Effect of High Magnetic Field on the Lifetime of Biradicals Generated from Benzophenone and Diphenylamine Bifunctional Chain Molecules

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The effect of high magnetic fields ($\leqq$ 13 T) on the lifetime of triplet biradicals (BPH$^{\bullet}$–O–$(CH_2)_n$–O–DPA$^{\bullet}$, n = 2, 4, 8, 16) composed of a protonated diphenylketyl radical (BPH$^{\bullet}$) and a diphenylaminyl radical (DPA$^{\bullet}$) is studied in *N,N*-dimethylformamide at room temperature by laser flash photolysis. On increasing the magnetic field from zero to ca. 2 T, the lifetime of BPH$^{\bullet}$–O–$(CH_2)_n$–O–DPA$^{\bullet}$ (n = 4, 8, 16) increases steeply, and then decreases gradually in higher magnetic fields. The lifetime of BPH$^{\bullet}$–O–$(CH_2)_2$–O–DPA$^{\bullet}$ decreases gradually with increasing the magnetic field with a shallow dip at ca. 2 T. The reversal of the effect observed in the lifetime of BPH$^{\bullet}$–O–$(CH_2)_n$–O–DPA$^{\bullet}$, n = 4, 8, 16 is interpreted in terms of spin-lattice relaxation which is induced by the anisotropic Zeeman interaction. The dip observed in the magnetic field dependence of the lifetime of BPH$^{\bullet}$–O–$(CH_2)_2$–O–DPA$^{\bullet}$ is attributable to the S–T$_-$ level crossing.

Studies on the effects of high magnetic field (> 2 T) in chemical, physical, and biological processes are important.[1,2] This is partly because superconducting magnets have become popular and partly because new phenomena which could not be observed in the lower magnetic fields have been discovered in the higher fields.

The effects in organic photochemical reactions have been researched very extensively.[1] Concerning the effect in the primary process of photochemical reactions, we have studied the effect of high magnetic field (< 14 T) in the lifetime of many biradicals,[3—8] prompted by the discovery of a reversal of the magnetic field effect (MFE) on the lifetime of a chain-linked triplet biradical composed of an anthrasemiquinone and a xanthenyl radical.[3] In the case of the triplet biradicals composed of two carbon-centered radicals,[3,6—8] the degree of the reversal (R%), which is tentatively defined as $-(\tau_{Bmax} - \tau_{max})/\tau_{max} \times 100$, is 5—20%; here τ_{Bmax} and τ_{max} mean the lifetime at ca. 13—14 T and the maximum lifetime at 1—2 T, respectively. On the other hand, R is about 70% in the case of a triplet biradical generated by the photoelectron transfer reaction of a γ-cyclodextrin inclusion complex of a chain-linked phenothiazine/viologen.[4] It is considered that a large anisotropic g value of a nitrogen-centered radical is responsible to the large R value in this case, since it is composed of two nitrogen-centered radicals. If this prediction is correct, a biradical which is composed of a carbon-centered radical and a nitrogen-centered one may show an R value which is intermediate between the two cases mentioned above. Furthermore, a previous paper[9] suggested that in a short chain biradical BPH$^{\bullet}$–O–$(CH_2)_2$–O–DPA$^{\bullet}$ composed of a protonated diphenylketyl radical (BPH$^{\bullet}$) and a diphenylaminyl radical (DPA$^{\bullet}$) the S–T$_-$ level crossing may occur at the magnetic field above 1 T. Therefore it is important to determine the energy of the level crossing.

For such reasons, the effect of high magnetic field ($\leqq$ 13 T) on the lifetime of triplet biradicals generated by α-(4-benzoylphenoxy)-ω-(4-anilinophenoxy)alkanes (BP–O–*n*–O–DPA, n = 2, 4, 8, 16) has been studied by laser flash photolysis in the present paper. Hereafter polymethylene chain, –$(CH_2)_n$–, will be abbreviated as –*n*–.

The level crossing energy of the biradical BPH$^{\bullet}$–O–2–O–DPA$^{\bullet}$ is estimated to be ca. 2 T. In the case of biradicals BPH$^{\bullet}$–O–*n*–O–DPA$^{\bullet}$ (n = 4, 8, 16), the R value is obtained to be about 35%, as expected. All the results are discussed in the framework of the radical pair mechanism.

Experimental

Synthesis of bifunctional chain molecules, BP–O–*n*–O–DPA (n = 2, 4, 8, 16) was described elsewhere.[9] Spectrograde *N,N*-dimethylformamide (DMF) was used as solvent. Sample solutions were deaerated by repeated freeze-pump-thaw cycles. The transient absorption of biradicals at 540 nm, which was assigned to the absorption of BPH$^{\bullet}$, was measured by a pulse-magnet laser flash photolysis system. The exciting light source was a Nd : YAG laser (Spectra Physics, GCR-11-1) (355 nm, 10 ns fwhm). The details of the apparatus were described elsewhere.[10] All measurements were carried out at room temperature.

Results

Reaction Scheme. In the nanosecond laser photolysis of BP–O–*n*–O–DPA in DMF, transient absorption spectra assigned to a protonated diphenylketyl radical, a diphenylaminyl radical, a diphenylketyl anion radical and a diphenylamine caion radical are observed, indicating the formation of both a neutral triplet biradical ^{3}(BPH$^{\bullet}$–O–*n*–O–DPA$^{\bullet}$) and an ionic one ^{3}(BP$^{-\bullet}$–O–*n*–O–DPA$^{+\bullet}$) composed of a diphenylketyl anion radical (BP$^{-\bullet}$) and a diphenylamine cation radical (DPA$^{+\bullet}$).[9,11] Their decays exhibit a significant magnetic field effect in the low magnetic field (< 1 T), as de-

scribed in a previous paper.[9] The primary photoprocess of BP–O–*n*–O–DPA is schematically depicted in Scheme 1, though it is complex within the time domain of a few nanoseconds.[11] The excited triplet of a benzophenone moiety ^{3}BP*–O–*n*–O–DPA is generated via the excited singlet of a benzophenone moiety ^{1}BP*–O–*n*–O–DPA upon photoirradiation. It undergoes both intramolecular electron transfer and hydrogen abstraction reactions, resulting in the formation of an ionic triplet biradical ^{3}(BP$^{-\bullet}$–O–*n*–O–DPA$^{+\bullet}$) and a neutral triplet biradical ^{3}(BPH$^\bullet$–O–*n*–O–DPA$^\bullet$). The neutral biradical is formed partly through the ionic biradical via a proton transfer reaction. ^{3}(BPH$^\bullet$–O–*n*–O–DPA$^\bullet$) may disappear via intersystem crossing (ISC) to the singlet state followed by recombination, whereas ^{3}(BP$^{-\bullet}$–O–*n*–O–DPA$^{+\bullet}$) may deactivate via ISC to the singlet state followed by a back electron transfer. The ratio of the neutral biradical to the ionic one is roughly estimated to be 4 : 1 to 3 : 1 in the nanosecond laser photolysis. Both neutral and ionic biradicals have experimentally an identical lifetime at zero field, and exhibit MFE very similar to each other in the low magnetic field region (< 1 T) as discussed in a previous paper.[9] For this reason the effect of high magnetic field (≦ 13 T) on the triplet neutral biradical ^{3}(BPH$^\bullet$–O–*n*–O–DPA$^\bullet$) is examined in the present study.

Magnetic Field Dependence of the Biradical Lifetime. Figure 1 and Table 1 show the magnetic field dependence (MFD) of the lifetime of ^{3}(BPH$^\bullet$–O–*n*–O–DPA$^\bullet$) (*n* = 2, 4, 8, 16) in DMF. In the low magnetic field region (< 2 T), the lifetime of ^{3}(BPH$^\bullet$–O–*n*–O–DPA$^\bullet$) (*n* = 4, 8, 16) increases rapidly with increasing the magnetic field. In the higher field region (> 2 T), it decreases gradually with increasing magnetic field up to 13 T. The degrees, R_s, of the reversal of MFE are 38 (*n* = 4), 34 (*n* = 8) and 36% (*n* = 16). The MFD of the lifetime of ^{3}(BPH$^\bullet$–O–2–O–DPA$^\bullet$) is very different from others. The lifetime decreases gradually with increasing the magnetic field. A shallow dip appears at the magnetic field of ca. 2 T.

Table 1. Lifetime (μs) of ^{3}(BPH$^\bullet$–O–*n*–O–DPA$^\bullet$) in Magnetic Field[a)]

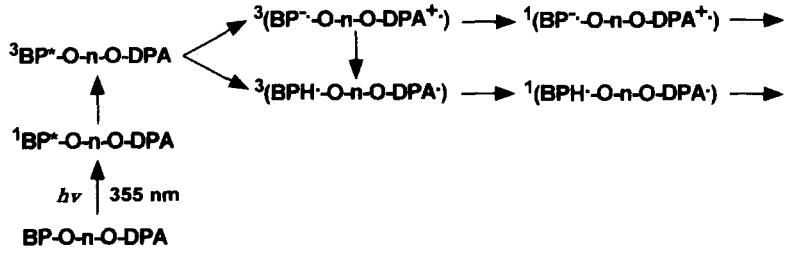
	B_0/T			
n	0	1.5	6.0	13.0
2	4.9	4.6	4.3	3.3
4	1.5	5.5	4.2	3.4
8	0.3	4.7	3.8	3.1
16	0.4	4.2	3.7	2.7

a) Experimental errors are ±10%.

Analysis of the MFD of Lifetime of ^{3}(BPH$^\bullet$–O–*n*–O–DPA$^\bullet$) with *n* = 4, 8, 16. Figure 2 depicts schematically energy levels and spin conversion process of a biradical when two radicals are linked by a long chain. In this case, the exchange interaction between two electron spins is negligibly small and, therefore, singlet (S) and triplet (T) states are nearly degenerate at zero field. The ISC among S and three triplet sublevels (T_+, T_0, T_-) occurs via electron-nuclear isotropic hyperfine (hf) interaction at zero field. By application of a magnetic field (> ca. 0.1 T), the hf-induced S–$T_\pm$ ISC is quenched because of the Zeeman splitting of T_+ and T_- sublevels. In the magnetic field, the T_0–S ISC due to the isotropic hf interaction remains and the T_0–S ISC induced by the difference of isotropic g-values in the two radicals (Δg mechanism) takes place. Furthermore, the spin lattice relaxation (SLR) among S, T_+, T_0, and T_- takes important roles in controlling the lifetime of biradicals. The SLR is induced by the anisotropic hf (δhf) interaction in component radicals in the δhf mechanism, whereas it is induced by the anisotropic Zeeman interaction in the δg mechanism. The SLR is also induced by the dipole–dipole interaction between two radicals (the dd mechanism).

In the case of BPH$^\bullet$–O–*n*–O–DPA$^\bullet$ with *n* = 8, 16, the distance between two radicals at the two ends of a chain is long (> 1 nm) and therefore S and T states are degenerate, since no S–T energy gap is observed in a previous study at the low magnetic field region.[9] For this reason, the MFD of the lifetime of ^{3}(BPH$^\bullet$–O–*n*–O–DPA$^\bullet$) with *n* = 8 or 16 is analyzed with a model shown in Fig. 2. In the case of the biradical composed of BPH$^\bullet$ and DPA$^\bullet$,the hf-induced S–T_0 ISC rate constant is estimated to be 10^7 s^{-1} or so and the S–T_0 ISC rate constant due to the Δg mechanism is of the order of 10^8 s^{-1} at 1 T. Therefore, the triplet biradicals optically detected in the presence of the magnetic field are those in T_+ and T_- sublevels, since their lifetime is as long as a few microseconds. Under these circumstances, the decay rate constant k_{BR} (or the lifetime τ_{BR}) of the biradical is controlled by the SLR rate constants and the spin-orbit induced ISC rate constant k_T from triplet sublevels to ground state product(s), which is magnetic-field independent. The quenching rate constant due to impurities may be included in k_T, if this process were to exist. Then k_{BR} is given by Eq. 1.[4,6–8]

$$k_{BR} = 1/\tau_{BR} = 1/2\{k(\mathrm{BPH}^\bullet : \delta\mathrm{hf}, \delta g) + k(\mathrm{DPA}^\bullet : \delta\mathrm{hf}, \delta g)\} + k(\mathrm{dd}) + k_T, \quad (1)$$



Scheme 1.

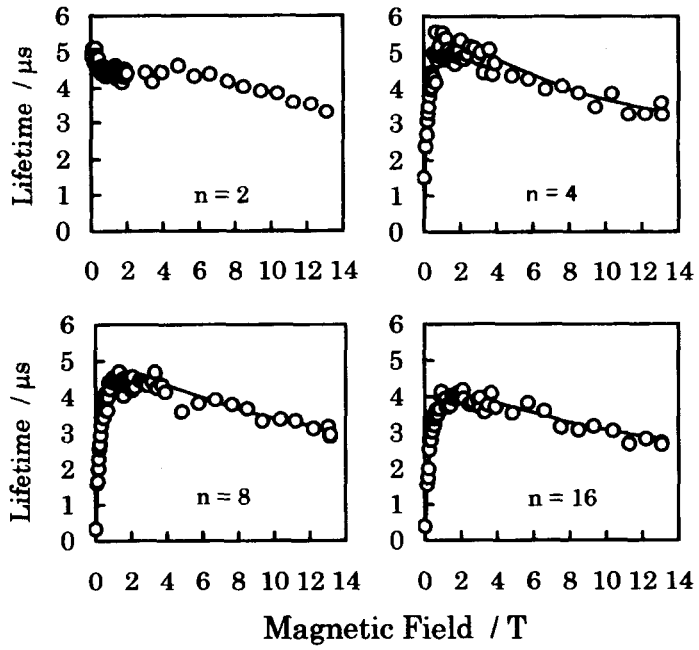


Fig. 1. Magnetic field effects on the lifetime of ^{3}(BPH$^\bullet$–O–n–O–DPA$^\bullet$) in DMF (n = 2, 4, 8, 16). Open circles are observed. Solid lines are simulated curves using Eq. 2. See text.

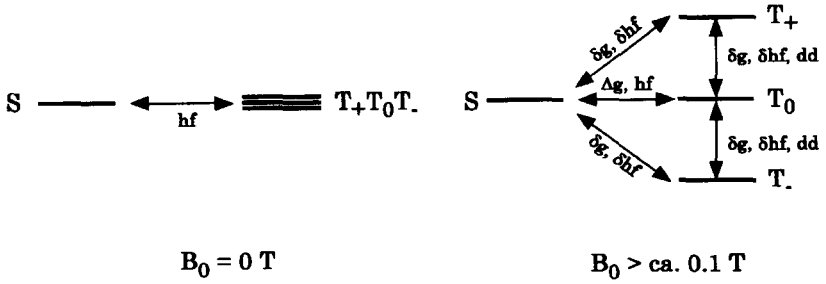


Fig. 2. Energy levels and spin conversion process of a biradical with a nearly degenerate S–T energy gap.

where k(BPH$^\bullet$: δhf, δg) and k(DPA$^\bullet$: δhf, δg) are the SLR rate constants at BPH$^\bullet$ and DPA$^\bullet$ which are governed by the δhf and δg mechanism and k(dd) is the rate constant due to the dd mechanisms. In general, the MFD of the lifetime of ^{3}(BPH$^\bullet$–O–n–O–DPA$^\bullet$) with n = 8 or 16 should be analyzed using Eq. 1. However, it is very difficult to separate the two rate constants: k(BPH$^\bullet$: δhf, δg) and k(DPA$^\bullet$: δhf, δg). Furthermore, the mathematical expression for k(dd) is also identical with that for the relaxation rate constant due to the δhf interaction. Thus, it is practically impossible to analyze the data using Eq. 1 For these reasons, the MFD of the biradical lifetime is analyzed using the following *empirical* expression:[6–8]

$$k_{BR} = 1/\tau_{BR} = k(\delta\mathrm{hf},\mathrm{dd}) + k(\delta g) + k_T, \tag{2}$$

where

$$k(\delta\mathrm{hf},\mathrm{dd}) = \gamma^2 H_{\mathrm{eff}}^2 \tau_c'' / (1 + \gamma^2 B_0^2 \tau_c''^2), \tag{3}$$

$$k(\delta g) = (1/5)(\beta/\hbar)^2 (g:g)_{\mathrm{eff}} B_0^2 \tau_c''' / (1 + \gamma^2 B_0^2 \tau_c'''^{\,2}). \tag{4}$$

The term $k(\delta\mathrm{hf}, \mathrm{dd})$ is the contribution from the δhf interactions at BPH$^\bullet$ and DPA$^\bullet$ and from the dd interaction between two radicals to the decay rate constant. $k(\delta g)$ is the contribution from the δg interactions at two radicals. H_{eff}, τ_c'', and γ are the effective locally fluctuating magnetic field due to the δhf interaction, its correlation time, and the magnetogyric ratio of an electron. β, $\hbar$, $(g:g)_{\mathrm{eff}}$, and τ_c''' are the Bohr magneton, the Planck constant devided by 2π, the effective inner product of the anisotropic g tensor and its correlation time, respectively. B_0 is the external magnetic field.

In the low magnetic field region (0.1—1 T), $k(\delta g)$ can be neglected from Eq. 2, since the contribution of the SLR due to the δg interaction to the biradical lifetime is considered to be small, giving the following equation:

$$1/(k_{BR} - k_T) = 1/\gamma^2 H_{\mathrm{eff}}^2 \tau_c'' + (\tau_c''/H_{\mathrm{eff}}^2) B_0^2. \tag{5}$$

Parameters k_T, H_{eff}, τ_c'', are calculated using Eq. 5. The $1/(k_{BR} - k_T)$ values are plotted against B_0^2 for a tentatively assumed k_T value. The k_T value is then determined from the one obtained when the plot of $1/(k_{BR} - k_T)$ vs. B_0^2 becomes linear. The parameters H_{eff}^2 and τ_c'' are obtained from the slope and intersection of the straight line calculated by the least squares method.

Figure 3 shows the plot of Eq. 5 for the lifetime of

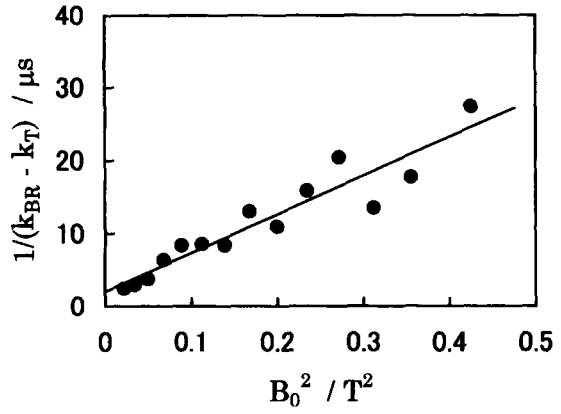


Fig. 3. Plot of $1/(k_{BR}-k_T)$ vs. B_0^2 for ^{3}(BPH$^\bullet$–O–16–O–DPA$^\bullet$).

^{3}(BPH$^\bullet$–O–16–O–DPA$^\bullet$). From this analysis, k_T, H_{eff}^2, and τ_c'' are obtained to be 2.38×10^5 s^{-1}, 5.84×10^{-7} T^2 and 30 ps (Table 2).

In the high magnetic field region (2—13 T), the lifetime of ^{3}(BPH$^\bullet$–O–16–O–DPA$^\bullet$) decreases gradually. The MFD of the lifetime of the biradical is analyzed by a numerical simulation method using Eq. 2. Only the values of $(g:g)_{eff}$ and τ_c''' are varied, whereas k_T, H_{eff}^2, and τ_c'' values obtained from the analysis in the low magnetic field are used and kept fixed.

Figure 4(a) shows the influence of $(g:g)_{eff}$ on the MFD of the lifetime for ^{3}(BPH$^\bullet$–O–16–O–DPA$^\bullet$), when the value of τ_c''' is fixed at 0.5 ps. If the value of $(g:g)_{eff}$ is 2.0×10^{-5}, the lifetime decreases very rapidly, and if it is 2.0×10^{-7}, it is almost constant. When the value of $(g:g)_{eff}$ is 2.0×10^{-6}, the calculated curve is in good agreement with the observed data. Figure 4(b) shows the influence of τ_c''' when $(g:g)_{eff}$ is fixed at 2.0×10^{-6}. The most reasonable value of τ_c''' is 0.5 ps. From the numerical analysis, the values of $(g:g)_{eff}$ and τ_c''' are obtained to be 2.0×10^{-6} and 0.5 ps.

Table 2. The Values of k_T, H_{eff}^2, and τ_C'' for ^{3}(BPH$^\bullet$–O–*n*–O–DPA$^\bullet$) [a)]

n	$k_T/10^5$ s^{-1}	H_{eff}^2/mT^2	τ_c''/ps
4	1.84	0.29	24
8	2.07	0.48	35
16	2.38	0.58	30

a) Experimental errors are ±20%.

The MFD of the lifetime of ^{3}(BPH$^\bullet$–O–8–O–DPA$^\bullet$) is similarly analyzed; all the parameters obtained in the low magnetic field region are summarized in Table 2. The MFD of the lifetime in the higher field is reproduced with combination of the above parameters and those for ^{3}(BPH$^\bullet$–O–16–O–DPA$^\bullet$) obtained from the analysis in the high field. The simulated curve is in good agreement with the experimental results, as shown in Fig. 1.

In the case of ^{3}(BPH$^\bullet$–O–4–O–DPA$^\bullet$), the S–T energy gap is 40 mT.[9] Thus the above model may not be applicable for the analysis of the lifetime of this biradical. However, in order to examine the applicability of Eq. 2 to the biradical with an S–T energy gap of 40 mT, we attempted to analyze the MFD of the lifetime of this biradical using Eq. 2. The parameters k_T, H_{eff}^2, τ_c'' are listed in Table 2. The MFD of the lifetime in the higher field is reproduced with combination of the above parameters and those for ^{3}(BPH$^\bullet$–O–16–O–DPA$^\bullet$) obtained from the analysis in the high field. The simulated curve is in good agreement with the experimental results, as shown in Fig. 1.

Lifetime of ^{3}(BPH$^\bullet$–O–2–O–DPA$^\bullet$). The MFD of the lifetime of ^{3}(BPH$^\bullet$–O–2–O–DPA$^\bullet$), shown in Fig. 1, is very different from those of the other biradicals studied here. In this biradical, the S–T energy gap is estimated to be ca. 2 T from a shallow dip which appears in the figure. The MFD is not analyzed because there is no theoretical model to apply for the biradical with a large S–T energy gap.

Discussion

Lifetime of ^{3}(BPH$^\bullet$–O–*n*–O–DPA$^\bullet$) with *n* = 4, 8, 16. The degrees, *R*, of the reversal of MFE are obtained to be 38 (*n* = 4), 34 (*n* = 8), and 36% (*n* = 16). They are intermediate between the value for the biradicals composed of two carbon-centered radicals (5—20%)[3,6–8] and the one composed of two nitrogen-centered radicals (ca. 70%).[4] The *R* values obtained here are reasonable for a biradical composed of one carbon-centered radical and one nitrogen-centered radical, though other parameters may also influence the MFD

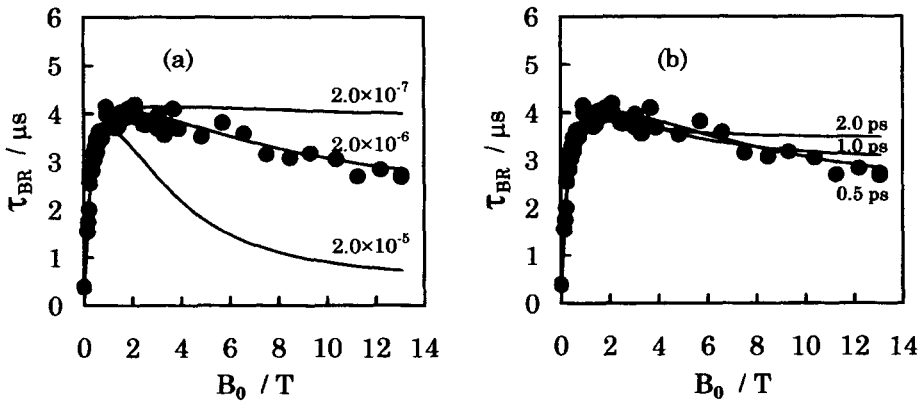


Fig. 4. Influence of $(g:g)_{eff}$ and τ_c''' on the MFD of the lifetime of ^{3}(BPH$^\bullet$–O–16–O–DPA$^\bullet$). (a) τ_c''' is fixed at 0.5 ps and $(g:g)_{eff}$ is varied from 2.0×10^{-5} to 2.0×10^{-7}. (b) $(g:g)_{eff}$ is fixed at 2.0×10^{-6} and τ_c''' is varied from 0.5 to 2.0 ps.

of the biradical lifetime. Furthermore, in the case of the biradicals composed of two protonated diphenylketyl radicals BPH$^{\bullet}$–O–$(CH_2)_n$–O–BPH$^{\bullet}$ (n = 10, 12), R is 6—7%.[7] This indicates that the large reversal of MFE observed in ^{3}(BPH$^{\bullet}$–O–n–O–DPA$^{\bullet}$) with n = 4, 8, 16 is attributable to the g anisotropy of DPA$^{\bullet}$. Deviation of the electron g value of a radical from that of a free electron arises from the spin-orbit interaction.[12] Since spin-orbit coupling constants for carbon atom and nitrogen atom are 28 and 76 cm^{-1}, respectively, it seems that the g anisotropy in a nitrogen-centered radical is larger than that in a carbon-centered radical.

In the case of ^{3}(XOH$^{\bullet}$–CO_2–$(CH_2)_n$–OCO–X$^{\bullet}$) with n = 3, 5, 6, 8, 12, 16, composed of a 9-hydroxy-9-xanthenyl radical (XOH$^{\bullet}$) and a 9-xanthenyl radical (X$^{\bullet}$), k_T, H^2_{eff}, and τ_c'' vary from 2.9×10^5 to 0.8×10^5 s^{-1}, from 1.54 to 0.39 mT^2, and from 10 to 30 ps, respectively, with increasing of n from 3 to 16.[8] The parameters obtained here are similar to those for ^{3}(XOH$^{\bullet}$–CO_2–$(CH_2)_n$–OCO–X$^{\bullet}$) with n = 8—16. In the present biradical, the k_T value for ^{3}(BPH$^{\bullet}$–O–16–O–DPA$^{\bullet}$) is slightly smaller than that for ^{3}(BPH$^{\bullet}$–O–8–O–DPA$^{\bullet}$), though the number of linkers is larger in the former than in the latter. This is consistent with the previous observation that the ratios of the biradical lifetime in the presence and absence of 0.56 T,[9] which may represent the magnitude of the MFE, are 11.8 (n = 16) and 14.2 (n = 8). With increasing n the MFE decreases. These facts suggest that the mean interradical distance is slightly smaller in ^{3}(BPH$^{\bullet}$–O–16–O–DPA$^{\bullet}$) than in ^{3}(BPH$^{\bullet}$–O–8–O–DPA$^{\bullet}$). Shrinkage in the end-to-end distance of bifunctional chain molecules may occur via solute–solvent specific interaction, though its mechanism is not understood.

The H^2_{eff} for ^{3}(BPH$^{\bullet}$–O–n–O–DPA$^{\bullet}$) decreases with increasing n, as shown in Table 2, though H^2_{eff} values are expected to decrease, as observed for the case of ^{3}(XOH$^{\bullet}$–CO_2–$(CH_2)_n$–OCO–X$^{\bullet}$). In the present biradicals, the seemingly small H^2_{eff} value for ^{3}(BPH$^{\bullet}$–O–4–O–DPA$^{\bullet}$) may arise from the fact that Eq. 1, which is applicable only for the biradical with *degenerate* S and T states, is tentatively used for analysis of the biradical with *non-degenerate states* ($2J$ = 40 mT). An unexpectedly large H^2_{eff} value for ^{3}(BPH$^{\bullet}$–O–16–O–DPA$^{\bullet}$) is attributable to the shrinkage in the end-to-end distance of the chain, since the increase of H^2_{eff} for this biradical is in parallel with that of k_T, as discussed above. Thus n-dependence of H^2_{eff} shown in Table 2 is not essential but accidental.

The correlation time τ_c'' of ca. 30 ps for the present biradicals may be chiefly attributable to that for the δhf interaction, by analogy with the value for XOH$^{\bullet}$–CO_2–$(CH_2)_n$–OCO–X$^{\bullet}$ with n = 8, 12, 16.[8]

The correlation time τ_c''' for ^{3}(BPH$^{\bullet}$–O–n–O–DPA$^{\bullet}$) with n = 8 or 16 is estimated to be 0.5 ps. This value is in agreement with the values (1 ps) for ^{3}(XOH$^{\bullet}$–CO_2–$(CH_2)_n$–OCO–X$^{\bullet}$) (n = 12, 16)[8] and for Ph$^{+\bullet}$–$(CH_2)_{12}$–V$^{+\bullet}$ composed of a 10-phenothiazinyl cation radical (Ph$^{+\bullet}$) and a N-propyl-4,4′-bipyridyl cation radical (V$^{+\bullet}$). As discussed in detail in a previous paper,[4] this short correlation time may be associated with a local motion such as an internal rotation of phenyl groups at a nitrogen atom in DPA$^{\bullet}$. It is interesting to note that short correlation times of 1 ps or less than 1 ps are also reported for the radical pairs in micellar solutions.[13,14] Biradicals and radical pairs undergo various conformational changes. From a wide spectrum of their frequencies, only a frequency energetically matched to a specific transition may be sorted out.

In the case of ^{3}(BPH$^{\bullet}$–O–4–O–DPA$^{\bullet}$) having an S–T energy gap of ca. 40 mT, parameters obtained are in reasonable agreement with the values for the biradicals having degenerate S and T states. This similarity may arise partly from the flexibility of the biradical conformation. The end-to-end distance of the biradical linked by a flexible chain is not fixed, but varies rapidly with time. Thus parameters obtained experimentally are the conformation-averaged values. This may imply that the S–T transition may take place considerably at the elongated chain conformation where an S–T energy gap is very small, while the transition at the closed conformation with a large gap does not contribute significantly to the biradical lifetime.

Lifetime of ^{3}(BPH$^{\bullet}$–O–2–O–DPA$^{\bullet}$).

With increasing the magnetic field from zero to 13 T, one finds that the lifetime of ^{3}(BPH$^{\bullet}$–O–2–O–DPA$^{\bullet}$) decreases gradually with a shallow dip at ca. 2 T, as shown in Fig. 1. This dip is attributable to the S–T$_-$ level crossing and corresponds to the S–T energy gap in this biradical. The energy gap of ca. 2 T is the largest value obtained by the transient absorption and fluorescence measurements. In a previous paper,[9] it is suggested that the level crossing occurs at > 1 T for ^{3}(BPH$^{\bullet}$–O–2–O–DPA$^{\bullet}$). The present observation is consistent with this prediction. As schematically shown in Fig. 5, the S–T energy gap due to the exchange interaction sharply increases on decreasing the chain length n.

In the higher magnetic field above ca. 4 T, the lifetime of ^{3}(BPH$^{\bullet}$–O–2–O–DPA$^{\bullet}$) decreases gradually. This decrease may be attributable to the relaxation due to the δg mechanism by analogy of MFD of the lifetime of other biradicals.

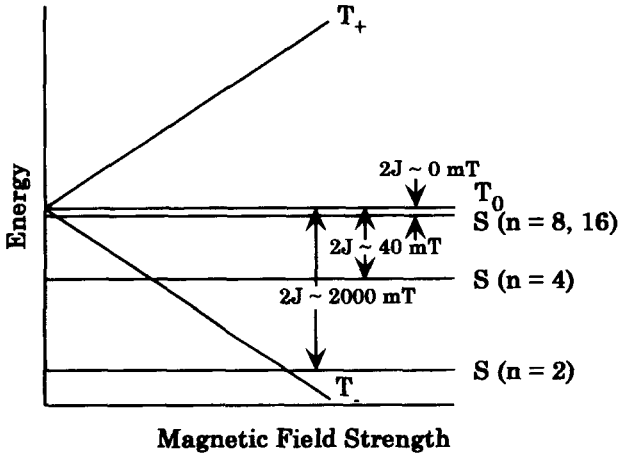


Fig. 5. Energy diagram of BPH$^{\bullet}$–O–n–O–DPA$^{\bullet}$.

Summary

The MFE ($\leqq$ 13 T) on the lifetime of ^{3}(BPH$^\bullet$–O–*n*–O–DPA$^\bullet$) with n = 2, 4, 8, 16 has been studied. On increasing the magnetic field from 0 to ca. 2 T, the lifetime of ^{3}(BPH$^\bullet$–O–*n*–O–DPA$^\bullet$) with n = 4, 8, 16, increases steeply, and then decreases gradually in higher magnetic field up to 13 T. The degree R of the reversal is ca. 34—38%. This value is consistent with the values estimated for the biradical composed of a carbon-centered radical and a nitrogen-centered radical. This drastic reversal of the effect is quantitatively interpreted in terms of the spin lattice relaxation which is induced by the anisotropic Zeeman interaction (δg mechanism). It is found that the g anisotropy of a nitrogen atom of DPA$^\bullet$ may take an important role in the large R value in the present biradicals. The MFE on the lifetime of ^{3}(BPH$^\bullet$–O–2–O–DPA$^\bullet$) is interpreted in terms of the level crossing and SLR. The S–T energy gap in ^{3}(BPH$^\bullet$–O–2–O–DPA$^\bullet$) is about 2 T.

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