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Photochemistry of Bifunctional Chain Molecules Containing Benzophenone and Anilino Chromophores. Magnetic Field and Magnetic Isotope Effects on Lifetimes of Triplet Biradicals

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The decay time of biradicals containing a benzophenone ketyl and an anilino-alkyl radical has been examined by nano-second laser photolysis in the presence of external magnetic fields up to 1 T. When sites with high spin densities are labeled with heavy carbon, noticeable magnetic isotope effects are observed on the decay kinetics for biradicals. Small kinetic effects are observed for deuterated species. The obtained results can be interpreted in terms of spin-lattice relaxation due to anisotropic hyperfine and dipole–dipole interactions. Procedures for preparing labeled species are also described.

The photoreduction of triplet benzophenone (BP) by amines is a well-characterized reaction that has been extensively investigated.[1—6)] Recently the primary process of photoreduction has been studied by femtosecond—picosecond photolysis.[7,8)] When the two reactive sites, i.e. benzophenone and amino chromophores, are linked by a polymethylene chain, a biradical intermediate is produced on photolysis. Since the primary reaction is caused by benzophenone in the excited triplet state, the initially prepared biradical is in the triplet manifold. It is, therefore, possible to investigate the dynamical behavior of triplet biradical by using nanosecond photolysis in the presence of an external magnetic field, if the chain length is sufficiently long.[9)] This work is concerned with the photochemistry of bichromophoric species containing benzophenone and anilino (AN) moieties. In other words, this paper describes the magnetic field and isotope effects on the decay kinetics for biradicals consisting of BP ketyl and 1-anilino-substitued alkyl radicals. Photoredox reactions of nitroaromatic-substituted chain species containing the anilino group have been reviewed by these authors.[10)] This work is an extension of photoredox studies on anilino chain molecules by changing the potential oxidant group from a nitroaromatic to a benzopheone moiety. We have examined the hydrogen abstraction reaction by BP in the excited triplet state for a series of bichromophoric chain molecules with benzylic hydrogen donors.[11—14)] Magnetic field and magnetic isotope effects were observed on decay profile of triplet biradicals composed of BP and benzyl and related radicals.

The following *para*-substituted benzophenone derivatives were prepared and used for the measurement.

$C_6H_5COC_6H_4O{-}(CH_2)_{12}{-}NHC_6H_5$ BP-12-AN **(1)**

$C_6H_5{}^{13}COC_6H_4O{-}(CH_2)_{12}NHC_6H_5$ 13BP **(1a)**

$C_6H_5COC_6H_4O{-}(CH_2)_{11}{-}{}^{13}CH_2{-}NHC_6H_5$ α13 **(1b)**

$C_6H_5COC_6H_4O{-}(CH_2)_{11}{-}CD_2{-}NHC_6H_5$ D2 **(1c)**

$C_6D_5COC_6D_4O{-}(CH_2)_{12}{-}NHC_6H_5$ D9 **(1d)**

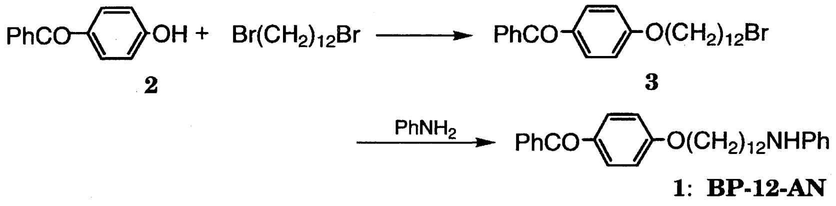
p-(12-Anilinododecyloxy)benzophenone BP-12-AN (**1**) with the natural abundance of the isotopes was prepared from *p*-hydroxybenzophenone (**2**) through a bromo ether as described in Scheme 1.

To prepare the compounds labeled with isotopes at appropriate positions of BP-12-AN, various synthetic courses were adopted as follows: The compounds 13BP (**1a**) labeled at the carbonyl carbon atom with ^{13}C and the nonadeuterio derivative D9 (**1d**) were obtained starting from the appropriately labeled *p*-hydroxybenzophenone (**2a** and **2d**) by the procedure shown in Scheme 1. The starting material **2a** was prepared by the Fries rearrangement of the corresponding phenyl benzoate (**4a**) in the presence of aluminum chloride, shown in Scheme 2. For the preparation of the decadeuterio compound **2d** from the benzoate **4d**, the photo-Fries rearrangement conditions were applied to avoid possible H–D exchange in the presence of a Lewis acid catalyst.

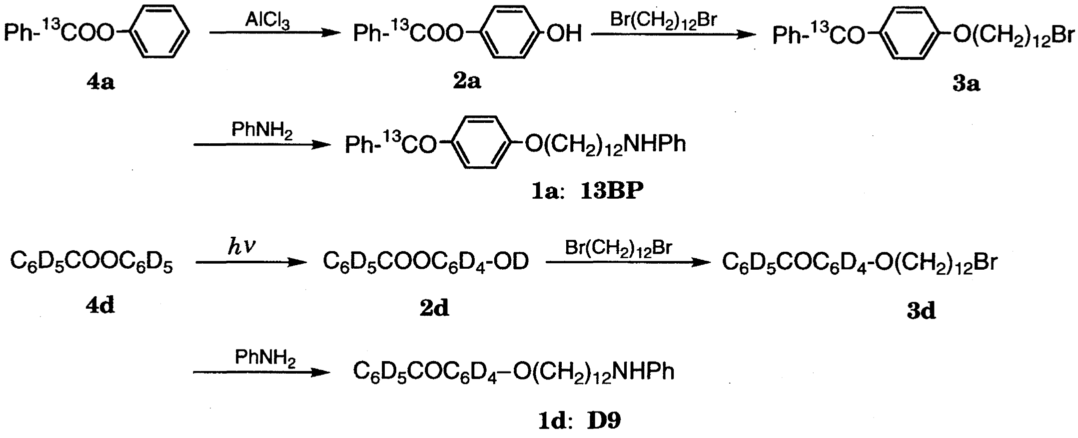
The compounds α13 (**1b**) and D2 (**1c**) labeled at the anilino-carrying end methylene group either with ^{13}C or deuteriums were prepared by reducing the corresponding ^{13}C-anilide (**7b**) with $LiAlH_4$ or unlabeled ^{12}C-anilide (**7**) with $LiAlD_4$ respectively as shown in Schemes 3 and 4. During the lithium aluminum hydride reduction, the carbonyl group in the benzophenone moiety was protected by acetalization.

Experimental

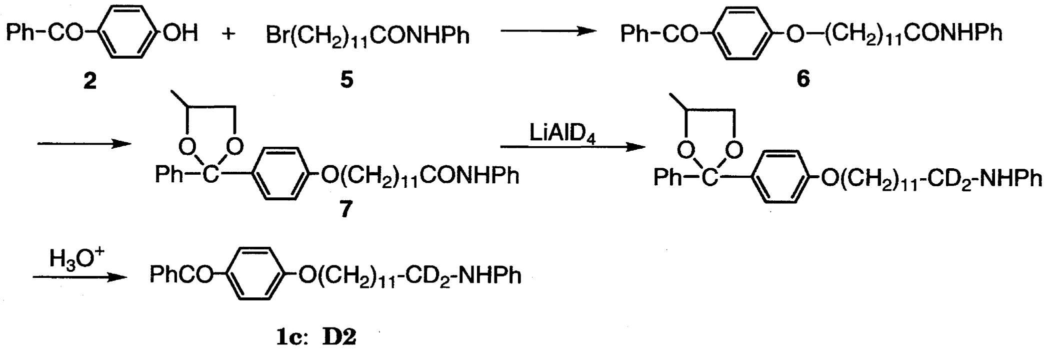
General. Melting points are uncorrected. ^1H NMR spectra



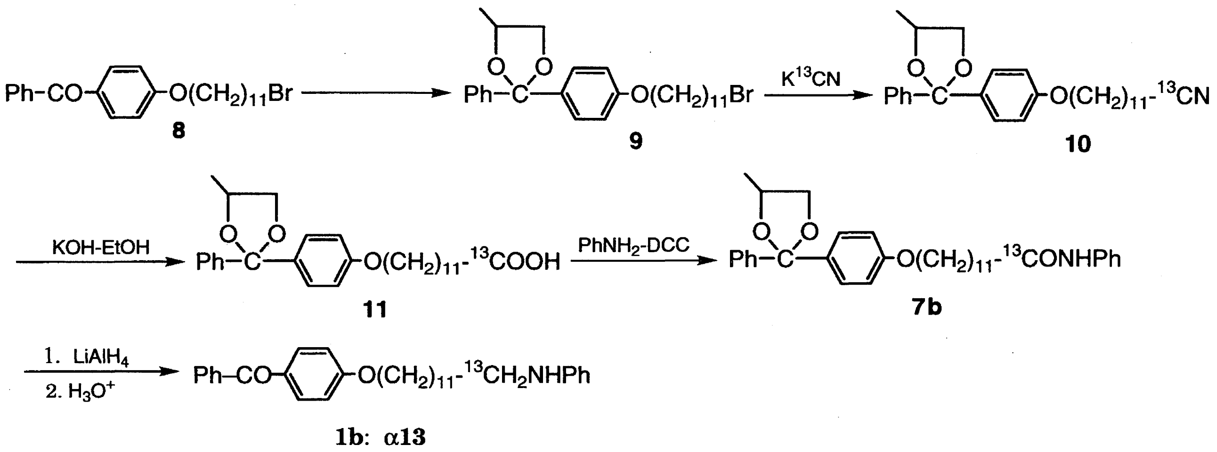
Scheme 1.



Scheme 2.



Scheme 3.



Scheme 4.

were recorded on a JEOL-GSX 500 MHz spectrometer. UV-spectra were recorded on a Hitachi U-3210 spectrophotometer.

***p*-(12-Bromododecyloxy)benzophenone (3).** A mixture of 1.50 g (7.6 mmol) of *p*-hydroxybenzophenone (**2**), 3.00 g (9.1 mmol) and 1,12-dibromododecane, 0.69 g (5 mmol) of K_2CO_3, and 0.1 g of tetrabutylammounium bromide was heated at 100 °C in 15 ml of water for 2.5 h. While warm, the reaction mixture was extracted with several 10-ml portions of chloroform. The combined extracts were dried over $CaCl_2$, and the solvent was removed with a rotary evaporator. The residue (about 4.9 g) was triturated with 15 ml hot benzene, and after cooling, the precipitates (mainly, diether) were removed by filtration. The filtrate was put on a chromatography column packed with 75 g of silica gel. Elution with benzene–CH_2Cl_2 mixture (1 : 1) gave 1.20 g (46%) of white crystals (recrystallized from hexane): Mp 73—74 °C; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.29$—1.51 (m, 16H), 1.79—1.88 (m, 4H), 3.41 (t, 2H), 4.04 (t, 2H), 6.95 (d, 2H), 7.47 (t, 2H), 7.56 (t, 1H), 7.75 (d, 2H), 7.82 (d, 2H); MS *m/z* 444, 446 (M^+); UV (λ_{max}/nm, CH_3CN), 223 (log $\varepsilon = 4.10$), 249 (3.97), 286 (4.26).

Found: C, 67.14; H, 7.61%. Calcd for $C_{25}H_{33}BrO_2$: C, 67.41; H, 7.47%.

***p*-(12-Anilinododecyloxy)benzophenone BP-12-AN (1).** A mixture of 0.31 g (0.7 mmol) of *p*-(12-bromododecyloxy)benzophenone (**3**) and 0.30 g (3.2 mmol) of aniline was heated at 95 °C for 2 h. The mixture was poured into 20 ml of 10% aqueous sodium carbonate solution and extracted with CH_2Cl_2. The extract was dried over anhydrous potassium carbonate. After the solvent was removed by distillation, the residue was put on a chromatography column packed with 70 g of silica gel and eluted with a benzene–CH_2Cl_2 mixture (1 : 1). Recrystallization of the second eluate gave 0.23 g (72%) of white crystals (recrystallized from ethanol): Mp 72—73 °C; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.26$—1.51 (m, 16H), 1.61 (m, 2H), 1.81 (m, 2H), 3.10 (t, 2H), 4.04 (t, 2H), 6.60 (d, 2H), 6.68 (t, 1H), 6.95 (d, 2H), 7.16 (t, 2H), 7.47 (t, 2H), 7.56 (t, 1H), 7.75 (d, 2H), 7.82 (d, 2H); MS *m/z* 457 (M^+); UV (λ_{max}/nm, CH_3CN), 249 (log $\varepsilon = 4.35$), 287 (4.28).

Found: C, 81.25; H, 8.77; N, 3.08%. Calcd for $C_{31}H_{39}NO_2$: C, 81.36; H, 8.59; N, 3.06%.

Phenyl Benzoate-*carboxy*-^{13}*C* (4a). A mixture of 10 ml of thionyl chloride and 1.0 g (8.1 mmol) of Ph-^{13}COOH (isotope content 99%) was refluxed for 6 h, and the unreacted reagent was removed with a rotary evaporator. Sodium phenoxide was prepared by the reaction of 310 mg (7.8 mmol) of sodium hydride washed with hexane and 800 mg (8.5 mmol) of phenol in 20 ml of anhydrous THF. To this suspension was added 1.0 g (about 7 mmol) of the crude benzoyl chloride obtained above and stirred for 25 min; then water was added and it was extracted with CH_2Cl_2. The extract was washed with 1 M aqueous NaOH ($1\ M = 1\ mol\,dm^{-3}$) and dried over anhydrous sodium sulfate. Removing the solvent with a rotary evaporator, 1.15 g (68%) of white crystals was obtained. Recrystallization from hexane gave colorless prisms: Mp 71—72 °C; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 7.22$ (d, 2H), 7.28 (m, 2H), 7.44 (t, 1H), 7.52 (t, 1H), 7.64 (m, 2H), 8.20—8.22 (m, 2H); MS *m/z* 199 (M^+); UV (λ_{max}/nm, CH_3CN), 231 (log $\varepsilon = 4.95$).

Found: C, 78.68; H, 5.13%. Calcd for $C_{12}{}^{13}CH_{10}O_2$: C, 78.88; H, 5.06%.

***p*-Hydroxybenzophenone-*carbonyl*-^{13}*C* (2a) by the Fries Rearrangement.** To a suspension of aluminum chloride in 1,2-dichloroethane was added 1.35 g (10 mmol) of phenyl benzoate-*carboxy*-^{13}*C* (**4a**). The mixture was refluxed for 3 h and cooled in an ice-water bath, to which 1 M hydrochloric acid was added till a clear water layer was formed. The water layer was extracted several times with ether, and the combined extracts were washed with a 1 M aqueous solution of NaOH to extract the product. This alkaline solution was acidified with 1 M hydrochloric acid and extracted with ether. The ether solution was washed with a saturated aqueous solution of NaCl, dried over anhydrous sodium sulfate; then the solvent was removed with a rotory evaporator, and the pale brown residue was charged on a chromatography column packed with silica gel. Elution with an ether–hexane mixture (1 : 2) gave 554 mg (50%) of colorless prisms (recrystallized from CH_2Cl_2–hexane): Mp 134—136 °C; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 5.80$ (s, 1H), 6.92 (d, 2H), 7.48 (t, 2H), 7.57 (t, 1H), 7.74—7.77 (m, 2H), 7.78—7.80 (m, 2H); MS *m/z* 199 (M^+); UV (λ_{max}/nm, CH_3CN), 221 (log $\varepsilon = 4.12$), 247 (4.00), 283 (4.23).

Found: C, 78.46; H, 5.16%. Calcd for $C_{12}{}^{13}CH_{10}O_2$: C, 78.88; H, 5.06%.

***p*-(12-Bromododecyloxy)benzophenone-*carbonyl*-^{13}*C* (3a).** This compound was prepared by the procedure described above for the unlabelled ketone in a yield of 62%: Mp 74—75 °C; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.29$—1.49 (m, 16H), 1.80—1.88 (m, 4H), 3.41 (t, 2H), 4.04 (t, 2H), 6.95 (d, 2H), 7.47 (t, 2H), 7.56 (t, 1H), 7.74—7.76 (m, 2H), 7.81—7.83 (m, 2H); MS *m/z* 445, 447 (M^+); UV (λ_{max}/nm, CH_3CN), 222 (log $\varepsilon = 4.22$), 249 (4.08), 286 (4.35).

Found: C, 66.95; H, 7.44%. Calcd for $C_{24}{}^{13}CH_{33}BrO_2$: C, 67.48; H, 7.45%.

***p*-(12-Anilinododecyloxy)benzophenone-*carbonyl*-^{13}*C* 13BP (1a).** This compound was prepared from the bromide (**3a**) and aniline by the procedure described for **2**: Mp 74—75 °C; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.26$—1.51 (m, 16H), 1.61 (m, 2H), 1.81 (m, 2H), 3.10 (t, 2H), 4.04 (t, 2H), 6.60 (d, 2H), 6.68 (t, 1H), 6.95 (d, 2H), 7.17 (t, 2H), 7.47 (t, 2H), 7.56 (t, 1H), 7.75 (m, 2H), 7.82 (m, 2H); MS *m/z* 458 (M^+); UV (λ_{max}/nm, CH_3CN), 249 (log $\varepsilon = 4.38$), 287 (4.31).

Found: C, 81.17; H, 8.60; N, 3.04%. Calcd for $C_{30}{}^{13}CH_{39}O_2N$: C, 81.40; H, 8.57; N, 3.05%.

Phenyl-*d*$_5$ Benzoate-*d*$_5$ (4d). This compound was prepared from phenol-*d*$_6$ (isotope content 99%) and benzoic acid-*d*$_5$ (isotope content 98%) as described above in a yield of 100%: Mp 64—65 °C; MS *m/z* 208 (M^+); UV (λ_{max}/nm, CH_3CN), 230 (log $\varepsilon = 4.33$).

Found: C, 74.86; D, 9.53%. Calcd for $C_{13}D_{10}O_2$: C, 74.97; D, 9.67%.

***p*-Hydroxybenzophenone-*d*$_{10}$ (2d) by the Photo-Fries Rearrangement.** A cylindrical quartz cell (50 mm in diameter and 50 mm in length) containing an acetonitrile solution of 250 mg (0.98 mmol) of phenyl-*d*$_5$ benzoate-*d*$_5$ (**4d**) was irradiated with a low-pressure Hg lamp for 24 h. After the solvent was removed by distillation, the remaining orange oil was put on a chromatography column packed with silica gel. Elution with CH_2Cl_2–hexane mixture (4 : 5) gave 50 mg (20%) of colorless prisms: Mp 126—127 °C; MS *m/z* 208 (M^+); UV (λ_{max}/nm, CH_3CN), 221 (log $\varepsilon = 4.33$), 248 (4.14), 283 (4.36).

Found: C, 74.84; D, 9.56%. Calcd for $C_{13}D_{10}O_2$: C, 74.97; D, 9.67%.

***p*-(12-Bromododecyloxy)benzophenone-*d*$_9$ (3d).** This compound was prepared by the procedure described for the compound with natural abundance of hydrogen in a yield of 55%: Mp 61—62 °C; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.25$—1.51 (m, 16H), 1.78—1.88 (m, 4H), 3.41 (t, 2H), 4.04 (t, 2H); MS *m/z* 453, 455 (M^+); UV (λ_{max}/nm, CH_3CN), 223 (log $\varepsilon = 4.31$), 247 (4.16), 285 (4.45).

Found: C, 65.49; H, 6.77%. Calcd for $C_{25}H_{24}D_9BrO_2$: C, 66.01; H, 9.31%.

***p*-(12-Anilinododecyloxy)benzophenone-*d*$_9$ D9 (1d).** This compound was prepared by the procedure used for BP-12-AN using *p*-(12-bromododecyloxy)benzophenone-*d*$_9$ (**3d**) in a yield of 54%: Mp 72—73 °C; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.26$—1.51 (m, 16H), 1.61 (m, 2H), 1.81 (m, 2H), 3.10 (t, 2H), 4.03 (t, 2H), 6.60 (d, 2H), 6.68 (t, 1H), 7.17 (t, 2H); MS *m/z* 466 (M^+); UV (λ_{max}/nm, CH_3CN), 228 (log $\varepsilon = 4.18$), 249 (4.34), 288 (4.26).

Found: C, 79.66; H, 10.05; N, 2.91%. Calcd for $C_{31}H_{30}D_9O_2N$: C, 79.78; H, 10.36; N, 3.00%.

12-Bromododecananilide (5). To 5 ml of thionyl chloride was added 1.00 g (3.6 mmol) of 12-bromododecanoic acid and the mixture was refluxed for 6.5 h. After the unreacted chloride was removed, the remaining pale yellow solid was dissolved in a small amount of ether, and added in small portions to a stirring mixture cooled at 0 °C of 10 ml of 10% aqueous NaOH and 10 ml of ether containing 0.4 ml (4.4 mmol) of aniline. White crystals were collected by filtration, and the filtrate was extracted with CH_2Cl_2. The extract was washed with water and dried over anhydrous sodium sulfate. After the solvent was removed by distillation, the remaining residue was combined with the white crystals and put on a chromatography column packed with silica gel. Elution with ethyl acetate–benzene mixture (1 : 20) gave 856 mg (67%) of colorless prisms (recrystallized from methanol): Mp 81—82 °C; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.25$—1.45 (m, 16H), 1.73 (m, 2H), 1.85 (m, 2H), 2.35 (t, 2H), 3.40 (t, 2H), 7.10 (t, 1H), 7.32 (t, 2H), 7.51 (d, 2H); MS *m*/*z* 353, 355 (M^+); UV (λ_{max}/nm, CH_3CN), 242 ($\log \varepsilon = 4.16$).

Found: C, 60.99; H, 7.88; N, 3.95%. Calcd for $C_{18}H_{28}BrNO$: C, 61.02; H, 7.96; N, 3.95%.

12-(*p*-Benzoylphenoxy)dodecananilide (6). A mixture of 102 mg (0.52 mmol) of *p*-hydroxybenzophenone (**2**), 267 mg (0.75 mmol) of 12-bromododecananilide (**5**), 394 mg (2.85 mmol) of K_2CO_3, and 30 mg (0.18 mmol) of KI in 10 ml of anhydrous THF was refluxed for 7.5 h. To the cooled reaction mixture was added 10 ml of water and the mixture extracted with three 10-ml portions of CH_2Cl_2. The combined extracts were dried over anhydrous sodium sulfate. Removal of the solvent gave pale yellow crystals, which were put on a chromatography column packed with silica gel. Elution with ethyl acetate–hexane mixture (1 : 3) gave colorless prisms: Mp 91—93 °C; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.25$—1.40 (m, 12H), 1.47 (m, 2H), 1.72 (m, 2H), 1.81 (m, 2H), 2.34 (m, 2H), 4.04 (t, 2H), 6.95 (d, 2H), 7.09 (t, 1H), 7.31 (t, 2H), 7.47 (t, 2H), 7.52 (d, 2H), 7.56 (t, 1H), 7.75 (d, 2H), 7.82 (d, 2H); MS *m*/*z* 471 (M^+); UV (λ_{max}/nm, CH_3CN), 243 ($\log \varepsilon = 4.36$), 285 (4.25).

Found: C, 78.95; H, 7.93; N, 2.96%. Calcd for $C_{31}H_{37}NO_3$: C, 78.95; H, 7.91; N, 2.97%.

12-[*p*-(4-Methyl-2-phenyl-1,3-dioxolan-2-yl)phenoxy]-dodecananilide (7). A mixture of 74.2 mg (0.15 mmol) of the above anilide (**6**), 13.8 mg (0.07 mmol) of *p*-toluenesulfonic acid, and 1.8 ml (25 mmol) of 1,2-propanediol in 10 ml of benzene was refluxed for 2 h. After cooling, a small amount of 10% aqueous NaOH solution was added, and the mixture was extracted with benzene. The benzene extract was washed with a saturated aqueous solution of sodium chloride and dried over sodium sulfate. After removing the solvent with a rotary evaporator, the residue was put on a chromatography column packed with silica gel. Elution with ethyl acetate–benzene mixture (1 : 20) gave colorless prisms (recrystallized from methanol): Mp 70—71 °C; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.24$—1.46 (m, 16H), 1.74 (m, 4H), 2.34 (t, 2H), 3.56—3.63 (m, 2H), 3.92 (m, 2H), 4.11 (m, 1H), 4.28 (m, 1H), 6.79—6.85 (m, 2H), 7.06—7.12 (t, 2H), 7.24—7.41 (m, 6H), 7.46—7.53 (m, 4H); MS *m*/*z* 529 (M^+); UV (λ_{max}/nm, CH_3CN), 234 ($\log \varepsilon = 4.42$).

Found: C, 77.10; H, 8.13; N, 2.69%. Calcd for $C_{34}H_{43}NO_4$: C, 77.09; H, 8.18; N, 2.64%.

***p*-(12-Anilinododecyl-12,12-*d*$_2$-oxy)benzophenone D2 (1c).** To a solution of 156 mg (0.29 mmol) of the unlabeled anilide (**7**) in 10 ml anhydrous THF was added 124 mg of $LiAlD_4$ (isotope content 98%), and refluxed for 5.5 h. A saturated aqueous solution of ammonium chloride was added to the reaction mixture and the mixture was extracted with benzene; the extract was dried over sodium sulfate. After the solvent was removed with a rotary evaporator, the residue was mixed with 10 ml of 5 M HCl, and warmed under stirring for 3 h. The reaction mixture was neutralized with a 10% aqueous solution of NaOH, extracted with three 10-ml portions of CH_2Cl_2. The combined extracts were dried over anhydrous sodium sulfate; then the solvent was removed by distillation, and the residue was put on a chromatography column packed with silica gel. Elution with ethyl acetate–hexane mixture (1 : 5) gave 50 mg (39%) of colorless prisms (recrystallized from CH_2Cl_2–hexane): Mp 72—73 °C; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.26$—1.51 (m, 16H), 1.60 (t, 2H), 1.81 (m, 2H), 4.04 (t, 2H), 6.60 (d, 2H), 6.68 (t, 1H), 6.95 (d, 2H), 7.16 (t, 2H), 7.47 (t, 2H), 7.56 (t, 1H), 7.75 (d, 2H), 7.82 (d, 2H); MS *m*/*z* 459 (M^+); UV (λ_{max}/nm, CH_3CN), 249 ($\log \varepsilon = 4.44$), 287 (4.36).

Found: C, 80.70; H, 8.90; N, 3.12%. Calcd for $C_{31}H_{37}D_2NO_2$: C, 81.00; H, 8.99; N, 3.05%.

***p*-(11-Bromoundecyloxy)benzophenone (8).** This compound was prepared by the procedure described for the homologue above, using 1,11-dibromoundecane in a yield of 50%: Mp 69—70 °C; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.26$—1.51 (m, 14H), 1.79—1.88 (m, 4H), 3.41 (t, 2H), 4.04 (t, 2H), 6.95 (d, 2H), 7.47 (t, 2H), 7.56 (t, 1H), 7.75 (d, 2H), 7.82 (d, 2H); MS *m*/*z* 430, 432 (M^+)

Found: C, 66.70; H, 7.41%. Calcd for $C_{24}H_{31}BrO_2$: C, 66.82; H, 7.24%.

11-[*p*-(4-Methyl-2-phenyl-1,3-dioxolan-2-yl)phenoxy]undecyl Bromide (9). This compound was prepared from 1.72 g (3.99 mmol) of *p*-(11-bromoundecyloxy)benzophenone (**8**) and 1,2-propanediol in a similar procedure as described for the preparation of the above acetal in a yield of 88%: Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.28$—1.43 (m, 14H), 1.55 (d, 3H), 1.71—1.88 (m, 4H), 2.30—2.34 (t, 2H), 3.53—3.62 (m, 1H), 3.92 (t, 2H), 4.08—4.14 (m, 1H), 4.24—4.32 (m, 1H), 6.80—6.85 (m, 2H), 7.24—7.40 (m, 5H), 7.47—7.52 (m, 2H); MS *m*/*z* 488, 490 (M^+).

12-[*p*-(4-Methyl-2-phenyl-1,3-dioxolan-2-yl)phenoxy]-dodecanenitrile-1-^{13}*C* (10). A mixture of 1.72 g (3.52 mmol) of the above bromide (**9**), 380 mg (5.85 mmol) of $K^{13}CN$, and 496 mg (3.52 mmol) of 18-Crown-6 in 15 ml of acetonitrile was refluxed for 9 h. After cooling, water was added to the reaction mixture; then it was extracted with CH_2Cl_2. The extract was washed with a saturated aqueous solution of sodium chloride, then dried over anhydrous sodium sulfate, and the solvent was removed with a rotary evaporator. The residue (pale yellow oil) was put on a chromatography column packed with silica gel. Elution with ethyl acetate–hexane mixture gave 1.32 g (86%) of colorless oil: ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.29$—1.44 (m, 14H), 1.55 (d, 3H), 1.62—1.77 (m, 4H), 2.31—2.34 (t, 2H), 3.57—3.62 (m, 1H), 3.92 (t, 2H), 4.11—4.14 (m, 1H), 4.24—4.31 (m, 1H), 6.80—6.85 (m, 2H), 7.25—7.40 (m, 5H), 7.47—7.52 (m, 2H); MS *m*/*z* 435 (M^+).

This compound was used for the next step without further purification.

12-[*p*-(4-Methyl-2-phenyl-1,3-dioxolan-2-yl)phenoxy]-dodecanoic-1-^{13}*C* Acid (11). A mixture of 10 ml of 20% aqueous KOH solution and 1.32 g (3.03 mmol) of the nitrile in 30 ml of 70% ethanol was refluxed for 22 h; then, a saturated aqueous solution of ammonium chloride was added, and the mixture was extracted with ethyl acetate. From the extract, dried over sodium sulfate, the solvent was removed with a rotary evaporator, and the remaining colorless solid was put on a chromatography column packed with silica gel. Elution with ethyl acetate–hexane mixture (1 : 9) gave 905 mg (66%) of colorless crystals: ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.27$—1.78 (m, 21H), 2.31—2.36 (m, 2H), 3.56—3.62 (m, 1H), 3.93 (t, 2H), 4.08—4.14 (m, 1H), 4.23—4.32 (m, 1H), 6.80—6.84

(m, 2H), 7.24—7.40 (m, 5H), 7.46—7.52 (m, 2H); MS *m*/*z* 435 (M^+).

This compound was used for the next step without further purification.

***p*-(12-Anilinododecyl-12-^{13}C-oxy)benzophenone α13 (1b).** To a mixture of 863 mg (1.96 mmol) of the ^{13}C-labeled dodecanoic acid (**11**), 0.25 ml (2.5 mmol) of freshly distilled aniline, and 411 mg (1.99 mmol) of dicyclohexylcarbodiimide in 20 ml of CH_2Cl_2 was refluxed for 2 h. After the solvent was removed from the reaction mixture with a rotary evaporator, the remaining oil was put on a chromatography column packed with silica gel. Elution with ethyl acetate–hexane mixture (1 : 9) gave 952 mg (96%) of ^{13}C-labeled anilide (**7a**) as colorless oil. To a solution of 391 mg of the above oil in 10 ml of anhydrous THF was added 311 mg (8.18 mmol) of lithium aluminum hydride, and this was refluxed for 7 h. After addition of methanol to decompose the unreacted hydride, a saturated aqueous solution of ammonium chloride was added, and the mixture was extracted with CH_2Cl_2. The extract was washed with a saturated aqueous solution of sodium chloride and dried over anhydrous sodium sulfate. Removing the solvent with a rotary evaporator, the residue was dissolved in 15 ml of methanol, to which was added 3 ml of 5 M HCl solution. After this was left for 0.5 h, a part of the solvent was removed by distillation. The remaining reaction mixture was neutralized with an aqueous sodium hydrogencarbonate solution, and extracted with CH_2Cl_2. The extract was washed with a saturated aqueous solution of sodium chloride, dried over anhydrous sodium sulfate. After removing the solvent with a rotary evaporator, the residue was charged on a chromatography column packed with silica gel. Elution with ethyl acetate–hexane mixture (1 : 19) gave 117 mg (35%) of pale pink crystals: Mp 73—74 °C; ^{1}H NMR (500 MHz, $CDCl_3$) $\delta = 1.26$—1.84 (m, 16H), 2.96 (t, 1H), 3.23 (t, 1H), 4.04 (t, 2H), 6.60 (d, 2H), 6.68 (t, 1H), 6.95 (d, 2H), 7.17 (t, 2H), 7.47 (t, 2H), 7.56 (t, 1H), 7.75 (d, 2H), 7.82 (d, 2H); MS *m*/*z* 458 (M^+).

Found: C, 81.10; H, 8.68; N, 3.10%. Calcd for $C_{30}{}^{13}CH_{39}NO_2$: C, 81.40; H, 8.57; N, 3.05%.

Laser Photolysis. Benzene of spectroscopy grade (Nacalai Tesque) was used as received. Concentration of bifunctional species was 3.3×10^{-4} M in benzene. The benzene solutions were deaerated by several freeze-pump-thaw cycles. A laser photolysis setup with conventional electromagnet (Tokin SEE-9G) has been reported in previous papers.[11,12] The decay profiles at 340 nm were analyzed by the equation:

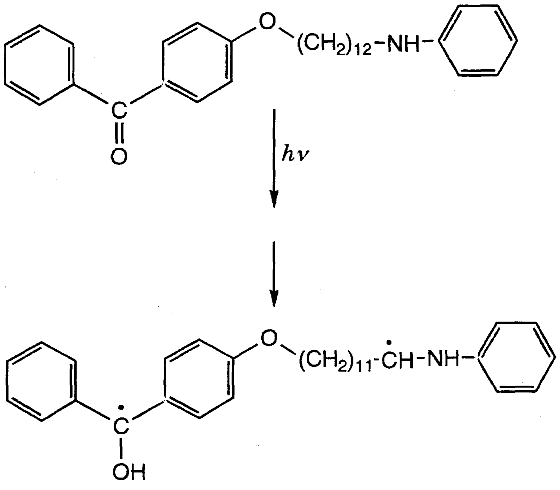
$$A(t) = A(1)\exp\left[-t/\tau(S)\right] + A(2)\exp\left[-t/\tau(L)\right] + A(3),$$

where $A(t)$ is absorbance at time t, $\tau(S)$ and $\tau(L)$ are lifetimes of short- and long-lived species.

Results and Discussion

Transient Absorption Spectra, Decay Kinetics, and Reaction Scheme. The transient absorption spectra obtained by nanosecond photolysis of BP-12-AN is closely related with those observed for the benzophenone–benzhydrol linked system with twelve methylene groups (BP-12-BH), from which biradicals with two equivalent ketyls (BPK-12-BPK) are produced.[14] In both cases the *p*-alkoxybenzophenone chromophore was excited and formation and decay of the excited triplet state was observed by monitoring the triplet–triplet absorption of the BP moiety. In addition, formation of the *p*-alkoxybenzophenone ketyl radical (BPK) was also traced by nanosecond photolysis. Decay curves of transient absorption at 340 nm consist of short- and long-lived components. The lifetime of the short-lived species is evaluated to be 50 ns in the absence and presence of magnetic fields. The short-lived component is assigned to a triplet–triplet transition of *p*-alkoxybenzophenone, which shows maxima at 340 and 540 nm. The long-lived one is due to a biradical intermediate consisting of the BP ketyl and 1-anilino-substituted alkyl radicals. The decay time of the long-lived species is lengthened on application of external magnetic fields. Absorption spectra of the biradical have broad maxima at 340 and 550 nm. The primary process shown in Scheme 5 is concluded from comparison of observed transient absorption spectra and those reported in Ref. 14. Since the absorption spectrum of the anilinoalkyl moiety may not appear in the longer wavelength region, the observed transient spectra of long-lived species are entirely due to the benzophenone ketyl.[15] The transient absorbance due to the biradical is reduced on going from BP-12-AN to D2. The observed mass isotope effects on biradical formation are consistent with the mechanism that a hydrogen of the methylene group adjacent to anilino nitrogen is abstracted by the benzophenone in the excited triplet state.[13]

Magnetic Field and Magnetic Isotope Effects on the Decay Profile. The decay times of long-lived species have been recorded as a function of magnetic field strength (B_0) for naturally abundant BP-12-AN and appropriately substituted species by deuterium and heavy carbon (see Figs. 1, 2, 3, 4, and 5). Although in the low-field region it was rather difficult to measure the lifetime of long-lived species precisely, it was reliably measured from a decay profile obtained in the high-field region. The decay times of BP-12-AN and its isotopomers are listed in Table 1. Up to 1 T, conspicuous magnetic isotope effects are discernible by comparing the data for BP-12-AN and its heavy carbon isotopomers. The heavy carbon substitution effects are reasonably interpreted on the basis of INDO MO calculations done for model radicals, i.e. 1-anilinopropyl and *p*-methoxybenzophenone ketyl radicals. The calculated spin density is shown in Table 2.



Scheme 5.

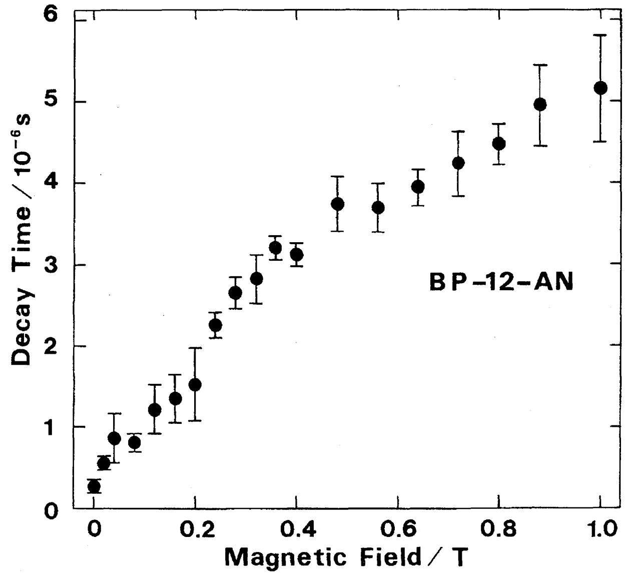


Fig. 1. Magnetic field effects on the decay time for biradical derived from BP-12-AN.

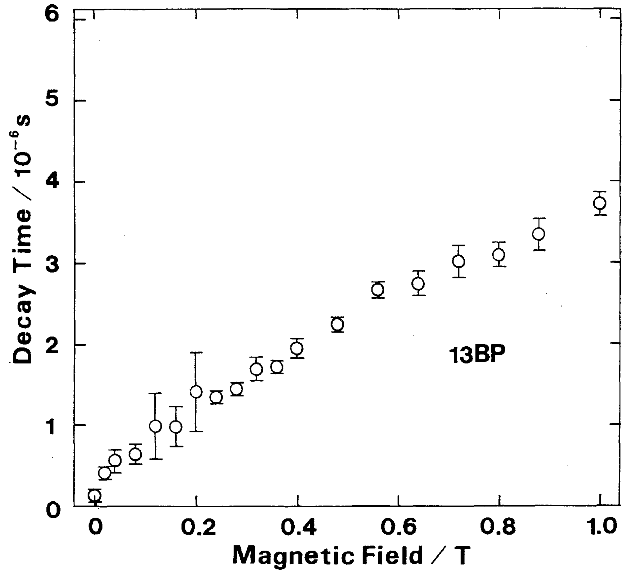


Fig. 2. Magnetic field effects on the decay time for biradical derived from 13BP.

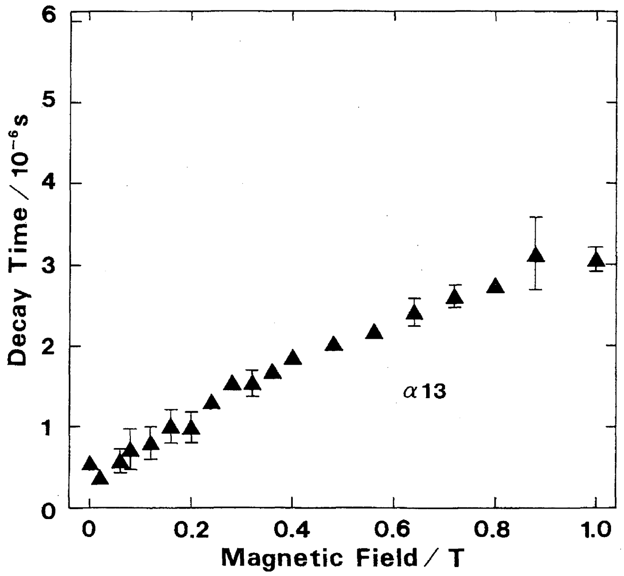


Fig. 3. Magnetic field effects on the decay time for biradical derived from α13.

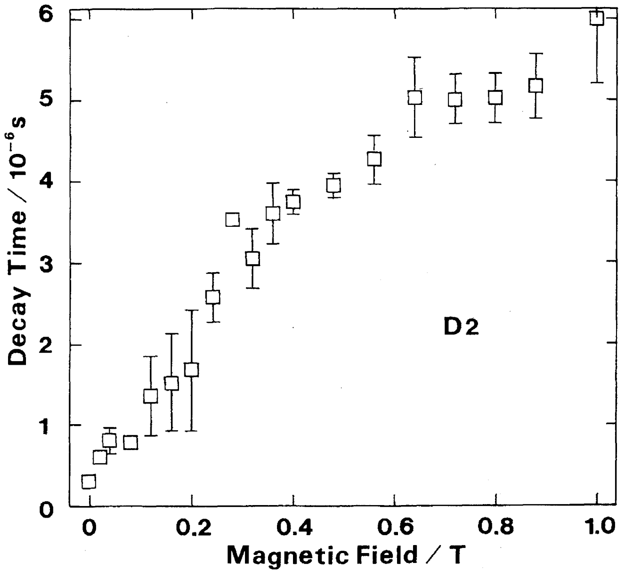


Fig. 4. Magnetic field effects on the decay time for biradical derived from D2.

The fact that the isotope substitution at the methylene group has larger effects on the decay rate than that at the carbonyl group corresponds to the results obtained by INDO MO calculations. The total spin at the N-terminal carbon of 1-anilinopropyl is higher than that at the benzylic site of the BP ketyl. Since the spin-lattice relaxation mechanism becomes significant in the high field region above 0.1 T, the data in Table 1 are interpreted in terms of spin-lattice relaxation induced by anisotropic hyperfine and dipole–dipole interactions.[13,14,16] These findings can be related with the magnitude of anisotropic hyperfine interaction[13] and summarized as follows:

1. On heavy carbon substitution the magnitude of hyperfine interaction is increased and the spin-lattice relaxation is mainly governed by anisotropic hf interaction.

2. Although the anisotropic hf interaction is reduced on deuteration, no significant difference in decay kinetics was observed for BP-12-AN and D9. In this case the dipole–dipole interaction may predominate in the spin-lattice relaxation process (vide infra).

The MO calculations show that spin density at the α-position is much higher than other sites. Therefore it is reasonably concluded that the anisotropic hyperfine field from the α-hydrogen is important in spin-lattice relaxation process. This is in agreement with the fact that the lifetime of the biradical derived from D2 is longer than those from BP-12-AN and D9. Similar deuteration effects have been observed for biradicals consisting of benzophenone ketyl and diphenylmethyl radicals. Longer biradical lifetimes are observed when the benzyl hydrogen of diphenylmethyl moiety

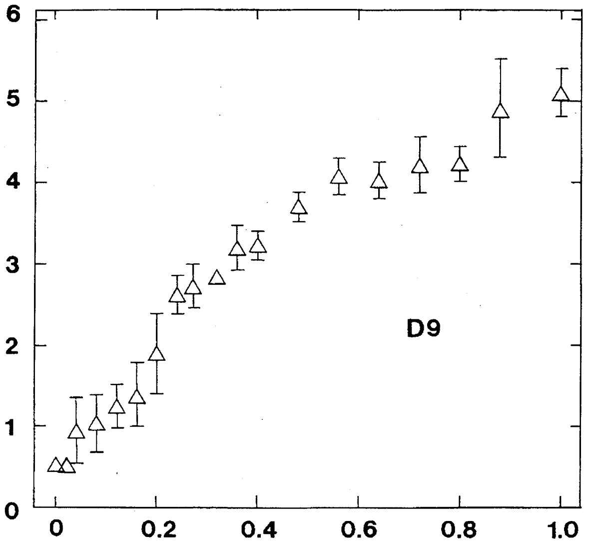


Fig. 5. Magnetic field effects on the decay time for biradical derived from D9.

Table 1. Magnetic Field Effects on Lifetimes of Biradicals[a)]

B_0/T	0.12	0.20	0.40	0.80	1.0
BP-12-AN	1.2	1.5	3.1	4.5	5.2
13 BP	1.0	1.4	2.0	3.1	3.7
α13	0.81	1.0	1.9	2.8	3.1
D2	1.4	1.7	3.8	5.0	6.1
D9	1.3	1.9	3.2	4.2	5.1

a) Lifetimes are given in μs. Experimental error is about 10%.

Table 2. Spin Density for Model Radicals

	α-Carbon[a)]	Benzylic carbon[b)]
2s-orbital	0.06036	0.04274
$2p_x$-orbital	0.02767	0.12030
$2p_y$-orbital	0.02587	0.04036
$2p_z$-orbital	0.69413	0.44760
Total	0.8080	0.6510

a) Calculated for model radical, 1-anilinopropyl. b) Calculated for model radical, *p*-methoxybenzophenone ketyl.

is replaced by deuterium in comparison with those for the species with natural isotopic abundance.[12)]

Changes in Anisotropic Hyperfine interaction Caused by Isotope Substitutions. Figure 6 summarizes a reaction scheme for biradicals in the high field region. Below 1 T anisotropic Zeeman mechanism plays a minor role in the spin-lattice relaxation process. The following factors, which may affect the spin-lattice relaxation process, should be measured: anisotropic hyperfine coupling tensor, rotational correlation times for the component radicals, and the magnitude of dipole–dipole interaction between the radicals. It is rather difficult to estimate all these quantities from analysis of observed results. In this study the increase in hf interaction caused by heavy carbon substitution is evaluated by the procedure described in our previous papers.[13,14)] The difference (Δk_{rlx}) in decay rates for BP-12-AN and isotopomers is attributed to the change in hf interaction by isotope substitution. This difference contains no contribution from the spin-lattice relaxation due to the dipole–dipole or the anisotropic Zeeman interaction. Since the difference between the data for BP-12-AN and deuterated species are rather small, the data for BP-12-AN and heavy carbon species are analyzed by taking the subtraction of two decay rates. Namely, the difference (Δk_{rlx}) is evaluated as follows:

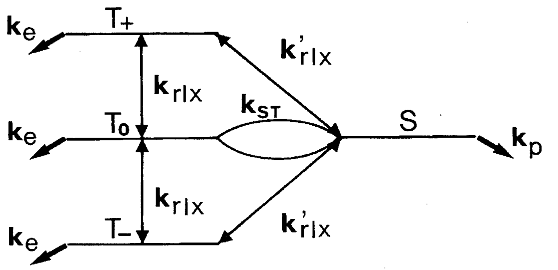


Fig. 6. Scheme for biradical reactions. Rate constants for the following processes: k_{rel}, spin-lattice relaxation among triplet sublevels; k'_{rel}, spin-lattice relaxation between T_+ (T_-) and S states; k_{ST}, intersystem crossing between T_0 and *S* states; k_{e}, bimolecular escape process (intermolecular biradical decay process); k_{p}, unimolecular cage product formation.

$$\Delta k_{\mathrm{rlx}} = \{1/\tau(\mathrm{L, isotopomer}) - 1/\tau(\mathrm{L, BP\text{-}12\text{-}AN})\}$$

The inverse of Δk_{rlx} was plotted as a function of the square of applied magnetic field strength, B_0. The results are shown in Fig. 7. Although some data points are scattered, approximately linear relationships are discernible in this figure.

The spin-lattice relaxation rate is expressed by the following equation:
$k_{\mathrm{rlx}} = (4\pi^2[\mathrm{V}]^2/h^2)\{\tau_{\mathrm{c}}/(1+\omega^2\tau_{\mathrm{c}}^2)\}$, where [V] refers to the magnitude of anisotropic hyperfine interaction, τ_{c} is rotational correlation time for the biradical, and $\omega = \gamma B_0$. Here γ is the gyromagnetic ratio for the electron on the biradical, which is assumed to be approximately equal to that of

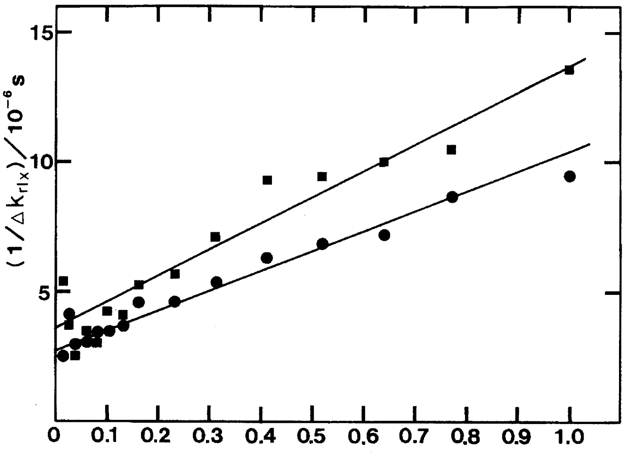


Fig. 7. Plot of $(\Delta k_{\mathrm{rel}})^{-1}$ against $B_0{}^2$. Circles for biradical derived from α13, squares for biradical derived from 13BP.

Table 3. Increase in Anisotropic Hyperfine Interaction Caused by Heavy Carbon Substitution [A]

Parent compound and substitution site	[A]/mT	τ_c/ps	Number of methylenes
BP-12-AN[a)]			
Benzylic carbon	1.0	10	11
α-Carbon	1.2	10	11
$BPCO_2$-12-DPM[b)]			
Benzylic carbon in DPM	0.75	10	12
BP-12-PEA[c)]			
Benzylic carbon in APK	0.98	12	12

a) Present work. b) *p*-Benzoylbenzoate(4-benzophenonecarboxylate)–diphenylmethane linked system. DPM: diphenylmethyl radical. Data taken from Ref. 13. c) Benzophenone-1-phenylethanol linked system. APK: acetophenone ketyl radical. Data taken from Ref. 13.

a free electron. It is reasonably assumed that the rotational correlation time is independent of isotope substitution. The magnitude of hf interaction in isotopomer can be estimated by taking the sum of squares:
$[V(\text{isotopomer})]^2 = [V(\text{BP-12-AN})]^2 + [A]^2$, where [A] corresponds to the increase in the anisotropic hf interaction due to heavy carbon substitution. The linear relationship is expected for the inverse of Δk_{rlx} and $B_0{}^2$:

$$1/\Delta k_{\text{rlx}} = 1/(\gamma^2 [A]^2 \tau_c) + \tau_c B_0{}^2/[A]^2.$$

From the intercept and slope, τ_c is estimated to be ca. 10 ps, and [A(13BP)] and [A(α13)] are evaluated to be 1.0 and 1.2 mT, respectively. These are compatible with previous results listed in Table 3 for biradicals composed of benzophenone ketyl and diphenylmethyl or acetophenone ketyl radicals.[13)]

The magnitude of the locally fluctuating magnetic field due to anisotropic hyperfine interaction in the BP ketyl has been calculated to be 0.176 mT for the normal BPK with natural isotopic abundance, 0.943 mT for the heavy-carbon-labeled BPK at the benzylic site, and 0.0746 mT for the nonadeuterio BPK.[14)] These values are in accordance with the observed increase in the anisotropic hyperfine interaction caused by the heavy carbon substitution (0.81 mT).[14)] Although the theoretical evaluation suggests that deuteration causes an appreciable change in a fluctuating local magnetic field due to anisotropic hyperfine interaction, small differences in the decay times were observed for BP-12-AN, D2, and D9. Observed deuteration effects indicate that anisotropic hyperfine interaction is of minor importance in the spin-lattice relaxation process of BP-12-AN, D2, and D9. The magnitude of the dipole–dipole interaction has been reported to be 0.35—0.48 mT for the biradical consisting of two equivalent ketyls (BPK-12-BPK).[14)] It can be concluded that the major contribution to spin-lattice relaxation is from the dipole–dipole interaction for the compound with natural abundance and the deuterated species.

Rate constants for reaction scheme shown in Fig. 6 were not completely evaluated from this analysis. The order of magnitude for k_p and k_e can be estimated from the magnetic field effects on cage and escape product yields. Although steady state photolysis data show distinct magnetic field effects on the quantum yield for parent molecule disappearance, major products are still unidentified at this stage of investigation. Our future work may be concerned with the magnetic field and magnetic isotope effects on end product yields and ultrahigh magnetic field effects on biradical decay kinetics.

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