Optical and Electron Paramagnetic Resonance Studies of the Excited States of 4-*tert*-Butyl-4′-Methoxydibenzoylmethane and 4-*tert*-Butyl-4′-Methoxydibenzoylpropane

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The excited states of 4-*tert*-butyl-4′-methoxydibenzoylmethane (BM-DBM) and 4-*tert*-butyl-4′-methoxydibenzoylpropane (BM-DBP), the model of the keto form of BM-DBM, have been studied through measurements of UV absorption, fluorescence, phosphorescence, and electron paramagnetic resonance spectra in ethanol at 77 K. The energy levels and lifetimes of the lowest excited triplet (T_1) states of BM-DBP, dibenzoylpropane (DBP), the model of the keto form of dibenzoylmethane (DBM), and the keto and enol forms of BM-DBM and DBM were determined. The energy level of the T_1 state of the keto form is much higher than that of the enol form in BM-DBM. The effect of tautomerization on the T_1 lifetime is small in DBM but large in BM-DBM. The methoxy and *tert*-butyl groups play an important role in lengthening the T_1 lifetimes of BM-DBP and the keto form of BM-DBM. The nature of the T_1 states of the keto and enol forms of BM-DBM can be explained in terms of the mixing of the $^3n\pi^*$ and $^3\pi\pi^*$ states. The observed energy levels and the lifetimes of the T_1 states of the UV absorbers provide a useful suggestion for designing more photostable UV absorbers.

1. Introduction

The photochemistry of dibenzoylmethane (DBM) derivatives has been a subject of numerous investigations because these compounds are the most widely used ultraviolet-A (UV-A) blocking filters in cosmetic sunscreens.[1−21] The most widely used derivative of DBM in sunscreens is 4-*tert*-butyl-4′-methoxydibenzoylmethane (BM-DBM, trade names Avobenzone, Escalol 517, Eusolex 9020, Parsol 1789, etc.). BM-DBM has large molar absorption coefficients in the UV-A region (320−400 nm). In solutions, BM-DBM exists in two tautomeric forms: the enol form and the keto form, as shown in Figure 1. BM-DBM exists mainly in the chelated enol form in solution because of stabilization by an intramolecular hydrogen bond.[8,11,18]

A number of studies have been devoted to photostabilization of BM-DBM because it is well-known for its photoinstability. Quite recently, it has been shown that the excited triplet state of the keto form is responsible for photodegradation of BM-DBM.[1] In practice, UV absorbers are used in combination with other UV absorbers and many additives. It is especially important to determine the energy level of the lowest excited triplet (T_1) state of individual UV absorber because triplet−triplet energy transfer from a donor to an acceptor will occur between the UV absorbers. We have determined the energy levels of the T_1 states of UV absorbers by measuring the phosphorescence spectra in rigid solutions at 77 K and elucidated the nature of the T_1 states of the UV absorbers.[22−24]

The energy level of the T_1 state of the enol form of BM-DBM has been estimated through measurements of the phosphorescence spectra in rigid solutions at low temperatures.[20,21] However, to the best of our knowledge, the phosphorescence spectrum of the keto form of BM-DBM has not been reported. The nature of the T_1 state of BM-DBM is poorly known because the photochemistry of BM-DBM is complex and ambiguous.

In the present study, we synthesized 4-*tert*-butyl-4′-methoxydibenzoylpropane (BM-DBP, Figure 1), the model of the keto form of BM-DBM, for the first time. We observed the UV absorption, fluorescence, phosphorescence, and electron paramagnetic resonance (EPR) spectra of BM-DBM, BM-DBP, DBM, and dibenzoylpropane (DBP, Figure 1), the model of the keto form of DBM, in ethanol (EtOH) at 77 K. The nature of the excited states of BM-DBM is discussed.

2. Experimental Section

Materials. DBM (Wako Special grade), BM-DBM (Wako first grade), and EtOH (Wako Super Special grade) were used without further purification. DBP and BM-DBP were obtained from DBM and BM-DBM, respectively, by the modified method reported by Paris et al.[1] All reactions were performed under an argon atmosphere unless otherwise specified. No study has been reported on BM-DBP to our knowledge. BM-DBP was prepared following Scheme 1.

(i) At room temperature, to a stirred solution of *tert*-butanol (40 mL) was added potassium *tert*-butoxide (3.6 g, 32.1 mmol). After being stirred for 1 h, to the reaction mixture was added BM-DBM (5 g, 16.1 mmol) in a period of 10 min. After being stirred for 2 h, to the reaction mixture was added methyl iodide (2.0 mL, 32.1 mmol) in a period of 10 min. The reaction mixture was stirred for an additional 2 days at room temperature. To the stirred reaction mixture was added 1 N hydrochloric acid (20 mL), and the organic layer was separated. The aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and filtered, and the solvent was removed to give 4-*tert*-butyl-4′-methoxydibenzoylethane (BM-DBE) in 75% yield (3.9 g) as a pale-yellow oil.

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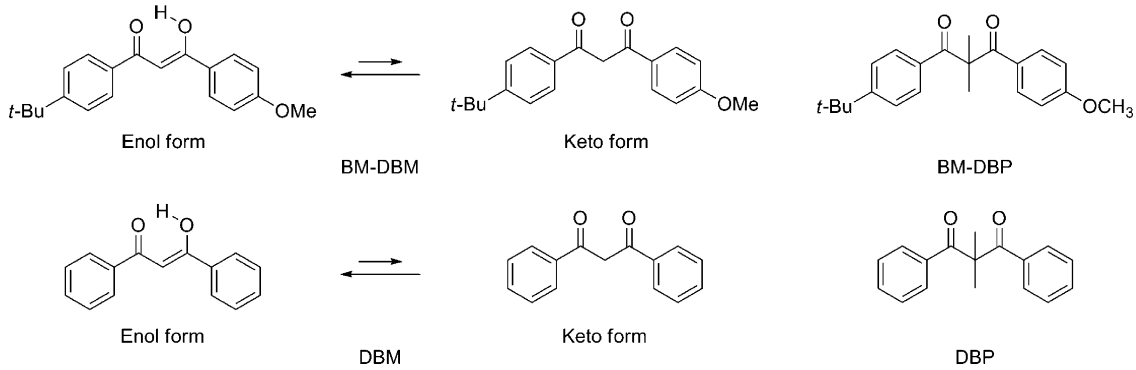
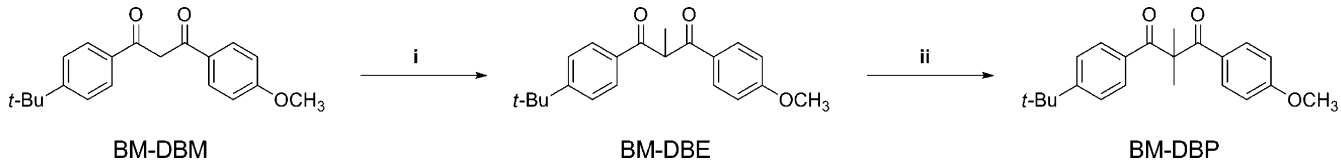


Figure 1. Molecular structures of BM-DBM, DBM, BM-DBP, and DBP.

SCHEME 1: Synthetic Procedure of BM-DBP[a]



[a] (i) K-*t*BuO, CH_3I, BM-DBM, *t*-BuOH, rt, 2 days (75%); (ii) NaH, BM-DBE, CH_3I, THF, rt, 2 days (14%).

(ii) At room temperature, to a solution of THF (200 mL) was added sodium hydride (0.95 g, 60% in oil). After being stirred for 1 h at room temperature, to the reaction mixture was added BM-DBE (3.9 g, 12 mmol) in a period of 10 min, and the reaction mixture was stirred for an additional 1 h. Then, to the reaction mixture was added methyl iodide (3.7 mL, 59.4 mmol) in a period of 10 min. After the addition, the reaction mixture was stirred for an additional 2 days at room temperature. To the stirred reaction mixture was added 1 N hydrochloric acid (50 mL), and the organic layer was separated. The aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and filtered, and the solvent was removed to give 4-*tert*-butyl-4′-methoxydibenzoylpropane (BM-DBP) as a yellow oil. The obtained yellow oil was purified on column chromatography (silica gel) using hexane/ethyl acetate (10:1, v/v) as eluent. After being dried in vacuo (20 mmHg), BM-DBP was obtained in 14% yield (0.57 g) as a colorless solid. Recrystallization from hexane gave BM-DBP as colorless plate crystal. ^{1}H NMR ($CDCl_3$, 270 MHz, δ): 7.86 (2H, d, $J = 5.4$ Hz), 7.77 (2H, d, $J = 5.4$ Hz), 7.30 (2H, d, $J = 8.1$ Hz), 6.80 (2H, d, $J = 8.1$ Hz), 3.78 (3H, s), 1.62 (6H, s), 1.25 (9H, s). FAB MS (*m*/*z*) Calcd for $C_{22}H_{26}O_3$, [M+1$^+$] 339.19; Found, 339. FT-IR (KBr) ν/cm^{-1}: 2969, 1657, 1599, 1569, 1509, 1457, 1417, 1382, 1364, 1319, 1267, 1248, 1175, 1163, 1138, 1108, 1030, 988, 955, 946, 880, 847, 778, 758, 720, 641, 621, 586, 553, 520. Anal. Calcd for $C_{22}H_{26}O_3$: C, 78.07; H, 7.74; O, 14.18. Found: C, 78.04; H, 7.801; O, 14.13.

Measurements. The sample solutions were prepared at a concentration of 3×10^{-5} or 3×10^{-3} mol dm^{-3} for the luminescence measurements or 3×10^{-3} mol dm^{-3} for the UV absorption and EPR measurements.

The UV absorption spectra were measured at 77 K with a Hitachi U-3210 spectrometer. To prevent the sample from cracking, the samples were prepared as follows: the sample solution was dropped on a quartz plate, and it was covered with another quartz plate. The sandwiched sample was rapidly immersed in liquid nitrogen. The optical path length was ~0.05 mm.

The fluorescence spectra were measured with a JASCO FP-6500 spectrofluorometer. For the phosphorescence and EPR measurements, a Keyence UV-400 UV-LED radiator (365 nm) equipped with a UV-50H radiation head and an Ushio USH-500D 500 W Hg lamp equipped with an Asahi Technoglass UV-D33S glass filter (transmits the wavelengths 250−400 nm), 5 cm of distilled water, and a Copal DC-494 electromechanical shutter were used as an exciting light source. For the phosphorescence measurements, the emissions from a sample were passed through a Jobin Yvon H-20UV spectrometer and detected by a Hamamatsu Photonics R453 photomultiplier tube. The phosphorescence−excitation spectra were measured with the JASCO FP-6500 spectrofluorometer.

The experimental setup for the EPR experiments is the same as that previously reported.[25,26] The EPR spectra were measured with a JEOL JES-FA200 spectrometer and a JEOL JES-FE1XG spectrometer with 100 kHz magnetic field modulation at microwave frequency close to 9.2 GHz. The external magnetic field was calibrated with an Echo Electronics EFM-2000AX proton NMR gauss meter. All measurements were carried out at 77 K.

3. Results and Discussion

Optical Properties. The UV absorption spectra of BM-DBM, DBM, BM-DBP, and DBP were measured at 77 K in EtOH. Figure 2 shows the UV absorption spectra of BM-DBM and BM-DBP. The observed UV absorption spectrum of BM-DBM shows strong absorption bands in the UV-A region (Figure 2a) and is similar to that of DBM in a 1:3 mixture of methanol (MeOH)−EtOH at 113 K.[19] The observed spectrum of BM-DBM (Figure 2a) is attributed to the enol form because BM-DBM exists mainly as the enol form in MeOH, dimethyl sulfoxide, cyclohexane, and ethyl acetate.[3] Tobita et al. reported that DBM exists mainly in the enol form in both polar and nonpolar solvents.[14] BM-DBP absorbs strongly at wavelengths shorter than 310 nm, as shown in Figure 2b. The UV absorption spectrum of the keto form of BM-DBM is considered to be blue-shifted compared with the enol form. The UV absorption spectrum of BM-DBP is similar to those of BM-DBE and 4-*tert*-butyl-4′-methoxydibenzoylundecane.[1,8]

Figure 3a shows the fluorescence and fluorescence−excitation spectra of BM-DBM in EtOH at 77 K. BM-DBM is fluorescent in EtOH at 77 K, and the fluorescence−excitation spectrum is

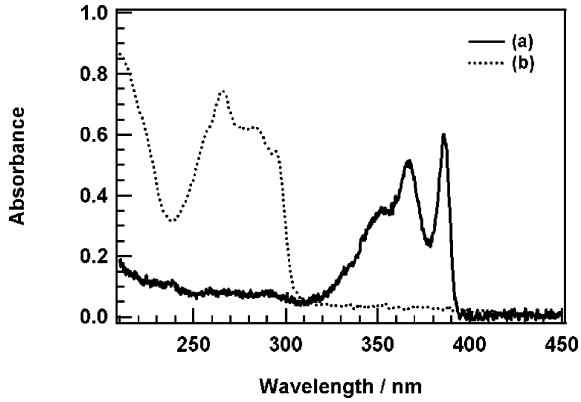


Figure 2. UV absorption spectra of (a) BM-DBM and (b) BM-DBP in EtOH at 77 K.

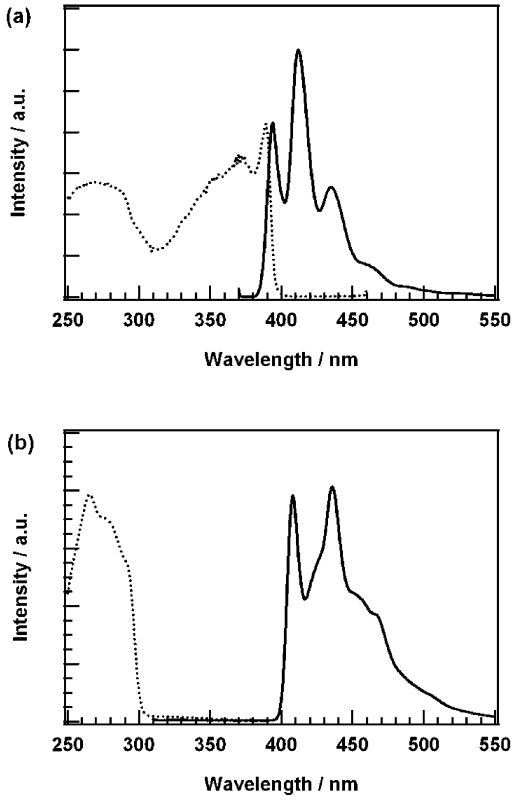


Figure 3. Emission (solid line) and emission−excitation (dotted line) spectra of (a) BM-DBM and (b) BM-DBP in EtOH at 77 K. Samples were excited (a) at 365 nm and (b) at 300 nm. Emissions were monitored (a) at 465 nm and (b) at 408 nm.

similar to the UV absorption spectrum shown in Figure 2a. Figure 3b shows the emission and emission−excitation spectra of BM-DBP. We used a phosphoroscope to separate the phosphorescence spectrum from the total emission spectrum. The sampling times were set at 2−7 ms after shutting off the exciting light. The phosphorescence spectrum thus obtained is shown in Figure 4c. The emission spectrum shown in Figure 3b is similar to the phosphorescence spectrum. Therefore, the emission−excitation spectrum of BM-DBP shown in Figure 3b can be regarded as a phosphorescence−excitation spectrum. These facts indicate that BM-DBP is phosphorescent but very weakly fluorescent in EtOH at 77 K. The observed luminescence properties of BM-DBP are similar to those of a typical aromatic ketone, benzophenone.

We can reasonably assume that the keto form of BM-DBM is very weakly fluorescent and the fluorescence spectrum shown

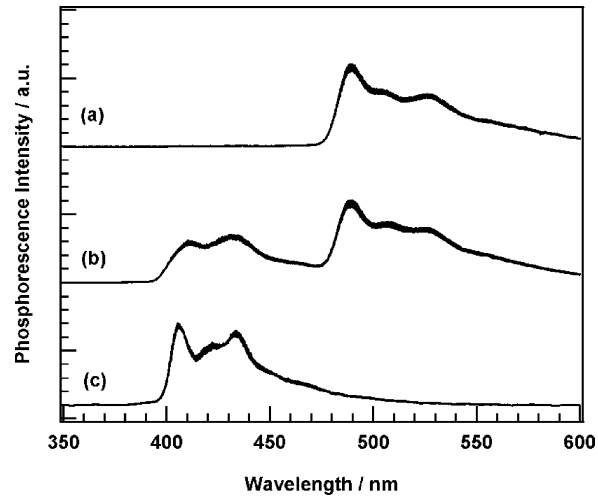


Figure 4. Phosphorescence spectra of BM-DBM (a) with the UV-LED excitation and (b) with the Hg-lamp excitation and (c) of BM-DBP with the Hg-lamp excitation in EtOH at 77 K.

in Figure 3a is attributed to the enol form of BM-DBM. The energy level of the lowest excited singlet (S_1) state of the enol form of BM-DBM was estimated to be 25 600 cm^{-1} from the intersection point of the UV absorption and fluorescence spectra.[27]

The phosphorescence spectra of BM-DBM, DBM, BM-DBP, and DBP were measured at 77 K in EtOH, as shown in Figure 4. The phosphorescence spectra of BM-DBM were measured using the UV-LED radiator and Hg lamp as an exciting light source. The results are shown in Figures 4a,b. The phosphorescence spectra of BM-DBP and DBP show the vibronic bands due to the C═O stretching vibration (∼1600 cm^{-1}).

As is clearly seen in Figure 4b, there are at least two phosphorescent species for BM-DBM in EtOH at 77 K. The first spectrum (first peak at 410 nm) disappears under the UV-LED excitation (365 nm). As shown in Figure 2b, BM-DBP does not have a strong absorption band at wavelengths longer than 310 nm. Therefore, the first spectrum is ascribed to the keto form of BM-DBM. This assignment is confirmed by the fact that the first phosphorescence is similar to the phosphorescence of BM-DBP although the former spectrum shows somewhat blurred vibronic bands. The second spectrum (first peak at 490 nm) is ascribed to the enol form of BM-DBM. This assignment is confirmed by the fact that the phosphorescence spectrum of BM-DBM under the UV-LED excitation (365 nm) is mainly composed of the second spectrum. The phosphorescence spectrum of the enol form of BM-DBM observed in EtOH at 77 K is similar to that of BM-DBM observed in 2-methylpentane.[20]

To examine the above-mentioned assignment of the dual phosphorescence more precisely, we observed the phosphorescence−excitation spectra of BM-DBM. As is clearly seen in Figure 5a, the phosphorescence−excitation spectrum monitored at 410 nm is similar to that of BM-DBP monitored at 408 nm (Figure 3b). On the other hand, the phosphorescence−excitation spectrum monitored at 490 nm is similar to the UV absorption and fluorescence−excitation spectra of the enol form of BM-DBM (Figures 2a and 3a), as shown in Figure 5b. These results show that the first and second phosphorescence spectra of BM-DBM observed with the Hg lamp excitation are reasonably assigned to the keto and enol forms of BM-DBM, respectively.

In the case of DBM, the phosphorescence spectrum is also composed of two spectra, as was reported by Gacoin.[19] The

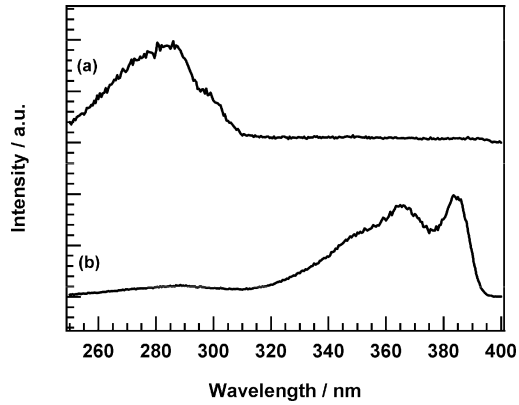


Figure 5. Phosphorescence−excitation spectra of the (a) keto and (b) enol forms of BM-DBM in EtOH at 77 K. Emission was monitored (a) at 410 and (b) at 490 nm.

TABLE 1: S_1 and T_1 Energies (E_{S1} and E_{T1}) and T_1 Lifetimes (τ) Observed in EtOH at 77 K

molecule	form	E_{S1}/cm^{-1a}	E_{T1}/cm^{-1b}	τ_{Phos}/ms^c	τ_{EPR}/ms^d
BM-DBM	enol	25 600	20 400	30	32
BM-DBM	keto		24 400	190	
BM-DBP	keto	27 000	24 500	160	
DBM	enol	26 300	20 500	20	17
DBM	keto		25 600	30	
DBP	keto	27 500	25 400	15	

[a] Obtained from the intersection point of the UV absorption and fluorescence spectra. [b] Obtained from the first peak of phosphorescence. [c] Obtained from the decay of the first peak of phosphorescence. [d] Obtained from the decay of the EPR B_{min} signal.

second spectrum is very similar to thallium and lanthanum chelate spectra.[19] In the same manner as for BM-DBM, the observed dual phosphorescence is attributed to the keto and enol forms of DBM.

The energy levels of the T_1 states of BM-DBM, DBM, BM-DBP, and DBP estimated from the first peaks of phosphorescence are listed in Table 1. The observed wavelength of the first peak of phosphorescence of DBP is the same as that observed in 2-methyltetrahydrofuran.[13] The lifetimes of the T_1 states of BM-DBM, DBM, BM-DBP, and DBP determined from the decay curves of the first peaks of phosphorescence are also listed in Table 1. As is clearly seen in Table 1, the T_1 lifetime of the keto form of BM-DBM is close to that of BM-DBP and longer than those of the other molecules studied. This fact also confirms the assignment of the first phosphorescence spectrum of BM-DBM mentioned above.

Andrae et al. reported that the steady-state UV irradiation of BM-DBM leads to the formation of the keto form.[12] Laser flash photolysis study of BM-DBM has reported the detection of the triplet state of the keto form.[10] However, the photochemistry of BM-DBM is complex. The photostability of BM-DBM is sensitive to the properties of the solvent environment. BM-DBM is relatively photostable in polar protic solvents and markedly photodegraded in nonpolar solvents.[1,12,15,16] However, it is important to note here that we carried out the phosphorescence measurements with great care because the stable photoproducts other than the keto form of BM-DBM might affect the phosphorescence measurements of BM-DBM in EtOH at 77 K. We observed the phosphorescence decay curves of BM-DBM by many scans. The results of less than about 10 scans were exponential over at least three lifetimes under our experimental conditions. The results of more than 10 scans slightly deviate from a single exponential decay. The T_1 lifetimes listed in Table 1 are the results of less than 10 scans.

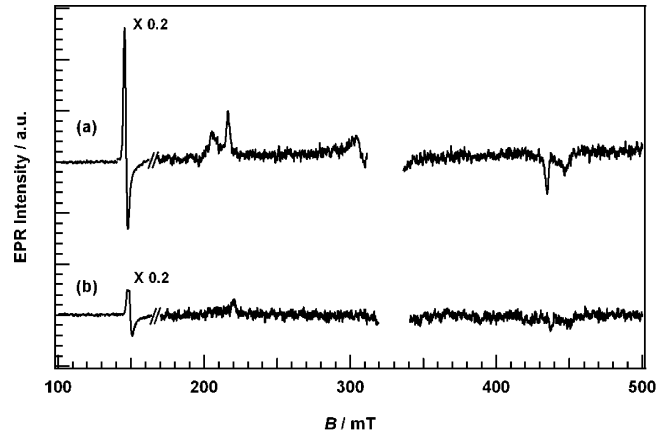


Figure 6. EPR spectra for the T_1 state of BM-DBM (a) with the UV-LED excitation and (b) with the Hg-lamp excitation in EtOH at 77 K.

Zero-Filed Splittings. The EPR spectra of the T_1 state of BM-DBM were measured in EtOH at 77 K, as shown in Figure 6. The EPR spectrum of BM-DBM is composed of one spectrum under the Hg lamp excitation. This spectrum is the same as that observed under the UV-LED excitation. Therefore, the observed EPR spectrum is ascribed to the enol form of BM-DBM. The ZFS parameters obtained from the $\Delta M_S = \pm 1$ transition signals are $|D| = 0.1117$ cm^{-1} and $|E| = 0.0302$ cm^{-1}. The D values of the T_1 states of benzene and formaldehyde were estimated to be 0.1581 and 0.42 cm^{-1}, respectively.[28,29] If the two unpaired electrons localize on the benzene or carbonyl fragment, then the $|D|$ value of BM-DBM should be >0.1117 cm^{-1}. The two unpaired electrons localize on neither the phenyl fragment nor the carbonyl fragment.

The lifetimes of the T_1 states of BM-DBM and DBM obtained from the decay curves of EPR signals are given in Table 1. All decays were exponential over at least three lifetimes within experimental error. The T_1 lifetime of the enol form of BM-DBM obtained from the decay of the EPR B_{min} signal is 32 ms. We find that the T_1 lifetime obtained from the decay curve of phosphorescence, 30 ms, is in good agreement with that obtained from the decay curve of the EPR signal. This agreement shows that the phosphorescence and EPR signals originate from the same photoexcited state.

The $\Delta M_S = \pm 1$ transition signals for DBM are too weak to be observed. The ZFS parameter obtained from the B_{min} signal with the UV-LED excitation is $D^* = 0.129$ cm^{-1}. The value of D^* is close to those observed for the metal-ion complexes with DBM.[30] The observed EPR B_{min} signal can be attributed to the enol form of DBM. The T_1 lifetime of the enol form of DBM obtained from the decay of the EPR B_{min} signal, ~17 ms, is in good agreement with that obtained from the decay curve of phosphorescence, 20 ms.

Nature of the S_1 and T_1 States. The observed ZFS values and T_1 lifetimes suggest that the T_1 states possess mainly a $^3\pi\pi^*$ character in both keto and enol forms of BM-DBM. As mentioned in the previous section, the enol form of BM-DBM is fluorescent and weakly phosphorescent, whereas BM-DBP is phosphorescent and very weakly fluorescent. We can reasonably assume that the keto form of BM-DBM is phosphorescent and very weakly fluorescent. One possible explanation of the luminescence properties arises from a consideration of a large spin−orbit coupling constant of the carbonyl oxygen and its important role in the mixing between the $n\pi^*$ and $\pi\pi^*$ states. The S_1 state of the keto form of BM-DBM possesses mainly a $^1n\pi^*$ character, whereas that of the enol form possesses mainly

a $^1\pi\pi^*$ character. The intersystem crossing (ISC) between $^1n\pi^*$ and $^3\pi\pi^*$ states should be much faster than that between $^1\pi\pi^*$ and $^3\pi\pi^*$ states, as suggested by El-Sayed.[31]

The phosphorescence spectrum of the keto form of BM-DBM was observed, although BM-DBM mainly exists as the enol form in EtOH. The T_1 state of the keto form gives no EPR signals, although the T_1 lifetime of the keto form is longer than that of the enol form. Both the phosphorescence and EPR spectra were observed for the T_1 state of the enol form. These unexpected properties of the keto form may be explained as follows: we can observe the phosphorescence spectrum of the strongly phosphorescent keto form, but the concentration of the keto form in the T_1 state is too low to be observed in the EPR experiment.

The T_1 lifetime of the keto form is expected to be shorter than that of the enol form because of the short-lived character of the $^3n\pi^*$ state. However, the observed T_1 lifetime of the keto form of BM-DBM is about six times longer than that of the enol form. This unexpected effect of the tautomerization on the T_1 lifetime of BM-DBM may arise from a fast nonradiative decay channel in the $^3\pi\pi^*$ state of the enol form.

Wetz et al. prepared the undecane derivative of BM-DBM, 1-(4-*tert*-butylphenyl)-2-decanyl-3-(4′-methoxyphenyl)-propane-1,3-dione (C10-BM-DBM), by grafting a 10-carbon aliphatic chain to the α-carbonyl position of BM-DBM.[8] They reported that the photochemical β-cleavage reaction of C10-BM-DBM possessing γ-hydrogen atoms produces the enol form of BM-DBM and 1-decene by the Norrish-II mechanism. As is known, this reaction is efficient if the T_1 state has an $n\pi^*$ character. At first glance, our assignment is not consistent with the Norrish-II photoreactivity of C10-BM-DBM. However, the T_1 states of aromatic carbonyls are well explained in terms of the mixing of the $^3n\pi^*$ and $^3\pi\pi^*$ states.[32−36] The T_1 state of the keto form of BM-DBM can be regarded to be a mixed character of the $^3n\pi^*$ and $^3\pi\pi^*$ states. Our assignment is not inconsistent with the observed Norrish-II photoreactivity of C10-BM-DBM because the $^3n\pi^*$ character plays an important role in the Norrish-II reaction, even if the $^3n\pi^*$ character is <50% in the T_1 state. Another possible explanation of the Norrish-II photoreactivity of C10-BM-DBM arises from a consideration of the thermal population of the higher $^3n\pi^*$ state, although there are no literature data concerning the energy level of the second excited triplet (T_2) state of C10-BM-DBM.

As is seen in Table 1, the effect of the tautomerization on the T_1 lifetime is small in DBM but large in BM-DBM. The T_1 lifetime of BM-DBP is much longer than that of DBP. It should be noted here that the methoxy and *tert*-butyl groups play an important role in lengthening the T_1 lifetimes of BM-DBP and the keto form of BM-DBM. The effects of the substituent on the nature of the T_1 states of aromatic carbonyls have been extensively studied through phosphorescence, optically detected magnetic resonance, and other optical techniques.[32−36] The methoxy and methyl groups decrease the energy level of the T_1 state (predominantly $^3\pi\pi^*$) and increase the T_2 (predominantly $^3n\pi^*$) energy and T_1 lifetime of benzaldehyde.[34−36] The decreasing $^3\pi\pi^*$ energy and the increasing $^3n\pi^*$ energy are the main cause for the increase in the $^3\pi\pi^*$ character in the T_1 states of *p*-methylbenzaldehyde and *p*-methoxybenzaldehyde. In the present work, we showed that the T_1 energy of the keto form of BM-DBM is lower than that of BM-DBM, and the T_1 energy of BM-DBP is lower than that of DBP. We also showed that the T_1 lifetimes of BM-DBP and the keto form of BM-DBM are much longer than those of DBP and the keto form of DBM, respectively. These facts show that the observed effects of methoxy and *tert*-butyl groups on the T_1 lifetimes of DBP and the keto form of DBM can be explained in terms of the mixing of the $^3n\pi^*$ and $^3\pi\pi^*$ states, as in many aromatic carbonyls reported.

Therefore, the observed influence of the methoxy and *tert*-butyl groups on the T_1 lifetimes may be explained as follows: the purity of the T_1 state is recovered by the electron-donating substituent because the $^3\pi\pi^*$ excitation energy decreases in BM-DBP and BM-DBM.

4. Conclusions

In the present work, the model of the keto form of BM-DBM has been used to study the excited states of BM-DBM. Our optical and EPR studies show that the energy level of the T_1 state of the keto form is much higher than that of the enol form in BM-DBM. The effect of tautomerization on the T_1 lifetime is small in DBM but large in BM-DBM. The methoxy and *tert*-butyl groups play an important role in lengthening the T_1 lifetimes of BM-DBP and the keto form of BM-DBM. The nature of the T_1 states of the keto and enol forms of BM-DBM can be explained in terms of the mixing of the $^3n\pi^*$ and $^3\pi\pi^*$ states. The energy levels and the lifetimes of the T_1 states of the UV absorbers obtained in the present work provide a useful suggestion for designing more photostable UV absorbers.

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