.7×10^{-3}.[17] Transient species surviving beyond 100 ns were studied by monitoring the optical absorption using the same picosecond Nd:YAG laser for excitation and a continuous-wave tungsten lamp, in combination with a Bausch & Lomb monochromator (350−800 nm) and a Hamamatsu R928 PMT, 500-MHz digital oscilloscope (Tektronix, TDS-540A) connected to a PC. Using the same setup, but without the probe light, phosphorescence lifetimes in rigid matrixes at 77 K were also determined.

Relaxation processes taking place in a time domain faster than 50 ps were studied using a home-built subpicosecond transient absorption spectrometer. Laser pulses of 100 pJ in energy and 70 fs in duration at 620 nm, generated from an argon-ion-pumped colliding-pulse mode-locked (CPM) dye laser oscillator, were amplified to about 300-μJ pulses of 100 fs in duration in a five-stage dye amplifier pumped by a Nd:YAG laser working at 30 Hz. Pump pulses at 310 nm were generated by doubling the 620 nm output from the amplifier in a 0.5-mm BBO crystal, and the residual fundamental was used to generate the white light continuum (400−950 nm) in a flowing water medium of 1-cm path length. The sample solutions were kept flowing through a quartz cell of 2-mm path length. The transient absorption spectra were recorded using the dual diode array optical multichannel analyzer, and the decay dynamics at a particular wavelength region (10 nm width) were monitored using two photodiodes coupled with boxcar integrators. The overall time resolution of the absorption spectrometer was determined to be about 500 fs by measuring the growth of the $S_1 \rightarrow S_n$ absorption of 1,4-diphenylbutadiene in cyclohexane solution at 650 nm.[18] The transient absorption spectra reported here were recorded only after a delay of more than 1 ps to avoid any distortion due to group velocity dispersion in the monitoring wavelength region, 400−950 nm.

Results and Discussion

Steady-State Studies. The steady-state absorption spectra of *p*-ABP in several solvents with different polarities and hydrogen-bonding abilities are presented in Figure 1A. Spectral characteristics of *p*-ABP in cyclohexane (CH) and 2-propanol have already been reported earlier.[9b] In cyclohexane, the spectrum is characterized by a broad high-intensity band centered at 303 nm and a long tail in the lower-energy region. Considering the very high extinction coefficient value (2.1×10^4 dm^3 mol^{-1} cm^{-1}) at 303 nm as compared to that at 350 nm (480 dm^3 mol^{-1} cm^{-1}), the former has been assigned to the $\pi\pi^*$ transition and the latter to $n\pi^*$ transition. Because, as a rule, the dipole moment of the singlet excited $n\pi^*$ state (Scheme 1) is lower than that of the ground state, the band due to the $n\pi^*$ transition suffers a hypsochromic shift in more polar solvents. In polar solvents, it is possibly masked by the high-intensity $\pi\pi^*$ band, which undergoes a bathochromic shift as the polarity of the solvent is increased. The maximum of the $\pi\pi^*$ band shifts from 303 nm

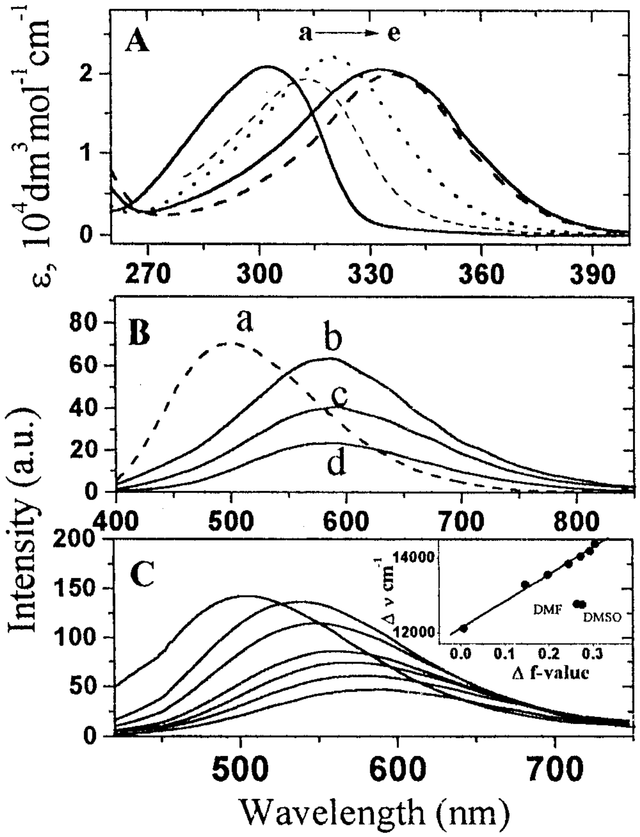

Figure 1. (A) Ground-state absorption spectra of *p*-ABP in (a) cyclohexane, (b) benzene, (c) acetonitrile, (d) methanol, and (e) DMSO. (B) Fluorescence spectra of *p*-ABP in (a) benzene, (b) acetonitrile, (c) DMF, and (d) DMSO. (C) Fluorescence spectra of *p*-ABP in benzene−acetonitrile mixed solvents with the following volume percentages of acetonitrile: (a) 0, (b) 10, (c) 20, (d) 40, (e) 60, (f) 80, and (g) 100. Inset: Plot of the Stokes shift $\Delta\nu$ vs Δf value of the solvent mixtures of benzene and acetonitrile. The plot also includes DMSO and DMF.

SCHEME 1

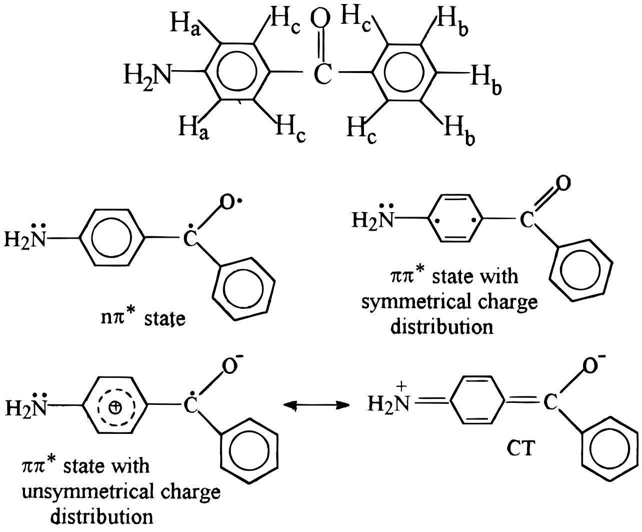

TABLE 1: Photophysical Parameters of *p*-ABP in Different Solvents

solvent	φ_f[a]	τ_S (ps)	φ_T[b]	τ_T (μs)
CH	−	12.1 ± 1	0.9 (0.82)	1.4 ± 0.2
BZ	1.2×10^{-3}	300 ± 20	0.6 (0.67)	3.2 ± 0.2
ACN	0.5×10^{-3}	150 ± 20	0.35 (0.32)	11.0 ± 0.3
DMF	0.21×10^{-3}	200 ± 30	0.13 (0.1)	4.8 ± 0.2
DMSO	0.15×10^{-3}	200 ± 30	0.04 (<0.1)	6.0 ± 0.3

[a] The error in the ϕ_f values is about 15%. [b] The ϕ_T values inside brackets are from refs 13 and 14.

in cyclohexane to 320 nm in acetonitrile, 332 nm in methanol, and 335 nm in DMSO. This large bathochromic shift in the maximum of the $\pi\pi^*$ absorption band with increased solvent polarity indicates the stabilization of the singlet excited $\pi\pi^*$ state in more polar solvents because of the increased dipole moment of the molecule in the excited state as compared to that of the ground state. The shift is seen to be larger in methanol than in acetonitrile, although both solvents have comparable solvent polarities (dielectric constants are 32.7 and 37.5, respectively). Note that the width of this band is also increased considerably in methanol (fwhm values are 32, 39, 43, and 36 nm in cyclohexane, acetonitrile, methanol, and DMSO, respectively). The larger bandwidth observed in methanol probably indicates a strong association of the solvent molecules with *p*-ABP molecules in the ground state via formation of intermolecular hydrogen bonds. Hoshino and Koizumi have reported the formation of an intermolecular hydrogen-bonded complex between *p*-HOBP and aliphatic alcohols.[19] The ^{1}H NMR spectra of *p*-ABP recorded in $CDCl_3$ shows the existence of three sets of clear signal peaks for three different kinds of protons (Scheme 1) present in the molecule in a 2:3:4 ratio of peak areas. The signal due to the protons in the amino group is very weak, as expected. However, in CH_3OD, the identities of these three kinds of protons are lost, and the peaks appear at a very high field as compared to those observed in $CDCl_3$. This fact probably indicates a strong association between *p*-ABP molecules and alcohol molecules, forming a network of hydrogen bonds.

Also note that the maximum in the $\pi\pi^*$ absorption band shows a shift of about 15 nm when the solvent changes from cyclohexane to benzene, both of which can be considered as the nonpolar solvents. Dielectric constants are 2.0 and 2.3 for cyclohexane and benzene, respectively. The source of this anomalous shift in benzene probably can be rationalized by following the classification of solvents by Maroncelli and coworkers.[20] They classified cyclohexane as a "simple dipolar" solvent but benzene as a "nondipolar" solvent. The nondipolar solvents are those that, by virtue of exact or near symmetry, have dipole moments that are approximately zero but that nevertheless contain bonds that are expected to be significantly polar, possibly leading to significant electrostatic solvation energies. These energies are not accounted for in a continuum model that employs only infinite-wavelength properties such as the dielectric constant.

Unlike benzophenone and hydroxy-substituted benzophenones, which are nonfluorescent, *p*-ABP has been seen to be weakly fluorescent in benzene (BZ) and also in polar and aprotic solvents. However, in cyclohexane and methanol, the emission is too weak to detect. The fluorescence spectra of *p*-ABP in different solvents are presented in Figure 1B. The fluorescence spectrum in benzene shows a maximum at ca. 506 nm, but in acetonitrile, DMF, and DMSO, the fluorescence maxima appear at ca. 586, 589, and 590 nm, respectively. The fluorescence quantum yields of *p*-ABP in the various solvents are given in Table 1.

Fluorescence spectra have also been recorded in benzene-acetonitrile mixed solvents of different compositions, which are presented in Figure 1C. The maximum of the fluorescence band shifts gradually toward the red as the polarity of the solvent mixture is increased. The values of the dielectric constant and the refractive index of the benzene−acetonitrile solvent mixtures of different compositions have been determined by Bakshi.[21] The values for the solvent mixtures used here were obtained by linear extrapolation of the reported values, and values for the polarity or "reaction-field" parameter, Δf, as defined by eq 1, were calculated.

$$\Delta f = \frac{D-1}{2D+1} - \frac{n^2-1}{2n^2+1} \qquad (1)$$

The variation of the Stokes' shift parameter, $\Delta\nu$, as a function of Δf is depicted in the inset of Figure 1C. This also includes the data for the other two solvents, DMF and DMSO. The linear increase of $\Delta\nu$ as a function of the reaction-field parameter, Δf, in benzene−acetonitrile solvent mixtures indicates the polar character of the fluorescent or S_1 state, which is stabilized by solvation in more polar solvents. The fact that a new band does not appear as the polarity of the solvent is increased excludes the possibility of formation of a new fluorescent state, such as the twisted intramolecular charge transfer (TICT) state, which is normally observed to form from the locally excited (LE) state after charge transfer.[6] For example, Borisevich et al. observed dual emissions from the LE and TICT states in solvents having moderately high polarity, following optical excitation of *N*,*N*-dimethylaminobenzophenone.[15] In the case of *p*-ABP, however, dual emission bands have not been observed, nor has any other indication, such as dual exponentiality of the decay of the excited singlet state (see later), been obtained in favor of the formation of a TICT state. The absence of TICT emission in *p*-ABP may be due to the fact that the rotation of the NH_2 group is barrier free and very fast compared to that of the dimethylamino group in *N*,*N*-dimethylaminobenzophenone. Hence, we conclude that the fluorescent S_1 state in benzene probably has the nearly symmetrical $\pi\pi^*$ configuration with little charge separation (Scheme 1). In polar solvents, the unsymmetrically charge-distributed $\pi\pi^*$ or CT state formed by intramolecular charge transfer from the aniline moiety to the carbonyl group becomes stabilized by solvation, and this intramolecular CT state is considered to be the fluorescent state in polar solvents. However, the smaller Stokes' shift values in DMSO and DMF, compared to those in benzene−acetonitrile mixed solvents, which should be considered as the non-hydrogen-bond-forming media, probably indicate the intermolecular hydrogen-bonding interaction between the DMF or DMSO solvent molecules, which are good hydrogen-bond acceptors, and *p*-ABP in both the ground and the excited states. From the slope of the least-squares fit of the linear plot of $\Delta\nu$ vs Δf, as shown in the inset of Figure 1C, the change in the dipole moment ($\Delta\mu = \mu_e - \mu_g$) in the singlet excited CT state with respect to the ground state has been calculated using the Lippert−Mataga equation (eq 2).[22]

$$\Delta\nu = \frac{2(\mu_e - \mu_g)^2}{hca^3}\Delta f + \text{constant} \qquad (2)$$

By applying the partial volume addition method suggested by Edward,[23] the Onsagar cavity radius, *a*, was estimated to be 3.52 Å. Then, by substituting the value of *a*, the change in dipole moment due to the transition from S_0 to the S_1 was estimated to be 7.9 D. This clearly indicates the CT character of the S_1 state.

Curves a and b in Figure 2 represent the phosphorescence spectra of *p*-ABP recorded in methylcyclohexane (MCH) and ethanol glass at 77 K. The phosphorescence spectra of BP (as shown by curve c) and those of *p*-HOBP and many other derivatives of BP, which have a T_1 state of $n\pi^*$ configuration, have been reported to have very similar features, including the position of the maxima as well as the fine structure characteristics, although these features are poorly resolved in hydroxybenzophenones.[11,24] However, the onset wavelengths of the phosphorescence spectra of *p*-ABP in both of the matrixes are shifted toward the red by about 30 nm compared to those of BP and *p*-HOBP. Also, the maxima of the phosphorescence spectra of *p*-ABP are considerably red-shifted, and the vibrational progression is completely absent in the spectrum in either of the matrixes. The phosphorescence spectrum in MCH glass is broad, with a single band having a maximum at 495 nm and a weak shoulder at 522 nm. The spectrum in ethanol glass shows two peaks at 477 and 504 nm. The energy levels for the lowest triplet excited states, as determined from the onset of the phosphorescence spectra, are at 66.6 kcal mol^{-1} in MCH and 65.6 kcal mol^{-1} in ethanol, as compared to those at 68.5 kcal mol^{-1} for BP and 67.5 kcal mol^{-1} for *p*-HOBP.[11,25] The phosphorescence decay of *p*-ABP is biexponential in MCH with lifetimes of 2.6 ± 0.3 and 55 ± 5 ms, whereas in ethanol matrix, the phosphorescence emission decays as a single exponential with a lifetime of 80 ± 5 ms. The ketones with T_1 states of $n\pi^*$ configuration have phosphorescence lifetimes not longer than a few milliseconds, and those with the T_1 states of $\pi\pi^*$ configuration have lifetimes of more than a few tens of milliseconds and, in many cases, up to several hundred milliseconds.[11,26,27] Hence, in the case of *p*-ABP, the double-exponential decay in MCH indicates the presence of two kinds of triplet states, namely, the $n\pi^*$ and $\pi\pi^*$ states, energetically very close to each other. The shorter lifetime (2.6 ms) might be associated with the $n\pi^*$ triplet state, whereas the longer lifetime (55 ms) might be associated with the $\pi\pi^*$ triplet state. This kind of dual phosphorescence has already been reported for a few of the aromatic carbonyl compounds, including benzophenone.[2b,26b,28] In ethanol, however, the unsymmetrically charge-distributed $\pi\pi^*$ or CT triplet state is the only emitting state, as, in this matrix, the energy level of the T_1 state of $\pi\pi^*$ or CT configuration is much lower than that of the triplet state of $n\pi^*$ configuration.

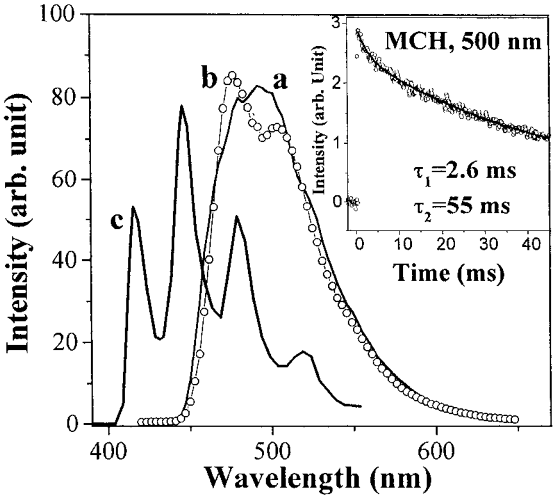

Figure 2. Phosphorescence spectra of *p*-ABP in (a) MCH and (b) ethanol matrixes. For comparison, the phosphorescence spectrum of BP in MCH is shown by curve c. Inset shows the phosphorescence decay of *p*-ABP in MCH.

Laser Flash Photolysis. Figure 3 presents the time-resolved absorption spectra of the transient species produced by photolysis of *p*-ABP in various organic solvents using 355-nm pulses of 35-ps duration and recorded (a) immediately, i.e., at 0 ps, and (b) at 660 ps after the laser pulse excitation. It is clearly evident from this figure that the spectral and decay characteristics of the transient species differ considerably in

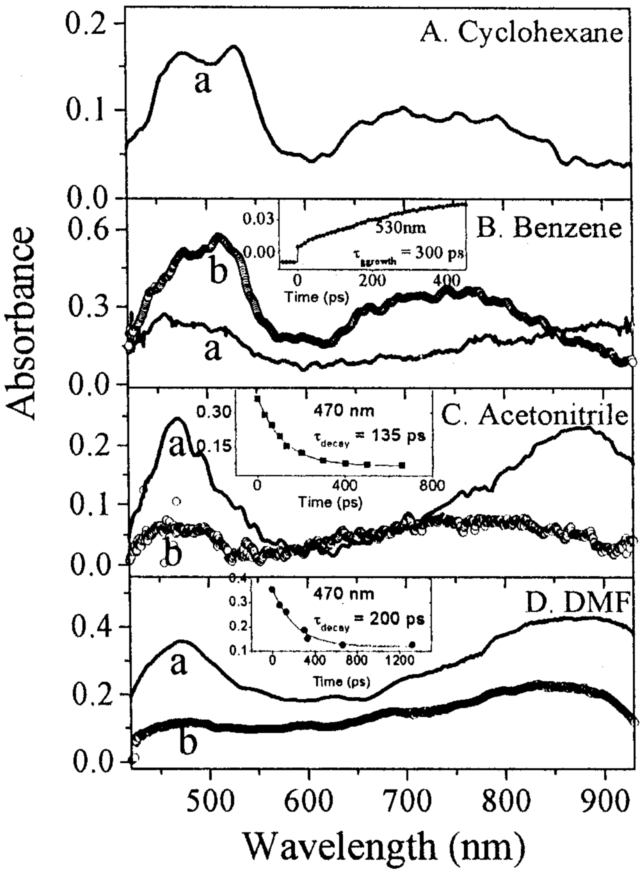

Figure 3. Absorption spectra of the transients recorded (a) immediately and (b) 660 ps after the photolysis of *p*-ABP by 35-ps laser pulses of 355-nm light in (A) cyclohexane, (B) benzene, (C) acetonitrile, and (D) DMF. The insets show the time evolution of the transient absorption monitored at 530 or 470 nm.

different solvents. In cyclohexane, the transient spectrum a, recorded immediately after the laser pulse, has two major bands; one is very broad in the range 600−930 nm and centered at ca. 750 nm, and the other one is in the range 420−600 nm, with two peaks at 470 and 530 nm superimposed on it. No further evolution of the spectral features has been observed at later times up to 6 ns. In benzene, however, we observe an evolution of the spectral characteristics with time, even though benzene is similar to cyclohexane with respect to polarity. The transient absorption spectrum recorded immediately after the laser pulse in benzene has distinctly different features from those observed in the spectrum recorded in cyclohexane. The former also has two major bands, but one is in the wavelength range of 600−930 nm, with a maximum at ca. 900 nm, and the other is in the 460−600 nm region, with a maximum at 460 nm and a shoulder at 530 nm. However, this spectrum evolves with time up to 1.5 ns, and the spectrum recorded at 1.5 ns has similar features to those in the spectrum obtained in cyclohexane. The growth of absorption of the transient was monitored at 530 nm, and the growth lifetime was determined to be 300 ps.

In the case of the polar and aprotic solvent, acetonitrile, the transient spectrum a, recorded at 0 ps, has two major bands with maxima at ca. 470 and 880 nm. The absorbance values monitored at both of these wavelengths decay at the same rate, and the lifetime of this transient has been determined to be 135 ± 15 ps (inset of Figure 3c). After the decay of this transient a new transient absorption spectrum (b), having one band centered at 750 nm and the other at 470 nm, evolves after 660 ps. Both bands are long-lived and do not show any further evolution up to 6 ns. In DMF and DMSO, the spectral characteristics of the transient species are very similar to those observed in acetonitrile. However, the transient spectrum recorded at 660 ps has the absorption maximum shifted to 850 nm for the lower-energy band (650−930 nm). The decay lifetime of the short-lived transient in either of these solvents has been determined to be about 200 ± 20 ps (inset of Figure 3D). We could not observe any transient absorption in the polar and protic solvent methanol.

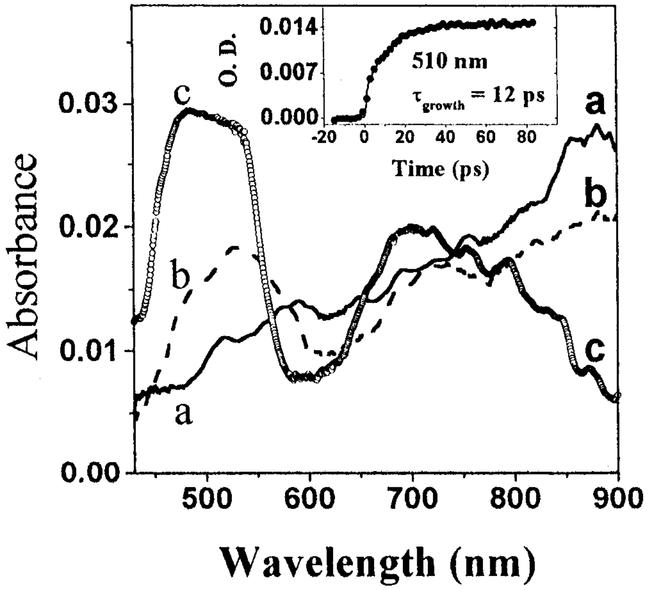

Figure 4. Absorption spectra of the transients recorded at (a) 1 ps, (b) 5 ps, and (c) 80 ps after the photolysis of *p*-ABP in cyclohexane by subpicosecond laser pulses of 310-nm light. The inset shows the growth of the transient absorption monitored at 510 nm.

Figure 4 shows the time-resolved transient absorption spectra obtained by flash photolysis of *p*-ABP in cyclohexane on excitation by 310-nm laser pulses of subpicosecond duration. The nature of spectrum a, recorded at 1 ps, is entirely different from that of the spectrum obtained upon excitation by 355-nm laser pulses. Spectrum a shows an increasing absorbance from 420 nm up to 900 nm with a maximum at about 890 nm. With an increase in the time delay, the absorbance at ca. 500 nm grows, and that at 890 nm decays to produce a transient species having spectrum c, which was recorded 80 ps after the laser pulse. Spectrum b was recorded 5 ps after the laser pulse. Spectrum c is very similar to that obtained on excitation by 355-nm light (curve a in Figure 3A) but with a slight difference in the shape of the band in the 420−600 nm wavelength region. In this wavelength region, the peaks at 470 and 530 nm in spectrum c are not as well resolved as those in spectrum a of Figure 3A. The growth of the transient absorption monitored at 510 nm is shown in the inset of Figure 4, and its lifetime has been determined to be 12 ± 1 ps.

The nature of the transient absorption spectrum of *p*-ABP in benzene recorded at 1 ps after photolysis by 310-nm laser pulses of subpicosecond duration is very similar to that of the spectrum obtained immediately after the 35-ps laser pulses of 355-nm light (Figure 3B). The growth lifetime of the transient of *p*-ABP produced by photolysis by 310-nm light has been determined to be 300 ± 30 ps (inset of Figure 3B). This growth lifetime of the transient is the same as was obtained by 355-nm excitation in picosecond flash photolysis experiments.

Absorption spectrum a of the transient produced by flash photolysis of *p*-ABP in acetonitrile on excitation by 310-nm light, shown in Figure 5A, has been observed to be very similar to that obtained on excitation by 355-nm light and recorded in

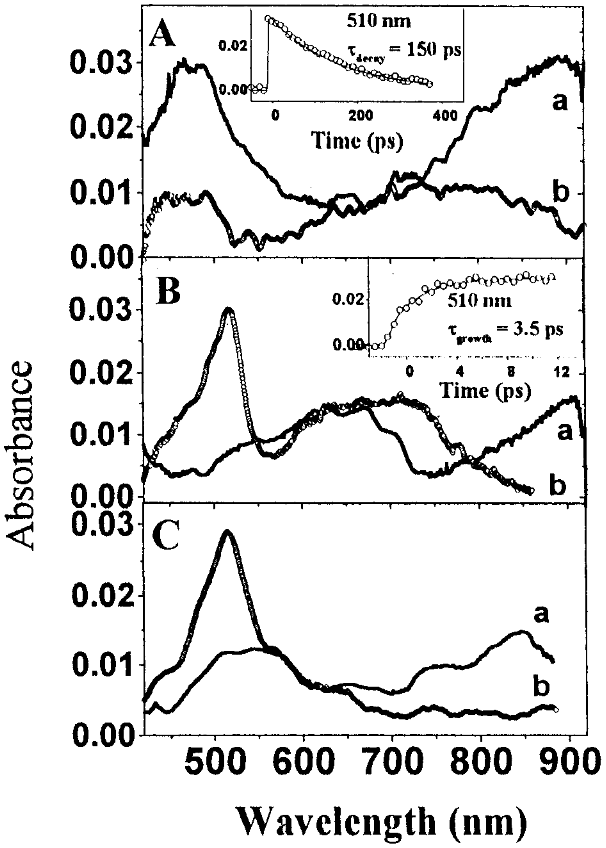

Figure 5. Absorption spectra of the transients recorded at (a) 1 ps and (b) 660 ps after the photolysis of (A) *p*-ABP, (B) *p*-HOBP, and (C) BP in acetonitrile by subpicosecond laser pulses of 310 nm. The insets show the time evolution of the transient absorption monitored at 510 nm.

the picosecond time domain (curve a in Figure 3C). The decay lifetime of the transient species obtained upon 310-nm excitation has been determined to be 150 ± 10 ps (inset of Figure 5A), which nearly agrees with the value determined from the picosecond flash photolysis experiments using the 355-nm excitation wavelength. Curves a and b in Figure 5B and C show the transient absorption spectra obtained by flash photolysis of *p*-HOBP and BP in acetonitrile upon excitation with 310-nm laser pulses of subpicosecond duration and recorded at 1 and 660 ps after the laser pulse, respectively. Curves a and b can be assigned to the S_1 and T_1 states of *p*-ABP, respectively.[1,2,11] The lifetime of the growth of the T_1 state has been determined to be 3.5 ± 0.2 ps for *p*-HOBP in acetonitrile, and those for BP have been reported earlier to be 9 ps in acetonitrile,[2,28] 10 ps in benzene, and 14 ps in ethanol.[2,29,30] Hence, a comparison between the spectral and decay characteristics of the S_1 and T_1 states produced by photolysis of BP, *p*-HOBP, and *p*-ABP in acetonitrile shows a clear difference between those of *p*-ABP and those of the other two.

In the studies here, we have used two excitation wavelengths, namely, 310 and 355 nm, for studying the transient absorption characteristics. Figure 1A reveals that excitation of *p*-ABP molecules by 310-nm light, in either nonpolar or polar solvents, induces the $\pi\pi^*$ transition. However, excitation by 355-nm light induces an $n\pi^*$ transition in the nonpolar solvent cyclohexane but a $\pi\pi^*$ transition in polar solvents. In benzene, probably transitions to both of these states are induced by 355-nm light because of the overlapping of the $n\pi^*$ and $\pi\pi^*$ absorption bands.

The S_1 state of BP is known to have an $n\pi^*$ configuration in almost all kinds of solvents.[1,2] Similarities in the features of the absorption spectra of the S_1 states of BP and *p*-HOBP (curve a in Figure 5B and C, respectively) indicate that the S_1 state of *p*-HOBP in acetonitrile also has the $n\pi^*$ configuration. However, we are not able to provide any explanation for the very short lifetime (3.5 ps) of the S_1 state of *p*-HOBP as compared to that of BP (10 ps). On the basis of a comparison of the lifetimes of the $n\pi^*$ S_1 states of BP and *p*-HOBP with that of the S_1 state of *p*-ABP in different solvents, it can be concluded that the S_1 state of *p*-ABP in cyclohexane should have the $n\pi^*$ configuration, because it has a short lifetime (12 ps). However, in the other solvents benzene, acetonitrile, DMF, and DMSO, the S_1 state has lifetimes longer than 100 ps, and hence, this state is expected to have the $\pi\pi^*$ configuration. In the polar solvents mentioned here, the situation is clear because excitation by either 310- or 355-nm light produces the S_1 state of $\pi\pi^*$ configuration. In cyclohexane, although we excite the molecules by 310-nm light to the $\pi\pi^*$ excited singlet state, because $n\pi^*$ is the lowest excited singlet (S_1) state, it becomes populated very rapidly (within less than 1 ps) by an internal conversion process from the higher $\pi\pi^*$ state initially prepared. However, the spectral features of the S_1 states of BP and *p*-HOBP are quite different from those of the S_1 state of *p*-ABP in cyclohexane (curve a in Figure 4). The latter has a very broad absorption band, increasing in absorbance from 420 nm up to 900 nm, with a shoulder at 600 nm. It has no well-defined band in the 500−700 nm wavelength region, as has been seen in the S_1 state spectra of BP and *p*-HOBP (Figure 5). Only the short lifetime (12 ps) of the S_1 state of *p*-ABP in cyclohexane indicates that the configuration of the S_1 state of *p*-ABP in this solvent should be $n\pi^*$, although the spectral features of the latter are quite different from those of the $n\pi^*$ states of BP and *p*-HOBP. This is the reason that *p*-ABP is nonfluorescent in cyclohexane. The very different spectral features and the longer lifetime (>100 ps) of the S_1 state of *p*-ABP in other solvents indicate the $\pi\pi^*$ or CT nature of this state.

It is evident from Figures 3 and 4 that the triplet absorption spectra of *p*-ABP in cyclohexane obtained by 310- and 355-nm excitation are found to be very similar in nature, as mentioned earlier. Hence, excitation to either $n\pi^*$ (by 355-nm light) or $\pi\pi^*$ (by 310-nm light) leads to the same kind of triplet state (or states) by intersystem crossing. However the triplet absorption spectrum of *p*-ABP in cyclohexane is very different from those of *p*-ABP in other solvents and also from those of BP and HOBP in any kind of solvents. Figure 6 compares the triplet absorption spectra of *p*-ABP in cyclohexane (curve a) and acetonitrile (curve b). The absorption spectra in both the solvents consist of two distinct bands: one in the near UV−visible region (450−600 nm, let us designate it as "band A") and the other in the 600−900 nm wavelength region (let us designate it as "band B"). It is observed that band B features of the triplet absorption spectra of *p*-ABP in cyclohexane and acetonitrile are very similar, but there are significant differences between the two spectra in the 420−600 nm wavelength region. The triplet absorption spectra of *p*-ABP in other solvents have features similar to those of the spectra in acetonitrile. The entire spectrum b of triplet *p*-ABP in acetonitrile can be assigned to the $\pi\pi^*$ or unsymmetrically charge-distributed $\pi\pi^*$, i.e., CT, configuration for two reasons. First, triplet *p*-ABP in acetonitrile or other polar solvents is not reactive to the hydrogen-abstraction reaction. The quantum yields of this kind of reaction in polar solvents have been reported to be less than 10^{-3}.[14] Second, the phosphorescence lifetime of *p*-ABP in polar solvents, such as ethanol, is very long (80 ms). The broad nature of the band A in cyclohexane indicates that the entire spectrum a is probably

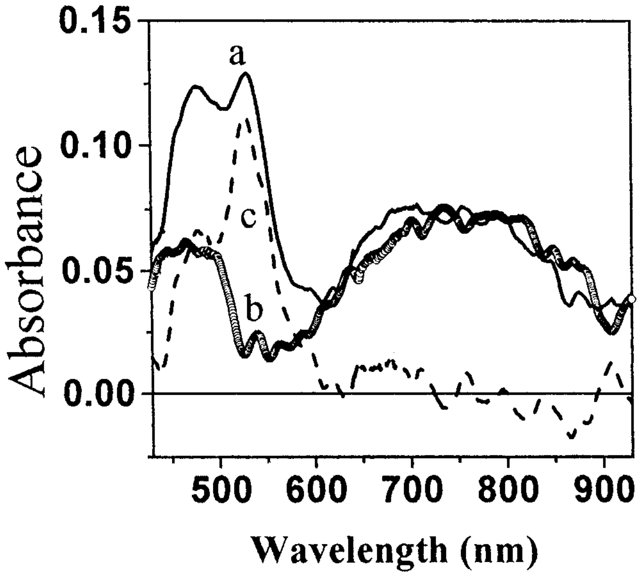

Figure 6. (a) Triplet−triplet absorption spectrum of *p*-ABP in cyclohexane, which is a combination of the spectra due to both the triplets of $n\pi^*$ and $\pi\pi^*$ configurations. (b) Triplet−triplet absorption spectrum of *p*-ABP in ACN, which is due to the $\pi\pi^*$ triplet. (c) Difference spectrum between a and b, which is due to the $n\pi^*$ triplet of *p*-ABP.

a combination of the spectra of the $\pi\pi^*$ triplet and some other transient, which might be the $n\pi^*$ triplet state. An indication of two kinds of triplet states that are energetically close to each other has already been obtained from the biexponential nature of the phosphorescence decay in MCH matrix. Spectrum c has been obtained by subtracting spectrum b from spectrum a, and it is very similar to the absorption spectrum of the $n\pi^*$ triplet of BP in acetonitrile (curve b of Figure 5B). Hence, assuming that the nature of the $n\pi^*$ triplet absorption spectrum does not change by substitution in the phenyl ring, we can conclude that the triplet absorption spectrum a of *p*-ABP in cyclohexane is a combination of the absorption spectra due to the triplets having $n\pi^*$ and $\pi\pi^*$ configurations. The energy levels of these two kinds of triplets are very close to each other, and in this solution, these states remain in thermal equilibrium during their stay in the excited triplet level. In benzene, too, the broad nature of the triplet absorption band in the 420−600 nm wavelength region indicates the presence of energetically proximate $n\pi^*$ and $\pi\pi^*$ states in the triplet manifold.

In the case of polar and hydrogen-bond-forming solvents such as methanol, the situation is entirely different. In both the singlet and triplet manifolds, the CT excited state is expected to be stabilized further in polar and hydrogen-bond-forming solvents by solvation and/or formation of a hydrogen-bonded complex. In methanol, no transient absorption could be observed in the spectral region of 400−900 nm. Probably, the singlet state of *p*-ABP in methanol is very short-lived, shorter than a picosecond, and also the triplet yield is negligibly small. This is due to the protic nature of the solvent, rather than its dielectric polarity, because the triplet yield is observed to be quite high in acetonitrile solvent. The reason could be either very fast quenching of the excited singlet CT state by proton transfer from the solvent or a very fast nonradiative relaxation process via intermolecular hydrogen-bond stretching vibrations.[19,31]

In Table 1, we provide the quantum yield values for triplet formation (ϕ_T) in different solvents, as determined within a few nanoseconds after the laser pulse excitation by 35-ps laser pulses. Also, in the same column, we have included the values reported in the literature for comparison. Although these two sets of ϕ_T values follow qualitatively the same trend, it should be mentioned here that they probably include the same error involved in the method of determination and only provide a rough estimate of the quantity. This is because it has not been possible to determine the extinction coefficient values for triplet absorption quite accurately for several reasons. As mentioned earlier, in nonpolar solvents, he T_1 state of *p*-ABP can be considered a thermal equilibrium mixture of $^3n\pi^*$ and $^3\pi\pi^*$ states; thus, it would be erroneous to report the extinction coefficient values determined by the conventional energy-transfer method and, hence, also the ϕ_T values determined using these values. To determine the ϕ_T values using the comparative method, we assumed the extinction coefficient value for the *p*-ABP triplet to be 6500 dm^3 mol^{-1} cm^{-1}, which was reported in the literature for the $n\pi^*$ triplet of benzophenone.[32] Also, we observed very rapid photochemical degradation of *p*-ABP in nonpolar solvents, probably because of hydrogen abstraction from the NH_2 group of another *p*-ABP molecule in the ground state.[11,14] This was evident from the concentration dependence of the triplet decay rate constants. The triplet lifetimes were seen to decrease with an increase in the concentration of *p*-ABP. Hence, the triplet lifetimes, which are reported in Table 1, are the inverse of the values of the intercepts obtained from the linear least-squares fit of the plots of the lifetimes as a function of concentration of *p*-ABP in the corresponding solvent. In polar solvents the T_1 state is not very reactive because of its $\pi\pi^*$ or CT character,[14] and hence, the lifetimes are not as sensitive to the concentration of *p*-ABP used and are also longer than those in nonpolar solvents.

Earlier, several mechanisms were proposed to explain the reactivity of the lowest-lying triplet state having the $\pi\pi^*$ configuration in an aromatic ketone. According to Wagner and co-workers,[10] in ketones in which the energy gap between the $n\pi^*$ and $\pi\pi^*$ triplet states is only a few kilocalories per mole, the mechanism of the reaction involves thermal excitation of the $\pi\pi^*$ state to the $n\pi^*$ state, from which the reaction occurs. However, Yang et al.[8a] explain the reactivity of the $\pi\pi^*$ state by the vibronic mixing of the $n\pi^*$ and $\pi\pi^*$ triplets in aromatic ketones. A small amount of $n\pi^*$ character mixed into the lowest $\pi\pi^*$ triplet gives the latter $n\pi^*$ reactivity. The theoretical analysis by Chandra[33] suggests that reaction from the triplet $\pi\pi^*$ state is possible through a crossing of the zero-order reaction surfaces of the $n\pi^*$ and $\pi\pi^*$ states of ketone. Our studies on the spectroscopic properties of the triplet state of *p*-ABP, however, probably support the view of Wagner and co-workers and suggest that, in nonpolar solvents, the energy gap between the lowest excited $n\pi^*$ and $\pi\pi^*$ triplet states should be very small, so that either of the two might be the lower in energy but both are still thermally accessible to each other, and hence, the $n\pi^*$ triplet state shows reactivity toward the hydrogen-abstraction reaction. In polar solvents, the $\pi\pi^*$ triplet state is probably more stabilized than the $n\pi^*$ triplet. For example, we have calculated that the triplet energy in ethanol (65.6 kcal mol^{-1}) is lower by about 1 kcal mol^{-1} than the corresponding energy in MCH (66.6 kcal mol^{-1}), a difference that is larger than the thermal energy at the room temperature (~0.6 kcal mol^{-1} at 296 K). This excludes the possibility of the existence of the $n\pi^*$ triplet in thermal equilibrium with the $\pi\pi^*$ triplet in solution, and hence, the triplet state of *p*-ABP in polar solvents is not as reactive toward the hydrogen-atom-abstraction reaction.

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Supporting Information Available: ^{13}C and ^{1}H NMR spectra of *p*-ABP in $CDCl_3$ and CH_3OD. This material is available free of charge via the Internet at http://pubs.acs.org.

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