December, 1989] © *1989 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.*, ***62***, *3923—3931 (1989)*

Laser Flash Photolysis Study of the Magnetic Field Effects on the Biradicals Generated from Aromatic Ketone-Xanthene Bifunctional Chain Molecules

Yoshifumi TANIMOTO,* Masanobu TAKASHIMA, and Michiya ITOH
Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920

(Received June 26, 1989)

The external magnetic field effects (MFE) on the biradicals generated from the intramolecular photoreactions of bifunctional chain molecules, α-(xanthone-2-carbonyloxy)-ω-(xanthene-2-carbonyloxy)alkanes (XO-*n*-XH, n=2—12) and Ar-12-XH (Ar=anthraquinone-4-carbonyloxy (AQ), 4-benzoylphenoxy (BP), and 4-acetylphenoxy (AP)) were studied by laser flash photolysis. All biradicals exhibit significant MFE. The simultaneous observation of the effects on the two radicals at the ends of the chain, generated from XO-12-XH, AQ-12-XH, and BP-12-XH, presents unequivocal evidence that the respective two radical centers correlate magnetically each other. The *n* dependence of the effects on biradicals generated from XO-*n*-XH indicates that the singlet-triplet degeneracy of the biradical occurs at the chain length of around n=6, i.e., the interradical distance of about 15 Å.

In the middle of 1970's, magnetic field effects (MFE) on radical reactions have been successfully interpreted in terms of the radical pair mechanism, in which the triplet (T)-singlet (S) intersystem crossing (isc) of a radical pair, a short-lived intermediate, is affected by a magnetic field.[1] It is speculated that the significant MFE could be observable when the lifetime of a pair is considerably long. In homogenous solution, however, the diffusive separation of the components of a pair competes with isc, leading to the shortening of the lifetime of the pair. These considerations suggest that MFE on bimolecular reactions in homogeneous solutions are rather insignificant, if any. In this regard, such a microheterogeneous solution as a micellar solution is expected to present us an ideal environment for sufficient T-S development of a radical pair. In an aqueous micellar solution, for example, the separation of the component radicals in a radical pair is considerably slow, because of the dimentionality of the micelle, and the microviscosity and polarity in it. Therefore, the isc, which is the magnetic field dependent process, can become the rate-controlling process. Based on the above-mentioned argument, quite a few numbers of research groups have studied MFE on photoreactions in micellar solutions and microemulsions.[2–7] Our main interest has been the MFE on the hydrogen abstraction reaction of aromatic ketones in micellar solutions.[5] Particularly, in order to confirm the mechanism, the MFE have been examined in detail in the hydrogen abstraction reaction of xanthone from xanthene.[5e] Then, new questions arise as for the roles of a micellar cage. a) What is the key factor for the significant effect, though dimentionality, polarity, microviscosity and others are expected to influence the lifetime of a radical pair? b) At what distance between the two radicals does the S-T degeneracy of a pair occur? However, the analysis of the photoreactions in microheterogeneous systems is too complex to answer these questions, since a micellar solution is the statistical ensemble of micelles with different sizes, and since microviscosity and polarity in a micelle depend on location in it.[8]

In order to answer these questions and to elucidate the governing factors in MFE, we have designed the end-to-end photoreactions of bifunctional chain molecules in homogeneous solutions as the intramolecular analogue of the bimolecular reaction of aromatic carbonyls in micellar solutions. First example was the intramolecular photoreaction of *n*-alkyl anthraquinone-2-carboxylates,[9] as the analogue of the reaction of anthraquinone in micellar solution.[5c,d] The hydrogen abstraction reaction of the excited triplet quinone from its methylene side chain generates the biradicals composed of alkyl and semiquinone radicals. It was shown that the S-T degeneracy of the biradicals occurs at the chain length of n=12 or so, from the MFE on the reaction yields under the steady-state photolysis. This system was, however, found to be inadequate for the dynamical study of MFE on the biradicals, since the rate-controlling step was not the isc but the generation of biradicals. In the present paper,[10] we report on MFE on the dynamics of the biradicals generated from the intramolecular abstraction reaction of the bifunctional chain molecules composed of the aromatic carbonyls (H acceptor) and xanthene (H donor) moieties, as the analogue of the radical pairs generated from the corresponding reaction in micellar solution.[5]

Experimental

Materials. Xanthone-2-carboxylic acid and xanthene-2-carboxylic acid were prepared with the literature procedure.[11,12] Xanthone-2-carboxylic acid (9.6 g, 0.04 M) in *N,N*-dimethylacetamide (DMAc, 130 ml) was slowly added into a hot DMAc solution (40 ml) of 1,12-dibromododecane (39.4 g, 0.12 M) and K_2CO_3 (6.1 g, 0.044 M), and the solution was then stirred at 90 °C for 6 h (1 M=1 mol dm^{-3}). The reaction mixture was treated with water, extracted with chloroform, and purified by chromatography, yielding a white solid of α-bromo-ω-(xanthone-2-carbonyloxy)dodecane (12.7 g): Mp 78—79 °C. ^{1}H NMR (60 MHz, $CDCl_3$): δ=1.18—2.00 (s, 20H, $-CH_2-$), 3.35 (t, 2H, $-CH_2-Br$), 4.32 (t, 2H, $-CO_2-CH_2-$), 7.10—8.92 (m, 7H, aromatic). IR (KBr): 2920—2850 (methylene), 1720 (aromatic ester), 1663 cm^{-1} (aromatic ketone). Calcd for $C_{26}H_{31}O_4Br$: C, 64.07; H, 6.41%. Found C, 64.26; H, 6.53%. M, 488.

α-Bromo-ω-(xanthone-2-carbonyloxy)dodecane (12.18 g, 0.025 M) was added into a hot DMAc solution (40 ml) of xanthene-2-carboxylic acid (5.99 g, 0.0265 M), and K_2CO_3 (4.14 g, 0.03 M), and the solution was stirred at 90 °C for 8 h. The reaction mixture was treated with water, extracted with chloroform, and purified by chromatography and recrystallization, yielding a white solid of α-(xanthone-2-carbonyloxy)-ω-(xanthene-2-carbonyloxy)dodecane (XO-12-XH, 6.6 g).

Other chain molecules, Ar-*n*-XH (Ar=xanthone-2-carbonyloxy (XO, *n*=2—10), anthraquinone-2-carbonyloxy (AQ, *n*=12), 4-benzoylphenoxy (BP, *n*=12), 4-acetylphenoxy (AP, *n*=12)), and 1-(xanthone-2-carbonyloxy)dodecane (XO-12) were prepared in an analogous manner. Their melting points are shown in Table 1, and the typical spectral data of chain molecules are given as follows:

XO-12-XH. ^{1}H NMR (60MHz, $CDCl_3$): δ=1.18—2.00 (s, 20H, $-CH_2-$), 4.02 (s, 2H, methylene of XH), 3.97—4.47 (m, 4H, $-CO_2-CH_2-$), 6.87—8.93 (m, 14H, aromatic). IR(KBr): 2910—2830 (methylene), 1725 (aromatic ester), 1673 cm^{-1} (aromatic ketone). Calcd for $C_{40}H_{40}O_7$: C, 75.93; H, 6.37%. Found: C, 75.71; H, 6.34%. M, 632.

AQ-12-XH. ^{1}H NMR($CDCl_3$): δ=1.18—2.00 (s, 20H, $-CH_2-$), 4.02 (s, 2H, methylene of XH), 4.2—4.46 (m, 4H, $-CO_2-CH_2-$), 6.83—8.87 (m, 14H, aromatic). IR(KBr): 2910—2840 (methylene), 1730 (ester), 1678 cm^{-1} (ketone). Calcd for $C_{41}H_{40}O_7$: C, 76.37; H, 6.25%. Found: C, 76.42; H, 6.25%. M, 645.

BP-12-XH. ^{1}H NMR ($CDCl_3$): δ=1.18—2.00 (s, 20H, $-CH_2-$), 4.03 (s, 2H, methylene of XH), 3.85—4.37 (m, 4H, $-CO_2-CH_2-$, $-O-CH_2-$), 6.76—7.84 (m, 16H, aromatic). IR(KBr) 2920—2840 (methylene), 1710 (ester), 1640 cm^{-1} (ketone). Calcd for $C_{39}H_{42}O_5$: C, 79.29; H, 7.17%. Found: C, 79.38; H, 7.19%. M, 591.

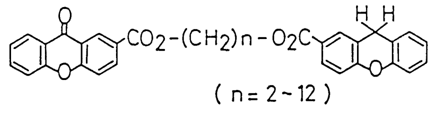
Table 1. Melting Points of Chain Molecules

Ar-*n*-XH	Mp/°C	Ar-*n*-XH	Mp/°C
XO-2-XH	214—215	XO-10-XH	165—166
XO-3-XH	140—141	XO-12-XH	121—122
XO-4-XH	189—190	AQ-12-XH	135—136
XO-5-XH	156	BP-12-XH	82—83
XO-6-XH	177—178	AP-12-XH	99—100
XO-8-XH	149—150	XO-12	79—80

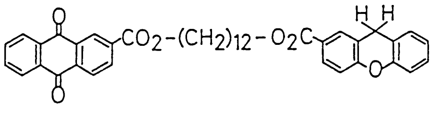
AP-12-XH. ^{1}H NMR($CDCl_3$): δ=1.18—2.00 (s, 20H, $-CH_2-$), 2.49 (s, 3H, $-CO-CH_3$), 4.02 (s, 2H, methylene of XH), 3.83—4.36 (m, 4H, $-O-CH_2-$, CO_2-CH_2-), 6.69—7.95 (m, 11H, aromatic). IR(KBr): 2920—2840 (methylene), 1710 (ester), 1670 cm^{-1} (ketone). Calcd for $C_{34}H_{40}O_5$; C, 77.24; H, 7.63%. Found C, 77.17; H, 7.91%. M, 528.

Spectrograde acetonitrile (AcCN) and benzene were used as received. Concentrations of solutes were ≈10^{-4} M and all solutions were deaerated by freeze-pump-thaw cycles.

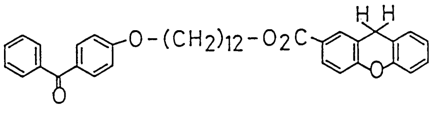
Laser Flash Photolysis. Figure 1 shows the experimental setup for a nanosecond laser flash photolysis. A sample cell (10×5 mm) placed between pole pieces of a small



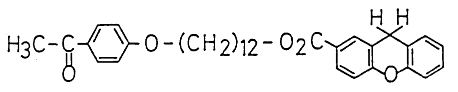
XO-n-XH



AQ-12-XH



BP-12-XH



AP-12-XH

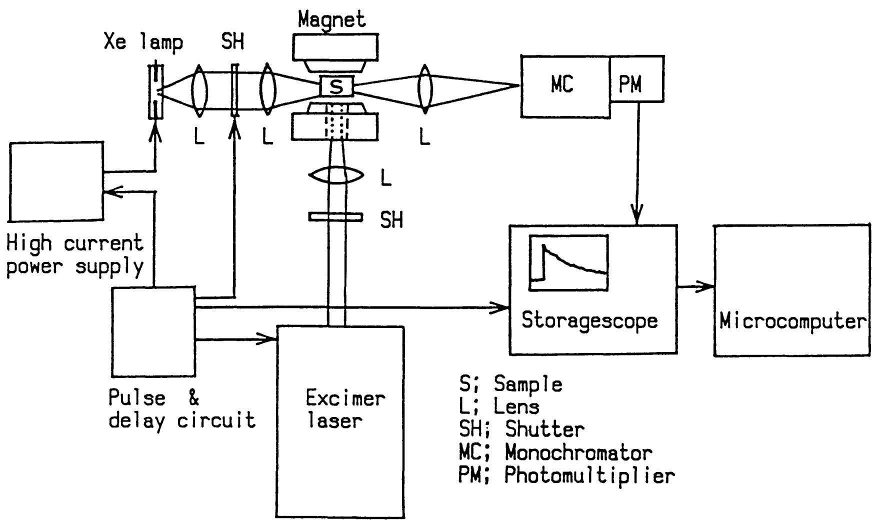


Fig. 1. Experimental setup of a laser flash photolysis apparatus.

electromagnet (Tokin SEE-9, <1 T) was irradiated by a light from an excimer laser (Lambda Physik EMG-50E, 308 nm) or an N_2 laser (Molectron UV-12, 337 nm) through a small hole (10 mm in diameter) on a pole piece. A xenon arc lamp (Ushio UXL-500-O) was used as a probe light source, whose intensity was intensified by applying a pulse of a high electric current (100 A, 3 ms). A laser, a probe light, and a high-speed electric shutter (Copal No. 0) were synchronized with a home-made pulse and delay circuit. The transient signal was detected by a combination of a monochromator (Ritsu NC-10N), a photomultiplier (HTV R-666), and a storagescope (Iwatsu TS-8123), and was fed into a microcomputer (Fujitsu FM-11BS) for analysis. Residual field of an electromagnet was canceled by applying a dc current (<0.3 mT).

In analysis of transient decay curves, the initial decaytime (1/e) was defined as the apparent lifetime (τ), as, in some cases, they deviated slightly from an exponential function.

Calculation of Interradical Distance. The radical-radical distance at the two ends of a methylene chain was calculated at 25 °C for biradicals generated from XO-*n*-XH by the direct enumeration method described in detail in the literature.[13] Here, the radical centers were assumed to be the carbon atoms at 9-position of XO and XH, respectively. The model considered for the methylene chain was the rotational isomeric state model, where all the C-C bonds of the methylene chain were assumed to be one of the three rotational isomers, trans (t), gauche (g^+, 120°), and gauche (g^-, −120°), and the relative orientation of C=O and O-C bonds at the ester was fixed in the trans form. Conformational energies were allotted as 0 cal mol^{-1} for t, 500 cal mol^{-1} for $g^\pm$, respectively. For $g^\pm g^\mp$ sequence, 2000 cal mol^{-1} was added.

Results and Discussion

1. Magnetic Field Effects on the Transient Absorption of Ar-12-XH.

XO-12-XH. Figure 2 shows transient absorption spectra of XO-12-XH and XO-12 in acetonitrile. An intense and broad band around 620 nm (τ, 2 μs) of XO-12, having no XH chromophore, is assigned to the triplet-triplet (T-T) absorption of the xanthone (XO) chromophore.[5c,14] Absence of the absorption band of a xanthone ketyl radical around 490 nm[14] indicates that the hydrogen abstraction of the excited triplet XO, ^{3}XO*, from its methylene chain and the solvent is insignificant in the present time scale (<10 μs).

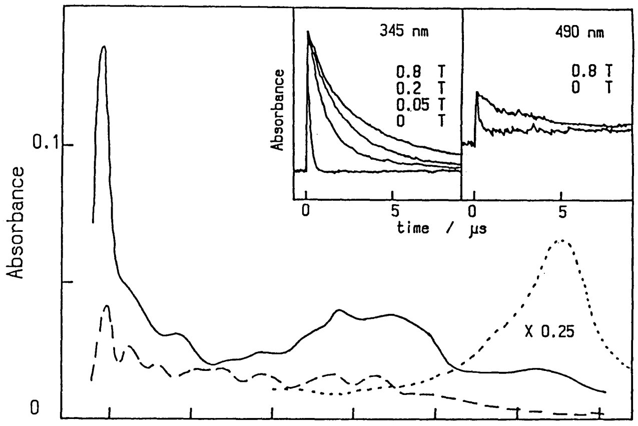


Fig. 2. Transient absorption spectra of XO-12-XH and XO-12 in acetonitrile. —— and ---- are the spectra of XO-12-XH monitored at 0.15 and 0.4 μs delay after laser excitation, respectively. ······· is the spectrum of XO-12 at 0.2 μs delay. Insets are magnetic field effects on the decay curves of transients.

In the spectra of XO-12-XH, a sharp band at 345 nm and a weak one around 500 nm are assigned to the xanthenyl ($\dot{\mathrm{X}}$) and xanthone ketyl ($\dot{\mathrm{X}}$OH) radical, respectively, from the comparison with the spectra reported in the literature.[5c,14,15] Since they appear concurrent with the rapid decrease (<10 ns) of the T-T absorption of XO around 620 nm, the hydrogen abstraction of the excited triplet, ^{3}XO*, of XO from the XH chromophore at the other end of the chain, results in the generation of a triplet biradical of $\dot{\mathrm{X}}$ and $\dot{\mathrm{X}}$OH, ^{3}($\dot{\mathrm{X}}$OH-12-$\dot{\mathrm{X}}$). Intermolecular photoreaction is not involved in the reaction of XO-12-XH in the present time scale, since the generation of a xanthenyl radical is very slow (risetime, 780 ns) in the corresponding intermolecular reaction of xanthone (1.4×10^{-4} M) and xanthene (1.4×10^{-4} M).

The effects of external magnetic fields on the decay curves of $\dot{\mathrm{X}}$ (345 nm) and $\dot{\mathrm{X}}$OH (490 nm) chromophores are shown in the insets of Fig. 2. Significant MFE were observed in the intramolecular reaction of XO-12-XH, though no appreciable effect was detected in the corresponding intermolecular reaction of xanthone and xanthene. Lifetimes of $\dot{\mathrm{X}}$ and $\dot{\mathrm{X}}$OH in the $\dot{\mathrm{X}}$OH-12-$\dot{\mathrm{X}}$ biradicasl are 0.14 and 0.18 μs at zero field, respectively, while they are 3 and 4 μs at 0.8 T, respectively. Small disagreement of the lifetimes determined from the two chromophores may result from the contamination of photoproducts. The simultaneous observation of MFE on the two radicals presents unequivocal evidence that the two radicals at the ends of the chain correlate magnetically each other. These findings are in good agreement with our previous observation that two radicals composing a pair exhibit MFE simultaneously in a micellar cage.[5f]

Furthermore, analogous MFE were observed for the transients of XO-12-XH in benzene solution (Table 2). The lifetime of $\dot{\mathrm{X}}$OH-12-$\dot{\mathrm{X}}$ in a magnetic field is about two times longer in benzene than in acetonitrile. This might be attributable to the conformational difference and/or the different reactivity of the biradical in the two solvents. Since XO-12-XH is less soluble in acetonitrlie than in benzene, its average conformation in acetonitrile may be rather compact compared with that in benzene. This difference of conformations may somewhat affect the lifetime in magnetic fields. An alternative explanation is the reactivity of the biradical The diffusion-controlled reaction-rate in benzene is considered to be about two times smaller than in acetonitrile, taking into account of the viscosity of two solvents (acetonitrile (0.345 cp; 1 p=0.1 Pa s) and benzene (0.649 cp)). Thus, in a high field, the lifetime of the biradical may be shorter in acetonitrile than in benzene, if diffusion-controlled bimolecular reactions take place substantially. The polarity of a solvent itself, therefore, does not affect the magnitude of MFE on the neutral biradical significantly.

Other Bifunctional Chain Molecules. Analogous chain molecules, AQ-12-XH, BP-12-XH, and AP-12-XH exhibit similar end-to-end photoreactions. Intramolecular hydrogen abstraction from the methylene chain may not be involved significantly in these reactions in the time scale of the present observation (<10 μs), since intramolecular hydrogen abstraction of alkyl anthraquinone-2-carboxylates and alkyl benzophenone-4-carboxylates is insignificant in that time scale,[9,16] and since the excited triplets of anthraquinone, benzophenone, and acetophenone react readily with xanthene in micellar solution.[5g]

In the transient spectra of AQ-12-XH in benzene (Fig. 3a), absorption bands of Ẋ and anthrasemiquinone radical (ȦQH) appear at 345 and 380 nm, respectively.[5b,17] Here, benzene is used as a solvent on account of solubility. The decay curves of both bands exhibit remarkable MFE as shown in the insets.

In the laser flash photolysis of BP-12-XH in acetonitrile, absorption bands appear around 340 and 530 nm (Fig. 3b). The former band is mostly attributable to the sum of absorptions of Ẋ, benzophenone ketyl radical ḂPH, and T-T absorption of BP.[3a,18] On the other hand, a weak band around 530 nm may be composed of T-T absorption of BP (≈510 nm) and that of ḂPH (≈540 nm), since its peak shifts slightly toward longer wavelengths with time.[3b] Indeed, the transient decay curve monitored at 510 nm is scarcely affected by a magnetic field, as expected. Hydrogen abstraction reaction in BP-12-XH is considered to be slower than XO-12-XH and AQ-12-XH, as the lifetime of the T-T absorption of BP monitored at 510 nm was estimated to be 0.2 μs. Significant MFE were observed on the decay curves at 345 nm (Ẋ and ḂPH) and at 545 nm (ḂPH) as shown in the insets of Fig. 3b, though the accurate determination of the biradical lifetime was difficult due to the interferrence of the T-T band of the BP chromophore in both wavelength region. The lifetime of the biradical determined from the former band, however, seems to be less contaminated by the decay of T-T band, because of high absorption intensities of Ẋ and ḂPH radicals.

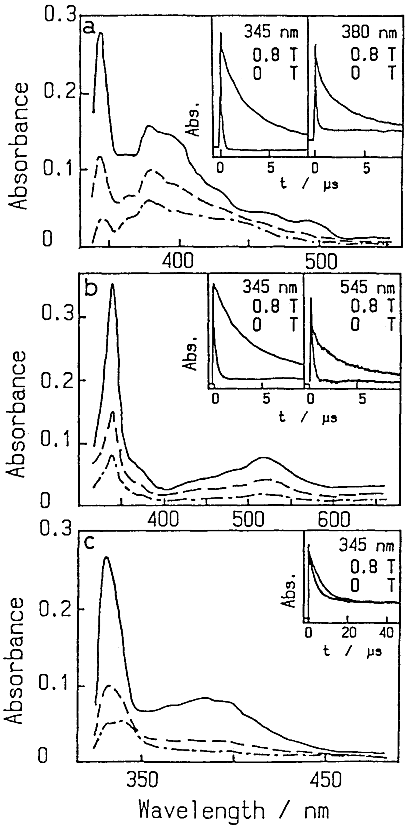


Fig. 3. Transient absorption spectra of bifunctional chain molecules. (a) AQ-12-XH in benzene. Delaytimes are 0.12 (——), 0.5 (----), and 1 μs (—·—). (b) BP-12-XH in acetonitrile. Delaytimes are 0.25 (——), 1 (----), and 5 μs (—·—). (c) AP-12-XH in acetonitrile. Delaytimes are 2 (——), 10 (----), and 20 μs (—·—). Insets in the respective figures are the magnetic field effects on the decay curves of transients.

In the case of AP-12-XH in acetonitrile (Fig. 3c), the rate of hydrogen abstraction is much slower than that of BP-12-XH. Absorption bands around 320 and 390 nm are mainly assigned to the T-T absorption of

Table 2. Lifetimes of Biradicals[a]

ArH-12-Ẋ Solvent	ẊOH-12-Ẋ AcCN	ẊOH-12-Ẋ Benzene	ȦQH-12-Ẋ Benzene	ḂPH-12-Ẋ AcCN	ȦPH-12-Ẋ AcCN
τ(0 T)	0.14 (345 nm)[b]	0.13 (345 nm)	0.14 (345 nm)	0.38[c] (345 nm)	8[c] (345 nm)
μs	0.18 (490 nm)	0.20 (490 nm)	0.17 (380 nm)	0.23[c] (545 nm)	
τ(0.8 T)	3.0 (345 nm)	4.2 (345 nm)	3.0 (345 nm)	5.1 (345 nm)	10[c] (345 nm)
μs	4.0 (490 nm)	4.8 (490 nm)	3.4 (380 nm)	5.7 (545 nm)	

a) Experimental errors are ±20%. b) Wavelength where transient decay curves were monitored. c) Measurements were difficult due to the interference from the T-T absorption. See text.

AP,[19,20] whose lifetime is estimated to be 3.3 μs. On the other hand, a band around 345 nm observed at 20 μs delay may be assigned to Ẋ, generated from the hydrogen abstraction reaction, indicating the generation of the triplet biradical of the acetophenone ketyl radical (ȦPH) and Ẋ, ^{3}(ȦPH-12-Ẋ). Indeed, only small MFE were detected on the decay curve of Ẋ at 345 nm (see inset of Fig. 3c), though no appreciable effect was detected in the decay curves monitored at 320 and 390 nm. The apparent lifetimes of the 345 nm band, presumably the mixture of the absorptions of ^{3}AP* and Ẋ, are approximately 8 μs at zero field and 10 μs at 0.8 T.

Magnetic field effects on the lifetimes of biradicals are summarized in Table 2. Drastic MFE were simultaneously observed on transient absorptions of two chromophores in ẊOH-12-Ẋ, ȦQH-12-Ẋ, and ḂPH-12-Ẋ. The facts present an unequivocal evidence that two radicals at the ends of methylene chain interact magnetically each other. Small disagreement in lifetimes determined from the respective two chromophores may be due to the contamination of the short-lived T-T absorption of the respective precursors and/or the absorption of photoproducts. In the case of ȦPH-12-Ẋ, its dynamics may be chiefly controlled by its slow formation process, and, for this reason, no significant MFE might be detected. Figure 4 shows the magnetic field dependence of the lifetimes of ẊOH-12-Ẋ, ȦQH-12-Ẋ, and ḂPH-12-Ẋ biradicals. Lifetimes are determined from the decay curves of the 345 nm band of Ẋ because of its high absorbance. In all cases, the lifetimes increase suddenly around 0.05 T and gradually in higher fields (>0.1 T). Saturation of the effects seems to occur at higher fields (>0.5 T).

Furthermore, the magnitude of MFE on these biradicals in both polar and nonpolar solvents is comparable with or greater than that observed in the radical pairs generated from the corresponding bimolecular reactions in micellar solution.[5] These facts indicate that the linking of two radicals by a methylene chain, to hinder their separation, is essential for significant MFE. Therefore, from comparison of results on the present biradicals with those on the radical pairs in micellar solution,[5] we can conclude that, in micellar solution, the dimentionality of a micellar cage, keeping the components of a pair in a short distance, is of the primary factor for significant MFE, as assumed so far in MFE on the photoreactions in micellar solutions. It is also likely that the high microviscosity in a micelle as well as the high solubility of hydrophobic radicals in a micellar phase acts all together to elongate lifetime of the pair in it.

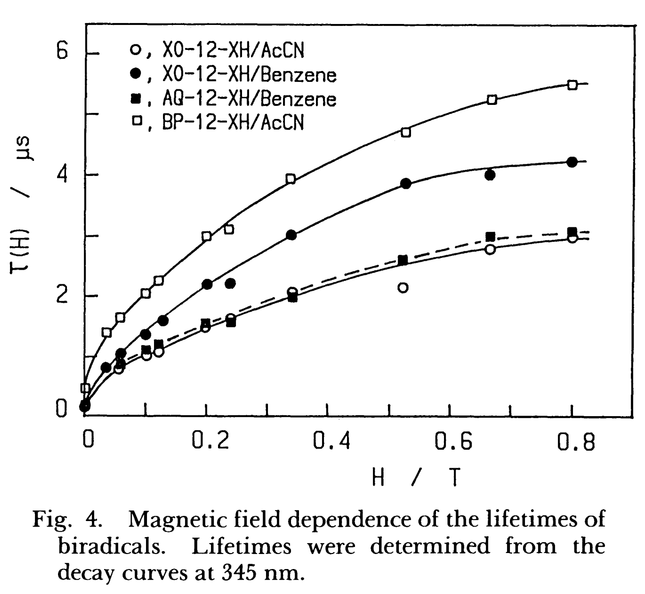


Fig. 4. Magnetic field dependence of the lifetimes of biradicals. Lifetimes were determined from the decay curves at 345 nm.

Reaction Mechanism. All the results mentioned above can be ascribed by the following reaction scheme:

$$\mathrm{Ar\text{-}12\text{-}XH} \xrightarrow{h\nu} {}^1\mathrm{Ar^*\text{-}12\text{-}XH} \tag{1}$$

$$ {}^1\mathrm{Ar^*\text{-}12\text{-}XH} \rightarrow {}^3\mathrm{Ar^*\text{-}12\text{-}XH} \tag{2}$$

$$ {}^3\mathrm{Ar^*\text{-}12\text{-}XH} \rightarrow {}^3(\dot{\mathrm{A}}\mathrm{rH\text{-}12\text{-}}\dot{\mathrm{X}}) \tag{3}$$

$$ {}^3(\dot{\mathrm{A}}\mathrm{rH\text{-}12\text{-}}\dot{\mathrm{X}}) \rightleftarrows {}^1(\dot{\mathrm{A}}\mathrm{rH\text{-}12\text{-}}\dot{\mathrm{X}}) \tag{4}$$

$$ {}^1(\dot{\mathrm{A}}\mathrm{rH\text{-}12\text{-}}\dot{\mathrm{X}}) \rightarrow \underbracket{\mathrm{ArH\text{-}12\text{-}X}} \tag{5}$$

$$ {}^1(\dot{\mathrm{A}}\mathrm{rH\text{-}12\text{-}}\dot{\mathrm{X}}) \rightarrow \mathrm{Ar\text{-}12\text{-}XH} \tag{6}$$

Here, ȦrH is the ketyl or the semiquinone radical generated from aromatic carbonyl, Ar, after the hydrogen abstraction. Upon photoexcitation of Ar in Ar-12-XH, the excited triplet, ^{3}Ar*, of Ar is generated ((1) and (2)). ^{3}Ar* abstracts a hydrogen atom from XH at the other end of the chain to generate the triplet biradical of ȦrH and Ẋ, ^{3}(ȦrH-12-Ẋ). ^{3}(ȦrH-12-Ẋ) deactivates via isc to the singlet biradical, ^{1}(ȦrH-12-Ẋ) (4), from which the product formation (5) and the back reaction (6) may occur. For simplicity, bimolecular reactions such as the reaction between two biradicals are not included in the scheme as the reaction of the triplet biradical, since the concentration of Ar-12-XH is as low as ca. 10^{-4} M. They may be of minor importance in the time scale shorter than 10 μs, though, in the presence of a high magnetic field, they might also take place to some extent.

Now let's consider the mechanism of MFE observed for the present biradicals. The magnetic field effects on a radical pair or a biradical can be interpreted in terms of four mechanisms, i.e., (a) the Δg mechanism, (b) the hyperfine coupling (hfc) mechanism, (c) the relaxation mechanism, and (d) the triplet mechanism.[1,21] In (a), a difference in the electron-spin Larmor frequencies of the two radicals caused by the different electron g values induces the T-S isc of the pair. In (b), a local field generated by nuclear spins (i.e., electron-nuclear hfc) induces the isc, and, in high field, the rates are reduced because of the electronic Zeeman splitting of triplet sublevels (T_+, T_0, and T_-). On the other hand, in (c), electron spin relaxation due to the dipole-dipole anisotropic interaction of an electron and nuclear spins is affected by the Zeeman splitting of triplet sublevels. Finally, in mechanism (d), spin polarization in an excited triplet precursor is transferred to a radical pair, when the pair formation is fast compared with the relaxation in the excited triplet. Unequal distribution among triplet sublevels in the pair may affect the magnetic field dependence of the lifetime of a radical pair.

Mechanism (a) is not operative in the present magnetic fields (<1T), since the g factors of a xanthenyl radical and a xanthone ketyl radical are the same within experimental error ($g=2.0033\pm0.0005$).[22] The hfc-induced isc rate constant $k_{\mathrm{isc}}(\mathrm{hfc})$ can be estimated from the effective hfc constants, B_{av}, of radicals in a pair:[23]

$$k_{\mathrm{isc}}(\mathrm{hfc})=g\mu B_{\mathrm{av}}/\hbar, \qquad (7)$$

where μ is the Bohr magneton, and $\hbar$ is the Planck's constant. In mechanism (b), the hfc-induced T-S isc occurs between the energetically degenerated three triplet sublevels and the singlet state at zero field, and the $T_\pm$-S isc is quenched in a field much higher than B_{av}, due to the Zeeman splitting of two triplet sublevels. The saturation of the effect appears at a relatively low field (around 0.1 T).

In the case of $\dot{\mathrm{X}}$OH-12-$\dot{\mathrm{X}}$, B_{av} is estimated to be 2.5 mT,[24,25] giving $k_{\mathrm{isc}}(\mathrm{hfc})=10^8\ \mathrm{s}^{-1}$ at zero field and $0.3\times10^8\ \mathrm{s}^{-1}$ at high fields. The observed lifetimes of the biradical are 0.14 μs at zero field and 3 μs at 0.8 T, and the saturation of the effect occurs around 0.8 T, which is much higher than B_{av} (2.5mT). These results indicate that hfc-induced isc is not the rate-determining step at zero field, though one of the three reaction processes (chain dynamics, isc, and cage recombination (product-forming step)) is considered to control the decay rate of the biradical. The chain dynamics may not control it, as the fact that this biradical is formed within a laser pulse width (15—20 ns) confirms the collision of two ends of the chain is a very fast process. The lifetime of $\dot{\mathrm{X}}$OH-12-$\dot{\mathrm{X}}$ at zero field is, therefore, most probably controlled by the recombination reaction in the singlet state. Furthermore, according to the mechanism (c) the relaxation rate is estimated to be in the order of 10^5—$10^6\ \mathrm{s}^{-1}$,[26,27] which is compatible with the lifetimes of the present biradical in the higher magnetic fields. On this basis, it is concluded that the lifetime of $\dot{\mathrm{X}}$OH-12-$\dot{\mathrm{X}}$ is determined by the recombination rate in the singlet at zero field, while in high fields it may be attributable to the relaxation rate, as predicted by the mechanism (c).

The lifetime increases dramatically even in a weak magnetic field (<0.1 T). For example, the lifetimes of this biradical are 0.14 μs (zero field) and 0.77 μs (0.05 T). In low magnetic fields, the hfc-induced isc among non-degenerate spin states may become slower than the cage recombination, and, therefore, the former may be the rate-controlling step at low magnetic fields (<0.1 T). Furthermore, mechanism (d) may be also operative to some extent in addition to the mechanism (c), since the short lifetime of ^{3}XO*-12-XH indicates that the reaction initiates from the spin-polarized triplet state. An analogous argument may hold as for the mechanism in the $\dot{\mathrm{A}}$QH-12-$\dot{\mathrm{X}}$ biradical. In the case of $\dot{\mathrm{B}}$PH-12-$\dot{\mathrm{X}}$ and $\dot{\mathrm{A}}$PH-12-$\dot{\mathrm{X}}$, however, mechanism (d) may not be involved, since the lifetimes of their precursors seem long enough to attain thermal equilibrium in the excited states.

2. Dependence of the Magnetic Field Effects on Methylene Chain Length of $\dot{\mathrm{X}}$OH-*n*-$\dot{\mathrm{X}}$. S-T energy gap of a radical pair or a biradical is considered to be the function of interradical distance, and, therefore, MFE may be affected by the interradical distance. Thus, the influence of the distance between two radical centers on MFE was examined as a function of chain lengths for XO-*n*-XH systems (n=2—12). All bifunctional molecules XO-*n*-XH (n=2—10) exhibit transient spectra similar to that with n=12 in acetonitrile. The magnetic field effect on the lifetimes of these biradicals is shown in Table 3. In the presence of a magnetic field (0.8 T), they increase very remarkably. At zero field, the lifetimes of $\dot{\mathrm{X}}$OH-*n*-$\dot{\mathrm{X}}$ (n=3—12) are almost independent of the chain length (0.1—0.2 μs), though that of $\dot{\mathrm{X}}$OH-2-$\dot{\mathrm{X}}$ is considerably long. The facts indicate that the lifetimes of $\dot{\mathrm{X}}$OH-*n*-$\dot{\mathrm{X}}$ (n=3—12) are likely controlled by the same reaction step, i.e., cage recombination reaction in the singlet state. The lifetime of $\dot{\mathrm{X}}$OH-2-$\dot{\mathrm{X}}$ may be controlled mainly analogous process to those of other biradicals, since it exhibits considerable MFE. The n dependence of MFE was , therefore, estimated from the lifetime ratio $R=\tau(\mathrm{H})/\tau(0)$ of biradicals, where $\tau(\mathrm{H})$ and $\tau(0)$ are the lifetimes in the presence and absence of a magnetic field (0.8 T) (Fig. 5). The ratio, R, which may represents the magnitude of the effect, increases with increasing n and reaches a plateau around n=6. The fact implies that the T-S degeneracy of the biradical occurs effectively at the chain length of around n=6. In the case of $\dot{\mathrm{X}}$OH-2-$\dot{\mathrm{X}}$, its lifetime (≈1 μs) at zero field is considerably long and the MFE are relatively small compared with those of other biradicals.

Table 3. Lifetimes of Biradicals Generated from XO-*n*-XH in Acetonitrile[a)]

n	τ(0 T) μs	μ(0.8 T) μs	R[b)]
2	0.98	2.7	2.8
3	0.18	0.8	4.4
4	0.22	1.7	7.7
5	0.13	1.1	8.5
6	0.11	1.7	15.5
8	0.16	2.3	14.5
10[c)]	0.29	6.0	20.7
12	0.14	3.0	21.4

a) Experimental errors are ±20%. b) Lifetime ratio τ(0.8 T)/τ(0 T). c) Experimental errors are ±30%, because of low solubility.

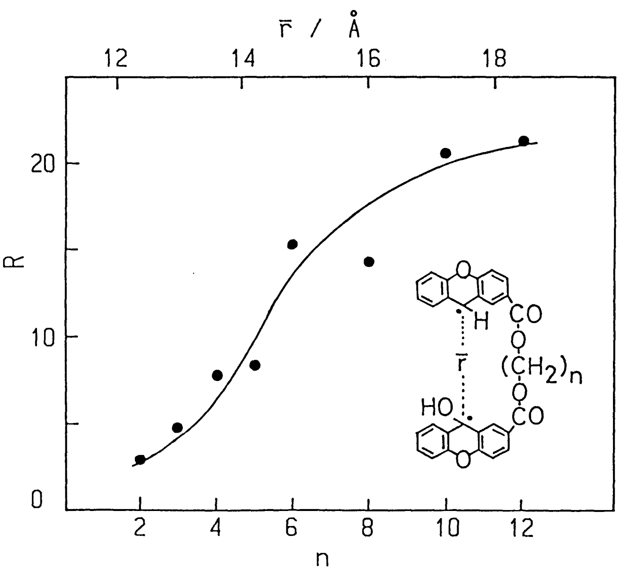


Fig. 5. Methylene chain length n dependence of R of ẊOH-n-Ẋ in acetonitrile. $R=\tau(0.8\ \mathrm{T})/\tau(0\ \mathrm{T})$ is the ratio of the lifetimes τ in the presence and the absence of a magnetic field, 0.8 T. Lifetimes were determined from the decay curves at 345 nm. Top of the figure is the mean distance $\bar{r}$ of two radical centers at the ends of methylene chain. See text.

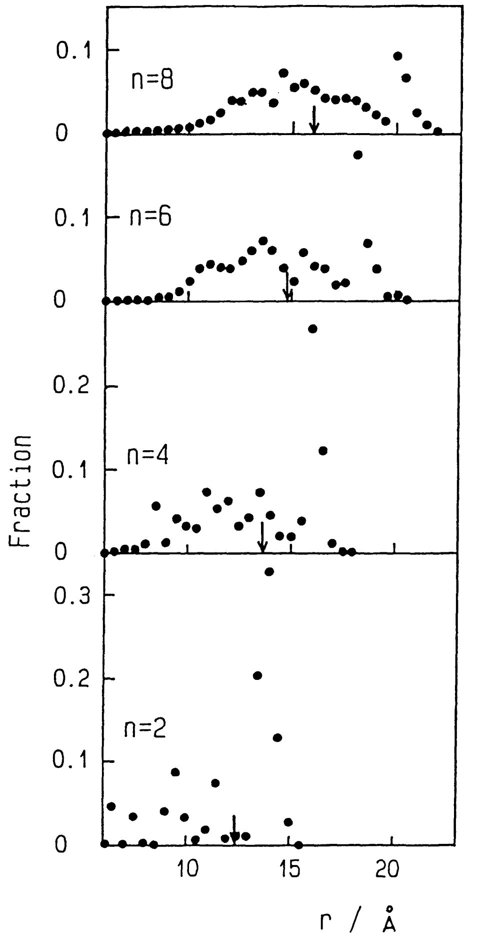


Fig. 6. Typical distribution of the interradical distance r of the ẊOH-n-Ẋ biradicals, the hydroxyl carbon atom of ẊOH and the methylene carbon atom of Ẋ being assumed to be the respective radical centers. Arrows indicate the respective mean interradical distance $\bar{r}$.

In this case, isc may occur among non-degenerate S and T states even at zero field. A steric hindrance and chain dynamics might not be very important, since the generation of this biradical is within the laser pulse width (15—20 ns) as observed for every other molecules.

In order to estimate the distance between the two radical centers at the ends of the chain, we calculated the distribution of interradical distance r and mean interradical distance $\bar{r}$ with the aid of the direct enumeration method, by assuming that the hydroxyl carbon atom of ẊOH and the methylene carbon atom of Ẋ are the respective radical centers. The typical results are shown in Fig. 6. Distribution of interradical distances, especially for short chain molecules, is deviated far from the normal distribution curve. It is mostly because the number of chain conformations are limited due to the fixed conformation of the carboxyl groups in the chain and to the steric hindrance of the bulky aromatic rings. The distance dependence of MFE was, thus, roughly estimated from the mean distance, $\bar{r}$, though it was not a good representative of the ensemble of the conformations. The mean interradical distance for the biradical ẊOH-6-Ẋ, where saturation of MFF occurs, was obtained to be about 15 Å (see Fig. 5). It is most likely that the triplet and singlet states degenerate each other at a mean interradical distance of about 15 Å, and at this distance, therefore, isc in the biradical occurs efficiently. In the case of ẊOH-2-Ẋ, the mean distance was estimated to be as long as about 12 Å, suggesting a very small S-T energy gap. For this reason, MFE might be observed even though the magnitude was relatively small compared with those of longer chain biradicals.

Next, the S-T energy gap ($2J$) of the ẊOH-n-Ẋ biradicals was estimated. $2J$ is usually expressed by an exponential function, when it is controlled by the through-space exchange interaction:[28,29]

$$2J=2J_0\exp(-ar). \qquad (8)$$

Assuming that $2J_0=1.896\times10^9$ mT and $a=2.136$ Å^{-1}, the $2J$ values were calculated (Table 4). The n dependence of $2J(r)$ values, calculated by weighting the distribution of r, does not reproduce the observed tendency of R shown in Fig. 5. This is attributable to the conformations of biradicals having short interradical distance r, as shown in Fig. 6. Since the exchange energy increases exponentially with decreasing r, averaged energy becomes considerable magnitude, even though fraction of such conformations is quite small. When the mean distance $\bar{r}$ is used for calculation, the trend of $2J(\bar{r})$ fits qualitatively the observed one,

Table 4. Mean Interradical Distance $\bar{r}$ (Å) and Electron Exchange Energy $2J$ (mT) of Biradicals, $\dot{\mathrm{X}}$OH-n-$\dot{\mathrm{X}}$

n	2	3	4	5	6	7	8
$\bar{r}$	12.4	12.8	13.6	14.3	14.8	15.5	16.1
$2J(r)^{\mathrm{a)}}$	21.8	0.05	0.08	30.7	0.45	30.8	1.1
$2J(\bar{r})^{\mathrm{b)}}$	0.006	0.003	0.001	0.000	0.000	0.000	0.000

a) Averaged over all of $2J(r)$ values for the distribution of r. b) Calculated by using mean distance $\bar{r}$.

though its magnitude is too small to explain the observed results. As was discussed in the CIDNP study of biradicals generated from cyclic ketones,[29] the exponential approximation of $2J$ is incomplete for complex systems like the present ones, since exchange interaction is influenced by mutual orientation of orbitals occupied by unpaired electrons.

Recently, MFE on the dynamics of radical pairs and radical ion pairs (rip) generated from bifunctional chain molecules have been reported. In studies of the MFE on the intramolecular exciplex fluorescence of phenanthrene-(CH$_2$)$_n$-*N*,*N*-dimethylaniline (n=3—10)[30] and pyrene-(CH$_2$)$_n$-*N*,*N*-dimethylaniline (n=3—16),[31] the S-T degeneracy of singlet intramolecular rip was reported to occur at the chain length of around n=10. These results are equivalent with the present ones for the triplet biradical, $\dot{\mathrm{X}}$OH-n-$\dot{\mathrm{X}}$, since they contain two ester groups in the chain. Analogous conclusion on the S-T degeneracy of triplet biradicals were also reported for Ph$\dot{\mathrm{C}}$H-(CH$_2$)$_n$-$\dot{\mathrm{C}}$=O (n=8—10) biradicals[32] and the biradicals generated from α-(4-benzoylphenoxy)-ω-[4-(phenylamino)phenoxy]alkanes (n=2—16).[33] Therefore, it is generally concluded that the S-T degeneracy of biradicals, independent from their spin multiplicity, occurs when the number of chain units becomes larger than 10 or so.

Conclusion

In this paper we have presented a detailed study of MFE on the dynamics of methylene chain linked biradicals. Drastic MFE were observed on the decay of $\dot{\mathrm{X}}$OH-12-$\dot{\mathrm{X}}$, $\dot{\mathrm{A}}$QH-12-$\dot{\mathrm{X}}$, and $\dot{\mathrm{B}}$PH-12-$\dot{\mathrm{X}}$ biradicals in both polar and nonpolar solvents. The facts present that the linking of two radicals to hinder their separation is essential for significant effects. These results also suggest that dimentionality of a micellar cage is the key for significant MFE on radical pairs observed previously in micellar solution.

The effects are qualitatively interpreted in terms of the relaxation mechanism, where relaxation in triplet sublevels of biradicals is a rate-controlling step in higher fields. The S-T degeneracy of biradicals, $\dot{\mathrm{X}}$OH-n-$\dot{\mathrm{X}}$, occurs at the chain length of around n=6, which corresponds to the interradical distance of about 15 Å.

The authors wish to express their thanks to Professor Masahiko Sisido, Kyoto University, for the use of his conformational calculation program, and to Professor Saburo Nagakura and Dr. Ryoichi Nakagaki, Institute for Molecular Science, for several illuminating discussions. This work was supported by the Yamada Science Foundation, the Takeda Science Foundation, and a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture.

References

1) "Spin Polarization and Magnetic Field Effects in Radical Reactions," ed by Yu. N. Molin, Elsevier, Amsterdam (1984).

2) a) N. J. Turro and B. Kraeutler, *J. Am. Chem. Soc.*, **100**, 7432 (1978); b) N. J. Turro and B. Kraeutler, *Acc. Chem. Res.*, **13**, 369 (1980); c) N. J. Turro, *Proc. Natl, Acad. Sci. U.S.A.*, **80**, 609 (1983); d) I. R. Gould, M. B. Zimmt, N. J. Turro, and B. H. Baretz, *J. Am. Chem. Soc.*, **107**, 4607 (1985); e) N. J. Turro, M. B. Zimmt, and I. R. Gould, *J. Phys. Chem.*, **92**, 433 (1988), and references therein.

3) a) Y. Sakaguchi, S. Nagakura, and H. Hayashi, *Chem. Phys. Lett.*, **72**, 420 (1980); b) Y. Sakaguchi, H. Hayashi, and S. Nagakura, *J. Phys. Chem.*, **86**, 3177 (1982); c) Y. Sakaguchi and H. Hayashi, *ibid.*, **88**, 1437 (1984); d) Y. Sakaguchi and H. Hayashi, *Chem. Phys. Lett.*, **106**, 420 (1984); e) H. Hayashi, Y. Sakaguchi, M. Tsunooka, H. Yanagi, and M. Tanaka, *ibid.*, **136**, 436 (1987).

4) a) J. C. Scaiano and E. B. Abuin, *Chem. Phys. Lett.*, **81**, 209 (1981); b) J. C. Scaiano, E. B. Abuin, and L. C. Stewart, *J. Am. Che. Soc.*, **104**, 5673 (1982); c) J. C. Scaiano and D. J. Lougnot, *J. Phys. Chem.*, **88**, 3379 (1984); d) J. C. Scaiano and D. -J. Lougnot, *Chem. Phys. Lett.*, **105**, 535 (1984); e) C. Evans, K. U. Ingold, and J. C. Scaiano, *J. Phys. Chem.*, **92**, 1257 (1988).

5) a) Y. Tanimoto and M. Itoh, *Chem. Phys. Lett.*, **83**, 626 (1981); b) Y. Tanimoto, H. Udagawa, and M. Itoh, *J. Phys. Chem.*, **87**, 724 (1983); c) Y. Tanimoto, H. Udagawa, Y. Katsuda, and M. Itoh, *ibid.*, **87**, 3976 (1983); d) Y. Tanimoto, K. Shimizu, and M. Itoh, *J. Am. Chem. Soc.*, **106**, 7257 (1984); e) Y. Tanimoto, M. Tahashima, and M. Itoh, *J. Phys. Chem.*, **88**, 6053 (1984); f) Y. Tanimoto, M. Takashima, and M. Itoh, *Chem. Lett.*, **1984**, 1981; g) Y. Tanimoto and M. Itoh, "Physical Organic Chemistry 1986," ed by M. Kobayashi, Elsevier, Amsterdam (1987), p. 257.

6) a) W. Schlenker, T. Ulrich, and U. E. Steiner, *Chem. Phys. Lett.*, **103**, 118 (1983); b) T. Ulrich and U. E. Steiner, *ibid.*, **112**, 365 (1984); c) T. Ulrich, U. E. Steiner, and W. Schlenker, *Tetrahedron*, **42**, 6131 (1986).

7) a) M. Okazaki, S. Sakata, R. Konaka, and T. Shiga, *J.*

Am. Chem. Soc., **107**, 7214 (1985); b) M. Okazaki and T. Shiga, *Nature (London),* **323**, 240 (1986); c) M. Okazaki, S. Sakata, R. Konaka, and T. Shiga, *J. Phys. Chem.*, **91**, 1131 (1987); d) M. Okazaki, S. Sakata, R. Konaka, and T. Shiga, *J. Chem. Phys.,* **86**, 6792 (1987).

8) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems," Academic Press, New York (1975), Chap. 2.

9) a) Y. Tanimoto, M. Takashima, M. Uehara, M. Itoh, M. Hiramatsu, R. Nakagaki, T. Watanabe, and S. Nagakura, *Chem. Lett.*, **1985**, 15; b) Y. Tanimoto, M. Takashima, M. Uehara, M. Itoh, M. Hiramatsu, R. Nakagaki, T. Watanabe, and S. Nagakura, XIIth International Conference on Photochemistry, Tokyo (1985), Abstr., No. 3P27; c) Y. Tanimoto, M. Uehara, M. Takashima, and M. Itoh, *Bull. Chem. Soc. Jpn.*, **61**, 3121 (1988).

10) A preliminary result has appeared: Y. Tanimoto, M. Takashima, K. Hasegawa, and M. Itoh, *Chem. Phys. Lett.*, **137**, 330 (1987).

11) M. Fckstein, H. Marona, and J. Mazur, *Pol. J. Pharmacol. Pharm.*, **35**, 159 (1983).

12) a) R. D. Hoffsommer, D. Taub, and N. L. Wendler, *Chem. Ind. (London),* **1964**, 482; b) A. L. Wilds, "Organic Reactions," John Wiley and Sons, New York (1944), **2**, p. 178.

13) M. Sisido, and K. Shimada, *J. Am. Chem. Soc.*, **99**, 7785 (1977).

14) A. Garner and F. Wilkinson, *J. Chem. Soc., Faraday Trans. 2,* **72**, 1010 (1976).

15) H. Masuhara, M. Okuda, and M. Koizumi, *Bull. Chem. Soc. Jpn.*, **41**, 2319 (1968).

16) M. A. Winnik, S. N. Basu, C. K. Lee, and D. S. Saunders, *J. Am. Chem. Soc.*, **98**, 2928 (1976).

17) N. K. Bridge and G. Porter, *Proc. R. Soc. London, Ser. A,* **244**, 259 (1958).

18) T. S. Godfrey, J. W. Hilpern, and G. Porter, *Chem. Phys. Lett.*, **1**, 490 (1967).

19) H. Lutz, E. Breheret, and L. Lindqvist, *J. Phys. Chem.*, **77**, 1758 (1973).

20) A. Beckett, A. D. Osborne, and G. Porter, *Trans. Faraday Soc.*, **60**, 873 (1964).

21) a) S. K. Wong, D. A. Hutchinson, and J. K. S. Wan, *J. Chem. Phys.*, **58**, 985 (1973); b) P. W. Atkins and G. T. Evans, *Chem. Phys. Lett.*, **25**, 108 (1974); c) F. J. Adrian, *J. Chem. Phys.,* **61**, 4875 (1974).

22) M. Terajima and T. Azumi, private communication.

23) a) K. Schulten and P. G. Wolynes, *J. Chem. Phys.*, **68**, 3292 (1978); b) A. Weller, F. Nolting, and H. Staerk, *Chem. Phys. Lett.*, **96**, 24 (1983).

24) a) M. D. Sevilia and G. Vincow, *J. Phys. Chem.*, **72**, 3635 (1968); b) L. Lunazzi, A. Mangini, G. Placucci, and C. Vincenzi, *J. Chem. Soc., Perkin Trans. 1,* **1972**, 2418.

25) a) R. Wilson, *J. Chem. Soc. B,* **1968**, 1581; b) R. S. Davidson, F. A. Younis, and R. Wilson, *J. Chem. Soc., Chem. Commun.*, **1969**, 826.

26) H. Hayashi and S. Nagakura, *Bull. Chem. Soc. Jpn.*, **57**, 322 (1984).

27) R. Kaptein, "Chemically Induced Magnetic Polarization," ed by L. T. Muus, P. W. Atkins, K. A. McLauchlan, and J. B. Pedersen, D. Reidel, Dordrecht (1977), p.1.

28) C. Herring and M. Flicker, *Phys. Rev.*, **134**, A362 (1964).

29) a) F. J. J. de Kanter, J. A. den Hollander, A. H. Huizer, and R. Kaptein, *Mol. Phys.*, **34**, 857 (1977); b) F. J. J. de Kanter, R. Z. Sagdeev, and R. Kaptein, *Chem. Phys. Lett.*, **58**, 334 (1978).

30) a) Y. Tanimoto, N. Okada, M. Itoh, K. Iwai, K. Sugioka, F. Takemura, R. Nakagaki, and S. Nagakura, *Chem. Phys. Lett.*, **136**, 42 (1987); b) Y. Tanimoto, N. Okada, K. Hasegawa, M. Itoh, K. Iwai, K. Sugioka, F. Takemura, R. Nakagaki, and S. Nagakura, *J. Phys. Chem.*, **93**, 3586 (1989).

31) H. Staerk, W. Kuhnle, R. Treichel, and A. Weller, *Chem. Phys. Lett.*, **118**, 19 (1985).

32) M. B. Zimmt, C. Doubleday, Jr. and N. J. Turro, *J. Am. Chem. Soc.*, **107**, 6726 (1985).

33) Y. Tanimoto, N. Okada, and M. Itoh, Symposium on Photochemistry, Tokyo (1988), Abstr. No. IA209.