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Magnetic Field Effects on the Dynamics of Biradicals Generated from Benzophenone and Diphenylamine Bifunctional Chain Molecules

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The magnetic field effects (MFE) on the lifetimes of triplet biradicals generated from the intramolecular photoreaction of bifunctional chain molecules, α-(4-benzoylphenoxy)-ω-[4-(phenylamino)phenoxy]alkanes (BP-O-n-O-DPA, n=2—16) were studied by laser flash photolysis. MFE on the biradical lifetimes are strongly affected by magnetic field, chain length, and solvent. The effects are interpreted in terms of the hf-relaxation mechanism. Lifetime change due to T_-—S level crossing was observed in the biradicals with n=2 and 4. The singlet and triplet degeneracy of biradicals occurs when $n \geqslant 6$.

Investigation of the magnetic field effects (MFE) on photochemical reactions continues to be an area of active research for the last decade.[1] Especially, recent studies of MFE on chain-linked biradicals have revealed the factors controlling the MFE in addition to the detailed knowledge of primary steps of the reaction.[2–8] In the previous papers, we have reported MFE on the dynamics of methylene chain-linked neutral triplet biradicals XOH·-COO-$(CH_2)_n$-OCO-X· composed of the xanthone ketyl radical (XOH·) and the xanthenyl radical (X·)[4] and ionic singlet biradicals $\text{Phen}^{\cdot-}$-$(CH_2)_n$-$\text{DMA}^{\cdot+}$ composed of the phenanthrene anion radical ($\text{Phen}^{\cdot-}$) and the N,N-dimethylaniline cation radical ($\text{DMA}^{\cdot+}$).[5] In spite of the great difference in the nature of the two biradical systems, MFE studies on both systems have reached analogous conclusion that the singlet (S)–triplet (T) degeneracy of biradicals occurs when the chain length becomes as long as about 10 chain units. However, if one compares the magnitude of MFE and magnetic field dependence of the lifetimes of both systems, one can find considerable difference between two systems. For example, the lifetime of XOH·-COO-$(CH_2)_6$-OCO-X· increases about 20 times in the presence of a magnetic field (0.8 T), whereas that of $\text{Phen}^{\cdot-}$-$(CH_2)_{10}$-$\text{DMA}^{\cdot+}$ increases about 2 times. We can observe T_-—S level crossing in $\text{Phen}^{\cdot-}$-$(CH_2)_n$-$\text{DMA}^{\cdot+}$ system, while no evidence of the crossing was observed in XOH·-COO-$(CH_2)_n$-OCO-X· system by laser flash photolysis. Is there any correlation between the magnitude and the chain length dependence of MFE? Is there any influence of electronic charge and spin multiplicity of chain-linked biradicals upon magnetic field dependence of their lifetimes and magnitude? With these questions in mind, we have attempted to extend studies of MFE to other chain-linked biradicals.

In the previous papers,[9] we have studied MFE on the photoreaction of aromatic ketones and amines in micellar solution, in which significant effects have been observed. In order to make deep insight into the mechanism of MFE, we have undertaken to study the MFE on the dynamics of methylene chain-linked triplet biradicals generated from the end-to-end reaction of excited triplet benzophenone and diphenylamine by laser flash photolysis.

Experimental

Materials. 1-(4-Benzoylphenoxy)-10-[4-(phenylamino)phenoxy]decane (BP-O-10-O-DPA) was synthesized with the following procedure. A 10 ml anhydrous N,N-dimethylformamide (DMF) solution of 4-hydroxybenzophenone (1 g) was slowly added to a 10 ml DMF containing NaH (240 mg) in an ice water bath, and the solution was stirred at room temperature for 18 h. Then a 10 ml DMF of 1,10-dibromodecane (4.5 g) was added into the solution and the solution was stirred at room temperature for 22 h. The reaction mixture was treated with ice water, extracted with benzene, and purified by chromatography, yielding a white solid of 1-(4-benzoylphenoxy)-10-bromodecane (1.67 g).

Mp 67—68 °C. ^{1}H NMR(60 MHz, $CDCl_3$) δ=1.05—2.11 (16H, br, methylene), 3.66 (2H, t, J=6 Hz, $-CH_2Br$), 4.00 (2H, t, J=6 Hz, $-CH_2O-$), and 6.65—7.90 (9H, m, aromatic). IR (KBr) 1635 (C=O), 2852, and 2920 cm^{-1} ($-CH_2-$). Calcd for $C_{23}H_{29}BrO_2$: C, 66.19; H, 6.95%. Found: C, 66.25; H, 6.99%. M, 416.

An 30% NaOH aqueous solution (5 ml) containing 1-(4-benzoylphenoxy)-10-bromodecane (400 mg), 4-hydroxydiphenylamine (342 mg), and tetrabutylammonium bromide (89 mg) was refluxed for 1 h. The reaction mixture was treated with ice water, extracted with $CHCl_3$, and purified by chromatography, yielding a light yellow solid of 1-(4-benzoylphenoxy)-10-[4-(phenylamino)phenoxy]decane (BP-O-10-O-DPA, 344 mg).

Mp 116—117 °C. ^{1}H NMR δ=1.01—2.05 (16H, br, methylene), 3.86 (2H, t, J=6 Hz, $-CH_2O$-Ph-NH), 3.96 (2H, t, J=6 Hz, $-CH_2O$-Ph-C=O), 5.40 (1H, bs, NH), and 6.45—7.81 (18H, m, aromatic). IR 1638 (C=O), 2850, 2910 ($-CH_2-$), and 3425 cm^{-1} (NH). Calcd for $C_{35}H_{39}NO_3$: C, 80.61; H, 7.46; N, 2.69%. Found: C, 80.61; H, 7.45; N, 2.65%. M, 521.

Other bifunctional alkanes composed with different chain

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Table 1. Melting Points of BP-O-*n*-O-DPA

n	Melting point/°C	*n*	Melting point/°C
2	139—141	8	114—115
3	92—93	10	116—117
4	131—133	12	116—117
6	116—117	16	119—120

length (BP-O-*n*-O-DPA, *n*=2—16) were prepared in an analogous manner. Their spectral data are very similar to those of BP-O-10-O-DPA. Their melting points are given in Table 1.

4-Methoxybenzophenone (MeOBP) and diphenylamine were purified by recrystallization and vacuum sublimation. Spectrograde *N,N*-dimethylformamide (DMF), acetonitrile (MeCN), and benzene were used as received. All solutions (10^{-3}—10^{-4}M) were deaerated by freeze-pump-thaw cycles (1 M=1 mol dm^{-3}).

Laser Flash Photolysis. Transient absorption spectra were measured at room temperature, by using an N_2 laser (337 nm, 10 ns) or a XeCl excimer laser (308 nm, 15—20 ns) as an exciting light source. The transient signal was detected by a combination of a monochromator, a photomultiplier, and a storagescope. Magnetic fields (<1 T) were applied with an electromagnet. The details of the apparatus were described elsewhere.[4] Lifetimes of biradicals were obtained from the initial decay of transient absorption monitored at 330—340 nm.

Results and Discussion

1. Magnetic Field Effects on the Transient Absorption Spectra of BP-O-10-O-DPA. Transient Spectra in DMF. Figure 1 shows the transient absorption spectra of BP-O-10-O-DPA in DMF, generated by the 337 nm excitation. Quite a few studies have been reported on the dynamics of intermolecular photoreactions of benzophenones and amines.[10—12] According to the literature, extinction coefficients and band maxima of the absorption spectra of reaction intermediates are as follows; benzophenone ketyl radical (20000 M^{-1} cm^{-1} at 330 nm, 4600—5100 M^{-1} cm^{-1} at 545 nm),[12,13] benzophenone anion radical (19000 M^{-1} cm^{-1} at 339 nm, 5000 M^{-1} cm^{-1} at 630 nm),[12,13] diphenylaminyl radical (4000 M^{-1} cm^{-1} at 760 nm),[14] and diphenylamine cation radical (19000—25000 M^{-1} cm^{-1} at 680 nm).[12,15] Thus, the transient absorption spectra of BP-O-10-O-DPA shown in Fig. 1 are reasonably assigned as follows: The strong band around 330 nm is the mixture of absorption of benzophenone ketyl radical (BPH·) and benzophenone anion radical(BP$^{\bar{\cdot}}$), and the bands around 550, 680, and 740 nm are attributable to the absorptions of BPH·, diphenylamine cation radical (DPA$^{\dot{+}}$), and diphenylaminyl radical (DPA·), respectively, though they are moderately complicated. The absence of the triplet-triplet (T-T) absorption band (6000—6500 M^{-1} cm^{-1} at 525 nm)[12,16] in nanosecond time scale, which is observed in the transients of MeOBP, indicates that both neutral biradical (BPH·-O-10-O-DPA·) and ionic one (BP$^{\bar{\cdot}}$-O-10-O-DPA$^{\dot{+}}$) are mainly generated from the intramolecular reaction of the excited triplet BP and DPA. The rate constant of the corresponding intermolecular reaction of the excited triplet MeOBP and diphenylamine was estimated to be around 10^9—10^{10} M^{-1} s^{-1}. Taking into account of the local concentration of DPA (>0.1 M) in BP-O-10-O-DPA, the intramolecular reaction was estimated to occur within a few nanosecond. The two biradicals may be generated simultaneously, as reported in the intermolecular reaction of benzophenone and diphenylamine studied by picosecond laser flash photolysis.[12] A preliminary picosecond photolysis study suggests that both neutral and ionic absorption bands appears in concomitant with a decay (1.8 ns) of ^{3}BP* in the case of BP-O-3-O-DPA in MeCN.[17] However, we could not determine whether two biradicals were generated simultaneously or successively by nanosecond laser photolysis, since they were generated within the pulse width (10 ns) of the laser used. The ratio of neutral biradical to ionic one is roughly estimated to be about 4:1 to 3:1, from the molar extinction coefficients of these radicals, though these absorption bands are overlapped.

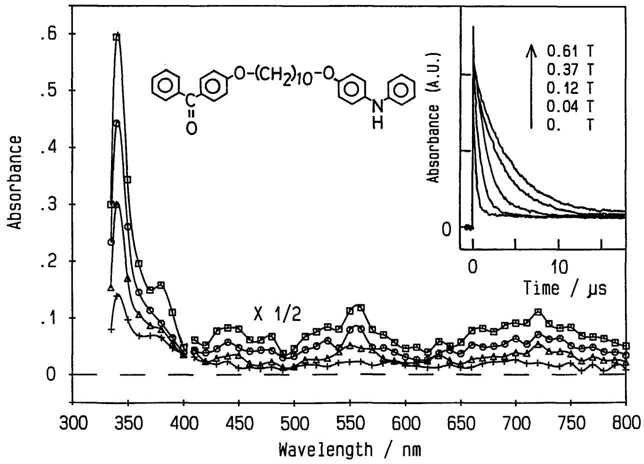


Fig. 1. Transient absorption spectra of BP-O-10-O-DPA generated by the 337 nm excitation in DMF. Delaytimes are 60 (□), 190 (○), 380 (△), and 800 ns (+) after the laser pulse. Inset: Magnetic field effects on the decay curves monitored at 340 nm.

Next, we examined the magnetic field effects on the lifetime of biradicals of BP-O-10-O-DPA generated by the 337 nm excitation in DMF. The external MFE were observed on the transient absorption bands in the whole wavelength region (300—800 nm), as a typical result is shown in inset of Fig. 1. The decay curves monitored around 340 nm and 680 nm consist of a short and a long decay component (see, Fig. 1). The long-lived component may be attributable to the monoradicals (BP-O-10-O-DPA$^{\dot{+}}$, BP$^{\bar{\cdot}}$-O-10-O-DPA) generated from the electron (hole) exchange between the ionic biradical and the neutral molecule, since it appears only in the absorption of ionic species and its fraction increases with increasing the solute concentration. Thus, lifetimes of biradicals were calculated from the initial slopes of the decay curves (1/*e*), since fraction of the long-lived component, which is magnetic field insensitive, is less than 10%.

The lifetimes determined from the absorption at 340 nm (mainly attributable to BPH· and BP$^{-\cdot}$), 540 nm (BPH·), 630 nm (BP$^{-\cdot}$), 680 nm (DPA$^{+\cdot}$), and 740 nm (DPA·) are approximately comparable with each other within experimental error (300 ± 30 ns at zero field and 4600±270 ns at 0.56 T), though the spectra are overlapped with each other and signal/noise ratio of absorption intensities in 500—800 nm is considerably low. This indicates that lifetimes in the absence and presence of a magnetic field are almost same within experimental error. Solvation of the ionic radicals in the ionic biradical may reduce the electrostatic Coulombic interaction between two radicals, though the interaction is expected to shorten the mean interradical distance from that of the neutral biradical, and, therefore, magnetic field dependence of lifetimes of two biradicals is expected to be different from one another. It is not clear from the present study whether the two biradicals are in dynamic equilibrium or not.

Hereafter, the lifetimes determined from the decay curves around 330—340 nm are used as the lifetimes of biradicals without distinguishing between two species, since magnetic fields affected decay curves of neutral and ionic biradicals in a similar manner, and since the best signal/noise ratio was attained at the absorption around 330 nm. Therefore, the lifetimes that will be discussed below are, in general, considered as the average lifetimes of neutral and ionic biradicals.

Excitation Wavelength and Solvent Dependence. Influence of the excitation wavelength and solvent on the transient spectra of BP–O–10–O–DPA was examined. By the 308 nm excitation in DMF, a considerable fraction of photons is absorbed by the DPA chromophore, since the absorption intensity ratio of DPA and BP is about 2 : 1 at 308 nm. However, transient spectra obtained by the 308 nm excitation are analogous to those obtained by the 337 nm excitation shown in Fig. 1. The 308 nm excitation does not affect seriously the relative yields of neutral and ionic biradicals monitored after several tens of nanosecond. In addition, lifetimes in the absence and presence of a magnetic field (0.56 T) are close to each other within experimental error (Table 2). In the case of DPA excitation, the energy transfer from the excited triplet DPA to BP may take place efficiently, as the excited triplet energy of diphenylamine is close to that of benzophenone.[18]

Table 2. Lifetimes (μs) of the Biradical Generated from BP–O–10–O–DPA[a]

Solvent	337 nm[b]		308 nm[b]	
	0 T	0.56 T	0 T	0.56 T
DMF	0.33	4.7	0.27	4.3
MeCN	—	—	0.14	0.64
Benzene	—	—	0.10	0.14

a) Experimental errors are ±15%. b) Excitation wavelength.

Solvent effects on the transients of BP–O–10–O–DPA were examined for the spectra obtained by the 308 nm excitation. Transient spectra of BP–O–10–O–DPA in MeCN (dielectric constant, 37.5) and benzene (2.3) are very similar to those in DMF (36.7) shown in Fig. 1, indicating the generation of two biradicals in these solvents. The relative yields of neutral and ionic biradicals are less sensitive to the solvent polarity. These observations are in parallel with those for the corresponding intermolecular reaction of benzophenone and diphenylamine.[12] In contrast to the spectra, the lifetimes of the biradicals in the absence and presence of magnetic fields are quite different from each other as shown in Table 2. MFE on the biradical lifetimes are in the order of DMF>MeCN>benzene.

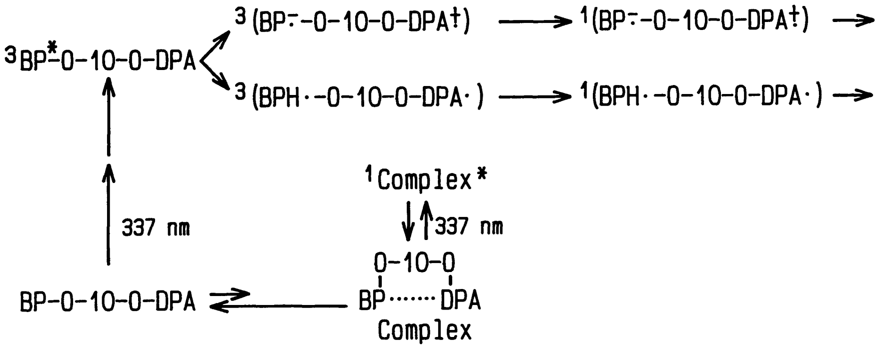
The solvent effects on the MFE of biradical lifetimes may be attributable to (1) formation of the intramolecular ground state complex or (2) conformational difference in the biradicals, since interradical distance in the biradicals affects strongly the magnitude of MFE as will be described later. Indeed, the UV spectral examination of MeOBP and diphenylamine reveals that intermolecular weak complex formation takes place in three solvents with the order of benzene> MeCN, DMF. The association constant in benzene was estimated to be 0.1 M^{-1} at room temperature, by assuming a 1 : 1 complex. Taking into account of high local concentration of DPA (>0.1 M) and of linking of the two chromophores in BP–O–10–O–DPA, considerable portion of BP–O–10–O–DPA may exist as intramolecular complex BP–O–10–O–DPA in benzene, while a little in DMF and MeCN.

According to product analysis studies,[19] triplet benzophenone reacts with diphenylamine in *t*-butyl alcohol and in acetonitrile but not in benzene, leading to 1-(4-anilinophenyl)-1,1-diphenylmethanol in the polar solvents. Furthermore, the excited singlet state of the intermolecular complex of benzophenone and diphenylamine deactivates into its ground state within picosecond time scale.[12] Thus, the excited state of the intermolecular complex does not generate radicals. Taking into account of the results mentioned above, in the intramolecular photoreaction of BP–O–10–O–DPA, it is not conceivable that intramolecular complex generates biradicals showing transient absorption in the nanosecond time scale. It seems that conformational difference of the biradicals in three solvents determines the magnitude of the effects. In a solution where complex formation takes place considerably, the mean distance between two chromophores at the ends of the chain in uncomplexed BP-O-10-O-DPA may become in close proximity, and, therefore, the two radical centers in the biradicals generated are in close proximity. This short interradical distance results in the reduction of the magnitude of the effects because the degeneracy of the triplet and singlet state of the biradicals is lifted (see, the next section). Furthermore, BP-O-10-O-DPA is less soluble in MeCN than in DMF. This indicates that the biradical conformation is rather compact in MeCN than in DMF, and, therefore, the magnitude of MFE is expected to be smaller in MeCN that in DMF. This expectation agrees well with the observed results shown in Table 2, though dielectric constants of two solvents are very similar. Conformational distribution of biradicals is considered to be very important to understand the magnitude of MFE. In the case of Phen-(CH$_2$)$_{10}$-DMA,[5] the ionic biradical generated from the excited singlet Phen does exhibit significant MFE, while the ionic biradical generated from the excited singlet DMA does not. This difference in MFE was attributed to the conformational difference between two biradicals.

Reaction Mechanism. A tentative reaction mechanism of BP-O-10-O-DPA in DMF is given in Scheme 1. In the ground state, BP-O-10-O-DPA may partly form the intramolecular complex BP-O-10-O-DPA.
:................:
The excited states of both the free BP-O-10-O-DPA and the complex may be generated by the 337 nm excitation. Intramolecular hydrogen abstraction and electron-transfer reactions take place simultaneously from the triplet excited state of free BP-O-10-O-DPA, leading to the generation of triplet biradicals linked by a methylene chain, i.e., the BPH·-O-10-O-DPA· biradical and the BP$^{\cdot-}$-O-10-O-DPA$^{\cdot+}$ biradical. These biradicals may undergo singlet (S)-triplet (T) intersystem crossing (isc), while recombination and/or back electron-transfer reactions may take place in the singlet state. On the other hand, the excited singlet of the complex does not give any net chemical reaction and deactivates into the ground state within picosecond time scale. Furthermore, when DPA is excited by a 308 nm laser, biradicals may be generated indirectly after the energy transfer from the excited triplet DPA to BP. The photoprocess in MeCN may be the same as that in DMF. Considerable fraction of BP-O-10-O-DPA may exist as the ground state intramolecular complex in benzene.

Mechanism of Magnetic Field Effects. In the previous papers,[4] we have discussed in detail the mechanism of MFE on the chain-linked triplet biradicals, XOH·-COO-(CH$_2$)$_n$-OCO-X·. Mechanism of MFE presented for the previous triplet biradicals seems to be applicable for the present systems, since magnetic field dependence of the lifetimes of the triplet biradicals generated from BP-O-10-O-DPA is very similar to that of the previous ones. The lifetimes of the biradicals generated from BP-O-10-O-DPA are 330 ns at zero field in DMF. The electron-nuclear hyperfine (hf)-induced T-S isc rate is estimated to be about 10^8 s^{-1} from their hf coupling constants,[20] while the relaxation rate among spin sublevels is considered to be in the order of 10^6 s^{-1}.[21] These facts indicate that neither hf-induced isc nor relaxation in triplet manifold is the rate-controlling step in the deactivation of the biradicals at zero field. The cage reaction in the singlet state may determine the lifetimes at zero field. In the presence of a weak magnetic field (<0.1 T), hf-induced isc rate among nondegenerate states becomes slower than the cage reaction rate, and, therefore, can be the rate-controlling step, as observed in the rapid increase in the lifetimes in the low field region (<0.1 T). In higher fields (>0.1 T), the hf-induced isc rate becomes slower than the relaxation rate among triplet sublevels. In this way, the relaxation may become the rate-controlling step in higher fields.

2. Chain Length Dependence of the Magnetic Field Effects. Bifunctional chain molecules BP-O-*n*-O-DPA (n=2—16) in DMF, generated by the 337 nm excitation, exhibit transient absorption spectra similar



Scheme 1.

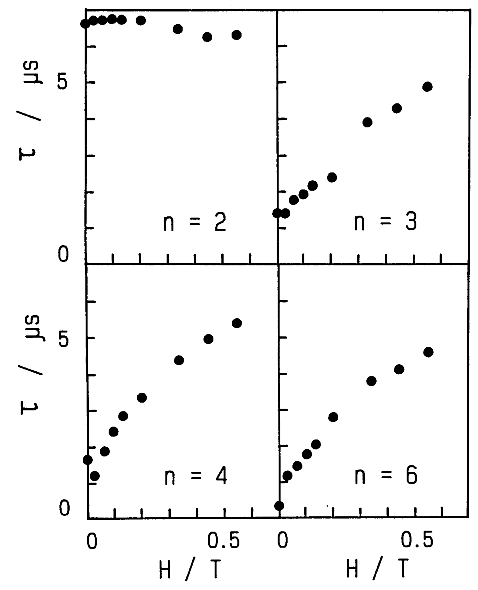


Fig. 2. Magnetic field effects on the lifetimes of biradicals generated from BP-O-*n*-O-DPA in DMF. Magnetic field dependences of biradicals with $n>6$ are not shown in this figure, since they are very similar to that of the biradicals with $n=6$.

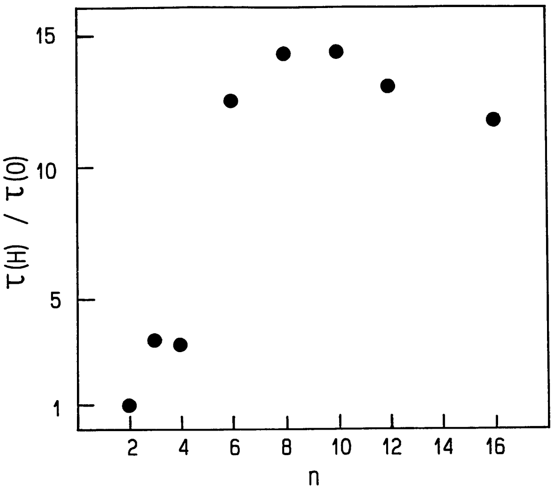


Fig. 3. Chain length dependence of the lifetime ratio $\tau(H)/\tau(0)$ of the biradicals generated from BP-O-*n*-O-DPA in the presence and absence of a magnetic field ($H=0.56$ T).

Table 3. Lifetimes (μs) of the Biradicals Generated from BP-O-*n*-O-DPA[a]

n	DMF[b]			MeCN[c]		
	0 T	0.56 T	*R*[d]	0 T	0.56 T	*R*[d]
2	6.6	6.2	0.9	4.4	4.0	0.9
3	1.4	4.9	3.5	1.1	2.2	2.0
4	1.6	5.4	3.4	0.75	1.1	1.5
6	0.36	4.5	12.5	0.14	0.52	3.7
8	0.36	5.1	14.2	0.14	0.64	4.6
10	0.33	4.7	14.2	0.14	0.64	4.6
12	0.37	4.8	13.0	0.24	0.69	2.9
16	0.40	4.7	11.8	0.15	0.48	3.3

a) Experimental errors are ±15%. b) 337 nm excitation. c) 308 nm excitation. d) Lifetime ratio in the presence and absence of a magnetic field.

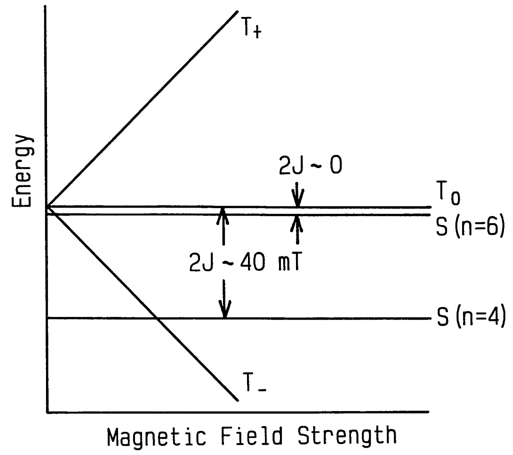


Fig. 4. Energy diagram of biradicals.

to those with $n=10$. The facts indicate that these molecules undergo photoreactions analogous to those of BP-O-10-O-DPA. The magnetic field dependence of the lifetimes of biradicals generated from these molecules was examined in detail (Figs. 2 and 3, and Table 3). The lifetimes of biradicals generated from BP-O-*n*-O-DPA are affected significantly by the chain length, *n*, as well as by the magnetic fields.

Chain length dependence of the MFE on the biradical lifetimes can be interpreted with the aid of the energy diagram schematically shown in Fig. 4. The energy gap between T and S biradical is caused by electron-exchange interaction, and is a function of interradical distance *r*, $\exp(-\alpha r)$, α being a constant. Thus, by changing the chain length, we can change the mean interradical distance and, therefore, the S–T energy gap of biradicals. Firstly, let's examine magnetic field dependence of biradical lifetimes shown in Fig. 2 in detail.

In the case of the biradicals with $n=6$—16, the lifetimes in the absence and presence of magnetic fields are rather independent from the chain length *n* (see also Table 3). In these biradicals, the chain length is so long that T and S states are almost degenerate with each other. Thus the transition occurs between nearly degenerate states (Fig. 4), and, for this reason, we can see significant MFE caused by the Zeeman splitting of triplet sublevels, as described in the previous section.

By decreasing the chain length, S and T states become nondegenerate at zero field because of electron-exchange interaction (Fig. 4). Therefore, by increasing a magnetic field, T_- shifts in lower energy, and the degeneracy between T_- and S occurs at a certain magnetic field (T_-–S level crossing). This happened in the case of the biradicals with n=4. As shown in Fig. 3, with increasing a magnetic field, the lifetime (1.6 μs at zero field) decreases initially up to 40 mT due to the level crossing (1.2 μs at 0.04 T), and then increases (5.4 μs at 0.56 T) by further increasing a magnetic field. T_0–S energy gap of this biradical is then considered to be about 40 mT.

In the case of the biradical with n=2, the S–T energy gap is so large that slow T–S transition (6.6 μs) occurs between nondegenerate T and S states at zero field. By increasing a magnetic field, however, a shift of T_- sublevel enhances slightly the T_-–S transition rate, observed as a small decrease in the lifetime (6.2 μs at 0.56 T). The T_o–S energy gap is likely greater than 0.9 T, since no minimum was observed in the magnetic fields up to 0.95 T.

On the other hand, no dip was observed in the magnetic field dependence of the lifetimes of the biradicals with n=3. The Zeeman splitting of triplet sublevels can influence the lifetimes of biradicals in two ways, when two states are nondegenerate; the lifetime increase due to the upward shift of T_+ and the decrease due to the downward shift of T_-. As the lifetime of biradicals with n=3 (1.4 μs at zero field) is in comparable with the biradical lifetime with n=4, its interradical distance may be compatible with that in the biradicals with n=4. However, because of conformational restriction posed for the chain, magnetic interaction between two radicals at the ends of the chain may be slightly different from one another. It is likely that, in the case of the biradicals with n=3, the increase of the lifetime due to the high energy shift of T_+ overcomes the depletion due to the T_-–S level crossing.

Degeneracy of two spin states was further confirmed from the chain length dependence of lifetime ratio in the absence and presence of a magnetic field (0.56 T) (Fig. 3 and Table 3). Significant increase in the lifetime ratio occurs at n=6, which is attributable to the S–T degeneracy. In this way, we can clearly conclude that the T–S degeneracy of present biradicals occurs when $n \geqslant 6$.

Chain length dependence of the MFE on the biradical lifetimes generated by the 308 nm excitation was also examined in MeCN. The dependence in MeCN is essentially the same as that shown in Figs. 2 and 3, and only the lifetimes at zero and 0.56 T are listed in Table 3 for comparison. We can also conclude that S–T degeneracy of the biradical occurs at around n=6. Observed scatter in the ratio may be due to the solubility of the chain molecules in MeCN. It is interesting that the analogous conclusion is obtained in two solvents, even though magnitude of the effects are considerably different.

As briefly discussed in Introduction, we reported the magnetic field dependence and chain length dependence of the lifetime of triplet biradicals, $\text{XOH}\cdot\text{-COO-(CH}_2)_n\text{-OCO-X}\cdot$ (n=2—12)[4] and singlet ones, $\text{Phen}^{\cdot-}\text{-(CH}_2)_n\text{-DMA}^{\cdot+}$ (n=3—10).[5] Present results on the S–T degeneracy of the biradicals are in parallel with those reported, though degeneracy occurs at slightly short chain length in the present biradicals. Indeed, in the present biradicals with n=6 in DMF and MeCN, linked by totally 8 chain units, no T_-–S level crossing occurs at 40 mT, while it occurs at 70 mT in the case of $\text{Phen}^{\cdot-}\text{-(CH}_2)_8\text{-DMA}^{\cdot+}$ in MeCN. This difference might be attributable to the chain conformations of these biradicals at the ester part (i.e., -O- or -OCO-). Furthermore, in the case of the present triplet biradicals exhibiting significant MFE, lifetime change due to T_-–S level crossing was observed when n=2 and 4. In the previous triplet biradical with n=2 (i.e., totally 6 chain units), we could still observe MFE as large as three times, and no depletion due to T_-–S level crossing was detected, in contrast to the present results. Therefore, whether T_-–S level crossing is observable or not is strongly affected by the dectivation rates associated with biradical spin states and the chain conformation.

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