

Inversion of 4-methoxybenzophenone triplet in aqueous solutions

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The triplet state of 4-methoxybenzophenone (4-MBP) has been investigated by laser flash photolysis and emission techniques in several solvents. In non-polar cyclohexane, 4-MBP triplet has an (n, π^*) configuration with the typical triplet–triplet absorption spectrum of benzophenone (λ_{\max} ca. 525 nm). However, due to the proximity of the two lowest triplet states of different configuration, some unusual features are observed in polar solvents. Thus, 4-MBP shows in aqueous solutions a transient absorption spectrum with λ_{\max} at 450 and 680 nm, which can be attributed to a T_1 (π, π^*) state. Further, transient absorption spectra due to T_1 (n, π^*) and T_2 (π, π^*) being simultaneously populated are observed upon laser excitation of 4-MBP in polar solvents such as acetonitrile or methanol. The triplet state inversion (n, π^* to π, π^*) is also detected by the measurement of triplet quenching rate constants by 1,4-cyclohexadiene (a good hydrogen donor) in acetonitrile and water (k_H ca. 2×10^8 and 5×10^5 M⁻¹ s⁻¹, respectively) and by the determination of room-temperature phosphorescence (the emission quantum yield at room-temperature decreases from 0.004 in acetonitrile to less than 1×10^{-6} in water). Further, the energy of the 4-MBP triplet state is ca. 288 kJ mol⁻¹ both in polar and non-polar organic solvents, while in water it drops to 275 kJ mol⁻¹. The photophysical properties of 4-MBP are compared with those of 4-aminobenzophenone (4-ABP), which also possesses an electron-donating group. In polar organic solvents such as acetonitrile, the transient absorption spectrum and the quenching rate constant of hydrogen abstraction for triplet 4-ABP are practically the same as those obtained for 4-MBP in aqueous solutions. On the other hand, a small T_2 (π, π^*) contribution is observed in the triplet–triplet absorption spectrum of 4-ABP in cyclohexane.

Introduction

Photoreduction of aromatic carbonyl compounds is one of the best studied photochemical reactions.^{1,2} The reactivity towards hydrogen atom abstraction has been associated with the nature of the lowest triplet excited state (n, π^* or π, π^*), which is in turn governed by the nature and position of the substituents in the aromatic rings, and the solvent polarity (polar solvents and electron-donating substituents stabilize π, π^* triplets and sharply decrease their reactivity).³ In this context, acetophenone has a T_1 (n, π^*) in non-polar solvents and a T_1 (π, π^*) in polar solvents; electron-donating substituents produce inversion (from n, π^* to π, π^*) of the electronic configuration of the acetophenone triplet.³ However, in the case of benzophenone (BP), its lowest triplet has n, π^* configuration in both non-polar and polar solvents; only the presence of strong electron-donating groups such as NH₂ or N(CH₃)₂ seems to produce a clear inversion of configuration.^{4–6} In fact, the only two reported cases of benzophenone derivatives with strongly solvent-dependent photoreduction quantum yields are 4-aminobenzophenone (4-ABP) and Michler's ketone [4,4'-bis(dimethylamino)benzophenone]. Thus, a decrease by two orders of magnitude is reported for the photoreduction quantum yield of these molecules in alcoholic solution compared to non-polar solvents.^{7,8} It was speculated on the possibility that T_1 (π, π^*) has charge-transfer character because 4-ABP shows a triplet–triplet absorption spectrum with λ_{\max} ca. 470 and 640 nm.^{5,9} Likewise, the spectrum of Michler's ketone shows maxima at ca. 480 and 680 nm.^{6,10} However, according to other studies the lowest trip-

let of Michler's ketone must be π, π^* in non-polar solvents, as its dipole moment is higher than that of the ground state ketone.¹¹ On the other hand, the results obtained by measuring the efficiency of singlet oxygen generation (S_A) are consistent with acetophenone, Michler's ketone and 4-ABP having lowest lying n, π^* triplet excited states in non-polar solvents, acetonitrile and alcohols (S_A between 0.3 and 0.4). The only exception appears to be Michler's ketone in ethanol (but not in isopropanol), where the lowest triplet is π, π^* and hence S_A is as high as 0.65.¹² In this context, laser flash photolysis studies have shown that the T–T absorption of 4-methoxybenzophenone (4-MBP) in acetonitrile–water mixtures shows two new absorption bands at ca. 450 and 680 nm.^{13,14} This was a marginal observation and therefore it was not studied in detail although the appearance of the new bands was tentatively attributed to a change in the character of the lowest n, π^* triplet by mixing a large amount of π, π^* character.¹³ The nature of the T_1 of these ketones, thus, remains a matter of discussion.

The present work has been undertaken to gain further insight into this problem. For this purpose, steady-state and time-resolved absorption and emission measurements of 4-MBP have been taken in several solvents. In some cases, 4-ABP has been used as a reference compound. Analysis of the triplet–triplet transient absorption spectra, determination of the rate constants of triplet quenching by 1,4-cyclohexadiene, combined with phosphorescence measurements at room temperature and at 77 K in different media, have been used as indicators of the electronic nature of the lowest lying triplet state.

Experimental

Materials

4-Aminobenzophenone (4-ABP), 1,4-cyclohexadiene, 4-methoxybenzophenone (4-MBP), naphthalene (NPT) and naproxen [6-methoxy- α -methyl-naphthalene-2-acetic acid, (NPX)] were purchased from Aldrich (Steinheim, Germany). All solvents were HPLC grade and were used without further purification. Water was purified through a Millipore MilliQ system. Phosphate-buffered solution (PBS) was 0.050 M (pH 7.2).

Nanosecond laser flash photolysis

A pulsed Nd-YAG SL404G-10 Spectrum Laser Systems was used for excitation at 355 and 266 nm. The single pulses were *ca.* 10 ns duration and the energy was \sim 6 mJ per pulse. A Lo255 Oriol xenon lamp was employed as the probe beam source. The laser flash photolysis apparatus consisted of the pulsed laser, the Xe lamp, a 77200 Oriol monochromator, an Oriol photomultiplier (PMT) system made up of 77348 side-on PMT tube, 70680 PMT housing and a 70705 PMT power supply. The oscilloscope was a TDS-640A Tektronix. The output signal from the oscilloscope was transferred to a personal computer.

The concentrations of 4-MBP and 4-ABP employed in the following experiments were in the range 0.3–1 mM. Samples were purged with nitrogen for 15 min prior to photophysical/photochemical studies. The molar absorptivity of triplet 4-MBP was determined in different solvents using the energy transfer method.¹⁵ For this purpose, a 0.1 M solution of naphthalene (NPT) was used when the solvent was cyclohexane (CH), while 5×10^{-3} M naproxen (NPX) was employed in the case of the other solvents. At these concentrations triplet quenching was always >95%. The molar absorptivity (ϵ) of the triplet state was calculated using eqn. (1):¹⁵

$$OD_{NP^*} \times \epsilon_{4-MBP^*} = OD_{4-MBP^*} \times \epsilon_{NP^*} \quad (1)$$

where the OD values refer to the optical density of the 4-MBP triplet state (510 nm) at the beginning of the reaction, and to the optical density of NP* [which stands for NPT* triplet state (412.5 nm) or NPX* triplet state (440 nm)] at the end of the reaction. The molar absorptivity of NPT* in cyclohexane was taken to be $24,500 \text{ M}^{-1} \text{ cm}^{-1}$.¹⁵ To obtain the molar absorptivities of the 4-MBP triplet state in acetonitrile or methanol (at 510 nm), or in different acetonitrile–PBS solutions (at 480 nm) NPX was used as triplet energy acceptor. The molar absorptivity of NPX* at 440 nm was taken to be $9500 \text{ M}^{-1} \text{ cm}^{-1}$, which is the value described in the literature for acetonitrile (ACN) solutions.¹⁶ In PBS aqueous solutions it was possible to determine a very similar ϵ for NPX* ($9500 \pm 250 \text{ M}^{-1} \text{ cm}^{-1}$ at 440 nm) by using BP as triplet energy donor (with an ϵ of $5800 \text{ M}^{-1} \text{ cm}^{-1}$ at 520 nm).¹⁵

The molar absorptivities of the 4-ABP triplet excited state were determined in the same way.

The 4-MBP intersystem-crossing quantum yield (Φ_{isc}) was calculated in different organic solutions by the comparative method, using benzophenone at the same absorbance (0.1). Thus, Φ_{isc} was obtained by application of eqn. (2):¹⁵

$$\Phi_{isc}(4-MBP) = \frac{\Phi_{isc}(BP) \times OD(4-MBP^*) \times \epsilon(BP^*)}{OD(BP^*) \times \epsilon(4-MBP^*)} \quad (2)$$

where the OD values refer to the absorbance of the 4-MBP triplet state at 510 nm and BP triplet state at 520 nm. The BP molar absorptivity and Φ_{isc} in acetonitrile were taken to be $6500 \text{ M}^{-1} \text{ cm}^{-1}$ and 1, respectively.¹⁵ For acetonitrile–PBS solutions the optical density of the 4-MBP triplet state was measured at 480 nm. A similar procedure was employed to estimate the intersystem crossing quantum yield of 4-ABP.

The studies on energy transfer between BP and 4-MBP in acetonitrile and acetonitrile–PBS mixtures (1 : 3 and 3 : 1 v/v) were performed by laser flash photolysis employing a 355 nm laser as the source of excitation, a BP solution with absorbance of 0.3 at the excitation wavelength, and a 4-MBP concentration of $0.3 \times 10^{-3} \text{ M}$.

The rate constants for quenching of 4-MBP triplets by 1,4-cyclohexadiene at concentrations of $1\text{--}10 \times 10^{-3} \text{ M}$ were determined in different acetonitrile–water mixtures using the kinetic traces at 700 nm. The same procedure was employed to determine the quenching rate constants for 4-ABP triplets in cyclohexane and acetonitrile. The values were obtained, upon kinetic corrections, as an average of four independent measurements.

Steady state measurements

Absorption spectra were recorded using a Varian CARY 1E spectrophotometer. Phosphorescence spectroscopy was carried out using a Perkin Elmer LS-50 luminescence spectrometer. The samples were excited at 300 nm and emission was measured in the region 350–600 nm. The phosphorescence quantum yields (Φ_{ph}) were determined at room temperature, under anaerobic conditions, using integrated peak areas and BP as standard for comparison ($\Phi_{ph} = 0.01$ in acetonitrile at room temperature).¹⁷ In the case of 4-MBP, phosphorescence spectra were also obtained in different glasses at 77 K. Samples with absorption values of *ca.* 0.8 in $1 \times 1 \text{ cm}$ cells were poured into a 5 mm NMR tube, which was subsequently inserted in a home-made quartz dewar containing liquid nitrogen. A delay of 1 ms and a gate time of 1 ms were employed in acquiring the spectra in methylcyclohexane and 4 : 1 methanol–ethanol. In water the delay employed was 30 ms, and the gate time was 50 ms.

Time-resolved phosphorescence

A Perkin Elmer LS-50 luminescence spectrometer was employed to record phosphorescence decay traces. The decays were monitored in all cases at 450 nm.

Results

Absorption and emission spectra

The absorption spectrum of 4-MBP is clearly solvent-dependent; while in cyclohexane the longest wavelength maximum appears at λ_{max} 279 nm, in more polar solvents a bathochromic shift is observed (Table 1).

The phosphorescence spectrum of 4-MBP was obtained in different solvents, at room temperature, and also at 77 K. From the 4-MBP phosphorescence at 77 K (Fig. 1A), a triplet energy level of 287 kJ mol^{-1} is estimated in methylcyclohexane and in 4 : 1 v/v methanol–ethanol, while in pure water the energy value is markedly lower (275 kJ mol^{-1}). This is accompanied by the disappearance of the typical “five-fingered” pattern of n,π^* benzophenone chromophores. Phosphorescence decay rate constants also vary with solvent composition. A value of 169 s^{-1} was registered in methylcyclohexane, similar to that measured in 4 : 1 methanol–ethanol (87 s^{-1}). In water the decay is biexponential, with rate constant values of 95 s^{-1} (and a weight of 79%), and 10 s^{-1} (and a weight of 21%) (see also Fig. 1B).

At 298 K, 4-MBP phosphorescence occurs from the lowest n,π^* triplet state in different acetonitrile–water mixtures (see Fig. 2). At this temperature, the phosphorescence quantum yield (Φ_{ph}) decreases with increasing amounts of water, becoming practically zero in pure water (see Fig. 2 and Table 1 for more details).

Nanosecond laser flash photolysis

In order to detect the T–T absorption of 4-MBP, laser flash photolysis experiments with solutions of 4-MBP in cyclo-

Table 1 Photophysical and photochemical properties of 4-MBP in different solvents

Solvent	$\lambda_{\max}^a/\text{nm}$	Φ_{isc}	Φ_{Ph} (25 °C)	$k_{\text{H}}^b/\text{M}^{-1} \text{s}^{-1}$
Cyclohexane	279	0.95	N.d. ^c	2.5×10^8
ACN	285	0.86	3.3×10^{-3}	2.0×10^8
3 : 1 v/v ACN-H ₂ O	290	N.d. ^c	2.3×10^{-3}	1.9×10^8
1 : 1 v/v ACN-H ₂ O	291	N.d. ^c	1.5×10^{-3}	1.4×10^8
1 : 3 v/v ACN-H ₂ O	294	0.56	0.3×10^{-3}	0.3×10^8
1 : 9 v/v ACN-H ₂ O	295	N.d. ^c	$< 0.01 \times 10^{-3}$	0.005×10^8

^a Absorption maximum of the longest wavelength π, π^* transition. ^b Quenching rate constant of 4-MBP triplet by 1,4-cyclohexadiene. ^c N.d. = not determined.

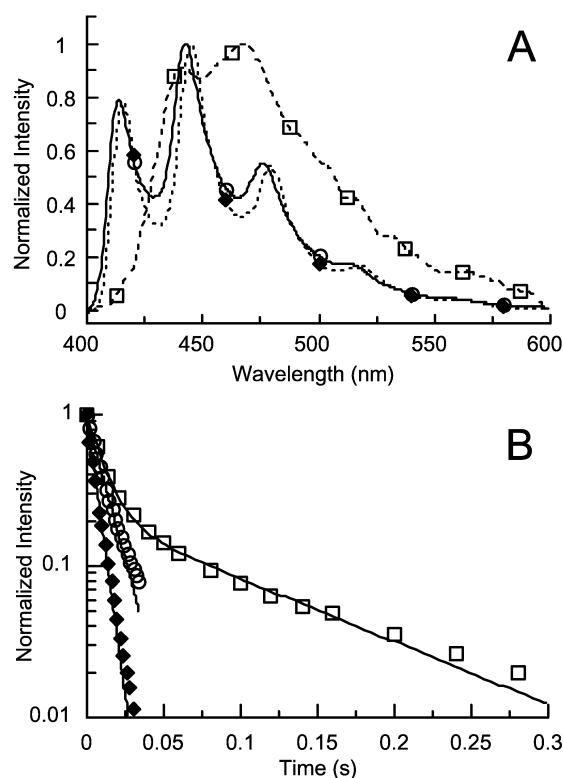


Fig. 1 (A) Phosphorescence emission and (B) phosphorescence decay traces of 4-MBP at 77 K in: (□) water, saturated solution, λ_{exc} 305 nm. (○) 4 : 1 v/v methanol-ethanol, λ_{exc} 303 nm. (◆) methylcyclohexane, λ_{exc} 294 nm.

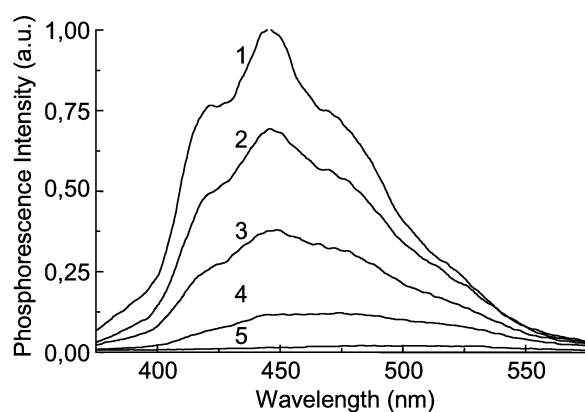


Fig. 2 Phosphorescence emission of 4-MBP at 298 K in different acetonitrile-water mixtures: (1) 1 : 0 (v/v), (2) 3 : 1 (v/v), (3) 1 : 1 (v/v), (4) 1 : 3 (v/v), (5) 1 : 9 (v/v). The spectra were obtained following excitation at 295 nm.

hexane, methanol, and different acetonitrile-water mixtures were carried out employing a 355 nm laser as the excitation source (Fig. 3).

In cyclohexane, the transient absorbing at λ_{\max} 540 nm, with a lifetime (τ_{T}) of *ca.* 0.3 μs , was assigned to 4-MBP triplet state.

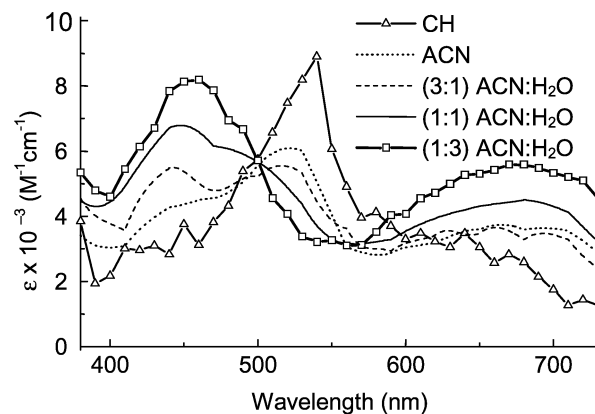


Fig. 3 Triplet-triplet transient absorption spectra of 4-MBP in cyclohexane (CH), acetonitrile (ACN) and different mixtures of acetonitrile-water (ACN-H₂O). The excitation wavelength employed was 355 nm, and all the spectra were obtained *ca.* 30 ns after the laser pulse.

The τ_{T} and absorption spectrum of this species are typical of benzophenone triplets.³ This transient is efficiently quenched by oxygen and NPT (quenching rate constants of *ca.* $2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). The spectrum obtained in acetonitrile is similar to that observed in cyclohexane (Fig. 3).

Upon addition of increasing amounts of water to acetonitrile, two new absorption bands appear in the red (680 nm) and in the violet-blue (450 nm) regions. The same transient absorption spectrum is obtained in different acetonitrile-PBS mixtures (data not shown). This transient is efficiently quenched by oxygen and NPX (a water-soluble naphthalene derivative). Thus, it can also be assigned as a 4-MBP triplet excited state.

The intersystem-crossing quantum yield measurements of 4-MBP, in the different solvents studied, reveal that higher amounts of water in the solvent mixture result in a decrease in the Φ_{isc} of this molecule (Table 1).

The transient absorption spectrum in pure water is very similar to that obtained in 1 : 3 v/v acetonitrile-water mixtures. However, when 266 nm is used as the excitation wavelength the solvated electron is clearly observed under anaerobic conditions (λ_{\max} *ca.* 720 nm¹⁸). Oxygen and N₂O efficiently quenched this species.

Laser flash photolysis experiments with $3 \times 10^{-3} \text{ M}$ solutions of BP in acetonitrile and acetonitrile-water mixtures (3 : 1 and 1 : 3 v/v) in the presence of $3 \times 10^{-4} \text{ M}$ 4-MBP were carried out in order to detect the transient absorption of 4-MBP triplet excited state generated following energy transfer from BP. The results show that this process occurs only in 1 : 3 v/v acetonitrile-water as solvent. Thus, as shown in Fig. 4, the decay of BP is concomitant with the generation of 4-MBP triplet (a rate constant larger than $10^9 \text{ M}^{-1} \text{ s}^{-1}$ was estimated for the quenching of BP triplet state by 4-MBP).

The analogous compound 4-ABP was also excited with a laser pulse at 355 nm, in a similar way to that employed with 4-MBP, in order to calculate its ϵ and Φ_{isc} in deaerated cyclohexane and acetonitrile solutions. The molar absorptivity

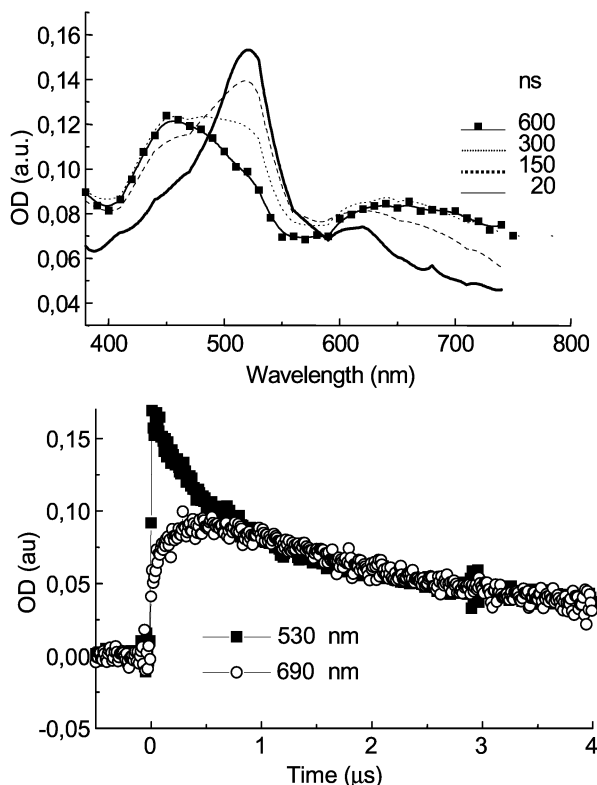


Fig. 4 Top: transient absorption spectrum of 3×10^{-3} M BP in the presence of 0.3×10^{-3} M 4-MBP, observed at different times after the laser pulse (355 nm) under anaerobic conditions and in 1 : 3 v/v acetonitrile–water as solvent. Bottom: kinetic traces obtained for BP triplet (λ_{\max} 530 nm) and 4-MBP triplet (λ_{\max} 690 nm).

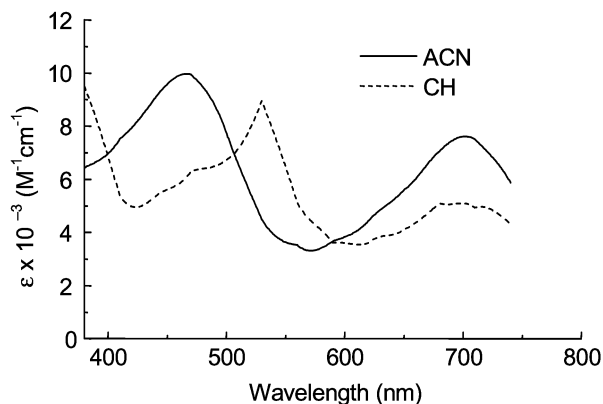


Fig. 5 Transient absorption spectrum of triplet excited state of 4-ABP in cyclohexane (CH) and acetonitrile (ACN). The excitation wavelength was 355 nm, and the spectra were obtained *ca.* 30 ns after the laser pulse.

of 4-ABP at 480 nm was found to be 6600 ± 300 M⁻¹ cm⁻¹ in cyclohexane and 9500 ± 400 M⁻¹ cm⁻¹ in acetonitrile (Fig. 5). The transient absorption spectrum of 4-ABP in cyclohexane is typical of benzophenone triplet while in acetonitrile it resembles that obtained for 4-MBP in 1 : 3 v/v acetonitrile–water. On the other hand, the Φ_{isc} of 4-ABP was found to be 0.95 in cyclohexane and *ca.* 0.1 in acetonitrile, which are similar values to those described in the literature.¹²

The quenching rate constants of 4-MBP and 4-ABP triplets by 1,4-cyclohexadiene were measured in different solvents (Table 1 shows the values obtained for 4-MBP). The values in cyclohexane are similar to that described for benzophenone in the same solvent (*i.e.*, 2.5×10^8 M⁻¹ s⁻¹). In the case of 4-ABP it is observed that the reactivity decreases sharply in acetonitrile solutions (k_{H} *ca.* 10^5 M⁻¹ s⁻¹); however, with 4-MBP there was no such decrease in acetonitrile, and substantial amounts of

water are needed to reduce the reactivity of the triplet to the level of 4-ABP in acetonitrile (thus in 1 : 9 v/v acetonitrile–water the k_{H} for 4-MBP triplet is *ca.* 5×10^5 M⁻¹ s⁻¹).

Discussion

The triplet state of 4-methoxybenzophenone (4-MBP) was investigated by laser flash photolysis and emission techniques in several solvents. These experiments show the influence of polar solvents on the photophysical and photochemical properties of 4-MBP, which are mainly associated with the electronic configuration of its lowest triplet excited state. Thus, in the non-polar cyclohexane, 4-MBP triplet has the typical properties of the parent benzophenone; a T₁ (n,π*) configuration, an absorption spectrum with λ_{\max} at 525 nm, a high quenching rate constant by 1,4-cyclohexadiene (2.5×10^8 M⁻¹ s⁻¹), a triplet energy level of 287 kJ mol⁻¹, a five-band phosphorescence spectrum, and a short phosphorescence lifetime. By contrast, in aqueous solutions or 1 : 9 v/v acetonitrile–water the transient absorption spectrum of 4-MBP triplet exhibits λ_{\max} at *ca.* 450 and 700 nm, much lower reactivity towards hydrogen abstraction (k_{H} by 1,4-cyclohexadiene of 5×10^5 M⁻¹ s⁻¹), a triplet energy level of 275 kJ mol⁻¹, and a phosphorescence decay rate constant with a component *ca.* 17 fold smaller than that in methylcyclohexane. These results support a T₁ (π,π*) configuration for 4-MBP in aqueous solutions. Further, the emission spectrum in water at 77 K does not have the characteristic “five-fingered” pattern of vibrational structure characteristic of benzophenone.

Interestingly, the related compound 4-ABP has a π,π* triplet excited state in acetonitrile,⁵ which shows a transient absorption spectrum similar to that found for 4-MBP in water (Figs. 3 and 5).

The reaction of triplet 4-MBP with 1,4-cyclohexadiene in cyclohexane or acetonitrile is *ca.* 500 times faster than in 1 : 9 v/v acetonitrile–water, in agreement with the previous observation that T₁ (n,π*) to T₁ (π,π*) inversion of aryl ketones produces a decrease by three orders of magnitude of their rates of quenching by potential hydrogen donors.^{19,20} The triplet energy decrease observed for 4-MBP in water could be due to the known stabilization of π,π* states relative to n,π* states in polar solvents.²⁰

In this context, the fact that two triplet levels of aryl ketones are strongly mixed when the energy difference is lower than 8 kJ mol⁻¹,^{20,21} is in agreement with the triplet energy levels of 4-MBP shown in Fig. 6. Thus, vibronic mixing of the n,π* and

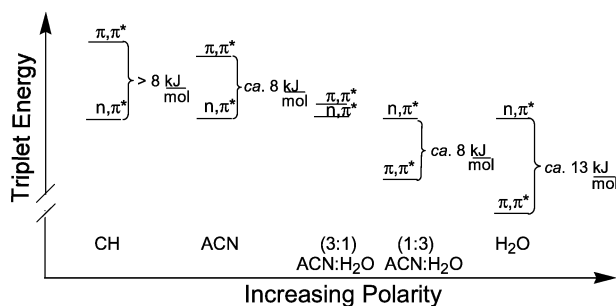


Fig. 6 Energetic diagram for the lowest triplet states of 4-MBP in solvents of different polarity.

π,π* triplets of 4-MBP is already significant in acetonitrile, where a small contribution is observed of T₂ (π,π*) to the T–T absorption spectrum of 4-MBP, and increases until the solvent mixture is formed by 1 : 3 v/v acetonitrile–water, where k_{H} is dramatically reduced. In cyclohexane, the lowest triplet state of 4-MBP has a pronounced n,π* character and its energy level must be at least 8 kJ mol⁻¹ lower than that of T₂ (π,π*). On the other hand, in water or 1 : 9 v/v acetonitrile–water T₂ (n,π*) is *ca.* 13 kJ mol⁻¹ higher than T₁ (π,π*) (data obtained from the low temperature phosphorescence spectrum). Accordingly, the

phosphorescence quantum yield of 4-MBP at room-temperature in acetonitrile–water mixtures with a high content of water are very low. It appears that the phosphorescence emission of 4-MBP is associated with the n,π^* triplet state character, in accordance with previous observations on related aryl ketones.^{17,22}

The decrease of the 4-MBP intersystem crossing quantum yield with increasing solvent polarity can be due to charge transfer deactivation of the singlet excited state (Table 1). Similar observations have been reported for other benzophenone derivatives such as 4-ABP or *p*-hydroxybenzophenone.^{4,5}

Conclusions

In the present work it has been established that the nature of the lowest triplet excited state of 4-MBP is clearly π,π^* in water; this is contrary to the previous assumption that triplet 4-MBP has always an n,π^* character.^{20,11,23,24} Moreover, 4-MBP is one of the few examples of solvent-dependent inversion of configuration in benzophenone derivatives.

Upon vibronic triplet mixing ($\pi,\pi^*/n,\pi^*$), only the properties of the most reactive level predominate, as has been observed for the 4-MBP triplet reaction with 1,4-cyclohexadiene. Further, this fact would explain the unexpected values of the dipole moment described for Michler's ketone or 4-ABP in non-polar solvents,¹¹ as well as the low singlet oxygen efficiency reported for acetophenone, Michler's ketone and 4-ABP in polar acetonitrile and hydrogen-bonding alcohols.¹²

Finally, it seems clear that the triplet–triplet absorption spectra of these benzophenone derivatives, which show two absorption maxima at *ca.* 450 and 690 nm, are of the T_1 (π,π^*) type.

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