Photolyses of Derivatives of Naphthyl and Anthryl Phosphates and Methylphosphonates

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Upon UV irradiation in acetonitrile, tri-1-naphthyl phosphate and di-1-naphthyl methylphosphonate underwent intramolecular rearrangement and *ipso*-coupling to give 1,2′-binaphthalen-1′-ol and 1,1′-binaphthalene, respectively. In the photolyses of tris(4-methoxy-1-naphthyl) phosphate and bis(4-methoxy-1-naphthyl) methylphosphonate in methanol, 4,4′-dimethoxy-1,1′-binaphthalene, 1′,4,4′-trimethoxy-1,2′-binaphthalene, and 2,4,4′-trimethoxy-1,1′-binaphthalene were generated. Tri-9-anthryl phosphate and di-9-anthryl methylphosphonate underwent intramolecular (4+4) photocycloaddition between two anthryl groups. The fluorescence spectra of the naphthyl derivatives had two emission bands ascribed to an intramolecular excimer and a monomer, but the fluorescence spectra of the anthryl derivatives had only a monomer emission band. These photoluminescence behaviors are closely related to the reactivities of the compounds.

It is known that two chromophores linked by a certain number of carbon atoms form an intramolecular excimer, for instance in compounds of types A-$(CH_2)_n$-A. The efficiency of intramolecular excimer formation is a function of n and often was optimal when $n=3$.[1—6]

Several studies of the intramolecular excimer or exciplex formation process and the kinetics of bichromophoric molecules containing naphthyl[7—16] and anthryl[17—22] groups have been reported. Although these compounds are almost unreactive, a few undergo (2+2) or (4+4) photocycloaddition to give cycloisomers. When the trimethylene chain connecting two chromophoric groups was replaced with an O–P–O chain, these chromophoric groups also formed an intramolecular excimer or exciplex and further underwent intramolecular reaction.[23—26] 4-Cyanophenyl 4-methoxyphenyl methylphosphonate gave 4-cyano-2-(4-methoxyphenyl)phenyl hydrogen methylphosphonate by an intramolecular electrophilic migration of one 4-methoxyphenyl group to another. 4-Chlorophenyl 4-methoxyphenyl methylphosphonate also gave 4-chloro-2-(4-methoxyphenyl)phenyl hydrogen methylphosphonate. In these reactions, a solvent effect was observed; the electrophilic solvent coordinating to the phosphoryl oxygen (P=O) enhanced the positive charge on the phosphorus atom, and as a result facilitated β-bond (O–Ar bond) cleavage.[27]

In this work, the photochemical behaviors of some derivatives of di- or trinaphthyl phosphate and methylphosphonate, and di- or trianthryl phosphate and methylphosphonate will be discussed.

Results and Discussion

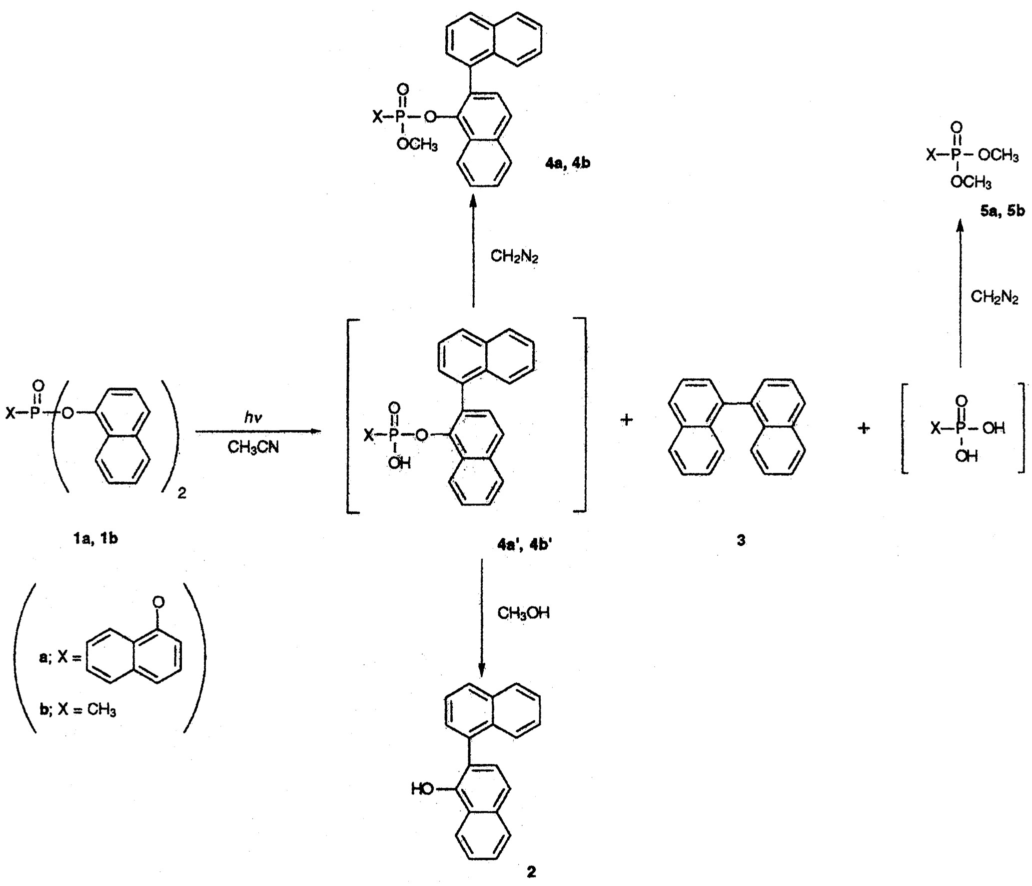
Photolysis of Naphthyl Derivatives. UV-irradiation of tri-1-naphthyl phosphate **1a** was carried out in acetonitrile (1.0×10^{-3} mol dm^{-3}) under argon atmosphere with a high-pressure mercury lamp for 20 min (26% conversion). After irradiation, methanol was added to the solution, which was allowed to stand overnight. 1,2′-Binaphthalen-1′-ol **2** was obtained in a 13% yield (quantum yield, $\phi=1.3\times10^{-2}$) accompanied by a trace amount of 1,1′-binaphthalene **3**. Treatment of the photolyzed products with diazomethane before methanolysis gave 1,2′-binaphthalen-1′-yl methyl 1-naphthyl phosphate **4a** (yield 46%) and a trace amount of dimethyl 1-naphthyl phosphate **5a**. Therefore, a precursor of **2** might be 1,2′-binaphthalen-1′-yl 1-naphthyl hydrogen phosphate **4a′**.

Upon UV-irradiation of di-1-naphthyl methylphosphonate **1b** for 1 h in the same manner as described above (69% conversion), product **2** was obtained in a 20% yield ($\phi=3.3\times10^{-3}$) as a main product, accompanied by a trace amount of **3**. In this case, a precursor of **2** might be 1,2′-binaphthalen-1′-yl hydrogen methylphosphonate **4b′** (Scheme 1).

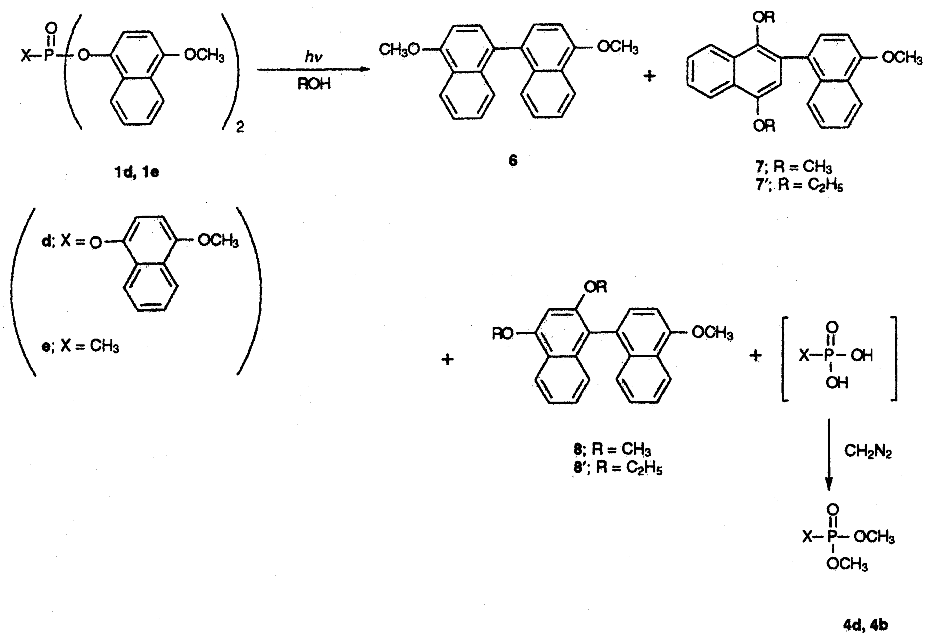
Tri-2-naphthyl phosphate **1c** was stable upon photoirradiation.

Photolysis of tris(4-methoxy-1-naphthyl) phosphate **1d** in methanol (1.0×10^{-3} mol dm^{-3}, irradiation for 5 min, 81% conversion) gave 4,4′-dimethoxy-1,1′-binaphthalene **6** (53%, $\phi=4.5\times10^{-3}$), 1′,4,4′-trimethoxy-1,2′-binaphthalene **7** (5%), and 2,4,4′-trimethoxy-1,1′-binaphthalene **8** (6%) (Scheme 2). After treatment with diazomethane, 4-methoxy-1-naphthyl dimethyl phosphate **5d** (74%) was also generated.

Photolysis of bis(4-methoxy-1-naphthyl) methylphosphonate **1e**, under similar conditions (irradiation for 1 min, 27% conversion), gave **6** (2%, $\phi=3.4\times10^{-3}$), **7**



Scheme 1.



Scheme 2.

(5%, ϕ=4.6×10^{-3}), and **8** (15%, ϕ=9.6×10^{-3}). When the conversion was increased to 65% (irradiation for 5 min), the yields of **6**, **7**, and **8** were 12, 14, and 20%, respectively. After treatment with diazomethane, dimethyl methylphosphonate **5b** (26 and 57%, respectively) was obtained.

When the photolysis of **1e** (conversion 47%) was performed in ethanol, **6** (2%), 1′,4′-diethoxy-4-methoxy-1,2′-binapthalene **7′** (6%), and 2,4-diethoxy-4′-methoxy-1,1′-binapthalene **8′** (14%) were obtained. It is noteworthy that products **7′** and **8′** were the diethoxy-homologues of **7** and **8**, respectively.

The photolysis of **1e** was carried out under triplet-sensitized conditions; a methanol solution of **1e** (1.0×10^{-3} mol dm^{-3}) containing benzophenone (2.0×10^{-2} mol dm^{-3}) was irradiated for 5 min (conversion 64%) with a high-pressure mercury lamp through a $BiCl_3$/HCl solution filter (cutoff below 355 nm). The yields of products **6** and **7** decreased to 2 and 4%, respectively, whereas the yield of **8** increased to 36%.

Fluorescence Spectra of Naphthyl Derivatives. The fluorescence spectra of **1a**, **1c**, and **5a** are shown in Fig. 1, and the fluorescence spectra of **1d**, **1e**, and **5d** are shown in Fig. 2. Compounds **5a** and **5d** were used as references of the monomer (singlet excited monomeric state) models of **1a**, **1c**, **1d**, and **1e**. The fluorescence spectra of **1a**, **1c**, **1d**, and **1e** consisted of two emission bands. The spectral shapes of **1a**, **1c**, **1d**, and **1e** were independent of the substrate concentration (from 1.0×10^{-4} to 1.0×10^{-6} mol dm^{-3}), therefore longer emission bands were ascribed to those of the intramolecular excimers.

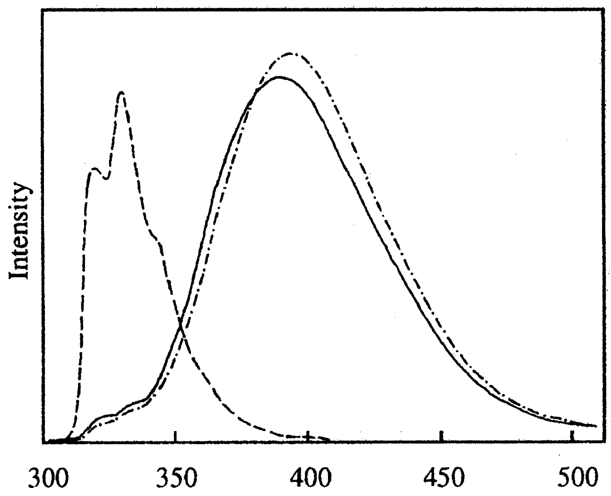


Fig. 1. Fluorescence spectra of **1a** (solid), **1b** (one dot broken), and **5a** (broken) in methanol (1.0×10^{-4} mol dm^{-3}, $\lambda_{ex}=280$ nm).

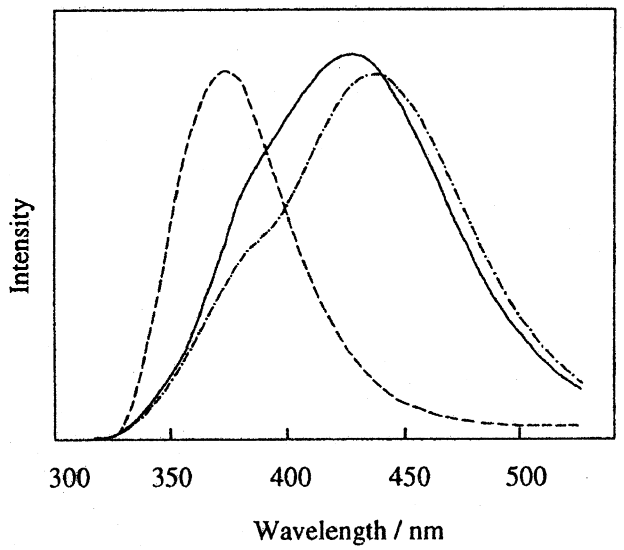


Fig. 2. Fluorescence spectra of **1d** (solid), **1e** (one dot broken), and **5d** (broken) in methanol (1.0×10^{-4} mol dm^{-3}, $\lambda_{ex}=280$ nm).

The fluorescence quantum yields of **1a**, **1c**, **1d**, and **1e** were determined as 0.14, 0.12, 0.11, and 0.11, respectively, by comparison with the fluorescence quantum yield of quinine sulfate.

Figure 3 shows the temperature dependence of the fluorescence spectra of **1d** and **1e**. The intramolecular excimer emission band of **1d** could be observed even

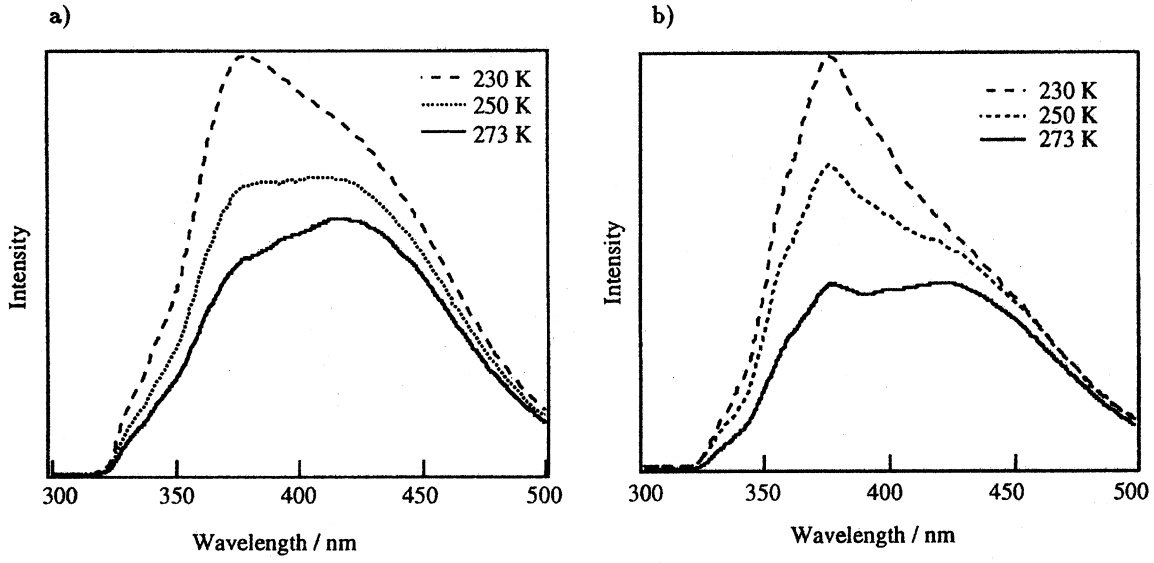


Fig. 3. Temperature dependence of fluorescence spectra of **1d** and **1e** in methanol (1.0×10^{-4} mol dm^{-3}, $\lambda_{ex}=280$ nm). a) **1d**; b) **1e**.

at a lower temperature of 230 K. On the other hand, the intramolecular excimer emission of **1e** at 230 K was concealed behind the monomer emission. This result suggests that the facility of formation of an intramolecular excimer may be greater in **1d** than **1e** because the number of methoxynaphthyl groups is larger in **1d** than **1e**, assuming the similarity of the temperature dependence of the fluorescence rate constant.

Quenching of 1e. The fluorescence spectra of the monomer and the intramolecular excimer of **1e** were quenched by dissolved oxygen in different manners; a linear correlation between the oxygen concentration and the fluorescence intensity of the monomer (350 nm) or intramolecular excimer (480 nm) emission band was found (Stern–Volmer analysis). The $k_{\mathrm{qm}}\tau_{\mathrm{m}}$ and $k_{\mathrm{qe}}\tau_{\mathrm{e}}$ values can be estimated by Eqs. 1 and 2, where ϕ_{m} and ϕ_{e}, or ϕ^0_{m} and ϕ^0_{e} are the quantum yields of the fluorescence of monomer and intramolecular excimer at the presence or the absence of oxygen, respectively, k_{qm} and k_{qe} are oxygen fluorescence quenching rate constants for the monomer and intramolecular excimer, respectively, and τ_{m} and τ_{e} are the fluorescence lifetimes of the monomer and intramolecular excimer, respectively.

$$\phi^0_{\mathrm{m}}/\phi_{\mathrm{m}} = 1 + k_{\mathrm{qm}}\tau_{\mathrm{m}}[\mathrm{Q}] \tag{1}$$

$$\phi^0_{\mathrm{e}}/\phi_{\mathrm{e}} = (1 + k_{\mathrm{qm}}\tau_{\mathrm{m}}[\mathrm{Q}])(1 + k_{\mathrm{qe}}\tau_{\mathrm{e}}[\mathrm{Q}]) \tag{2}$$

therefore,

$$(\phi^0_{\mathrm{e}}/\phi_{\mathrm{e}})/(\phi^0_{\mathrm{m}}/\phi_{\mathrm{m}}) = 1 + k_{\mathrm{qe}}\tau_{\mathrm{e}}[\mathrm{Q}] \tag{3}$$

For the monomer band (350 nm), $k_{\mathrm{qm}}\tau_{\mathrm{m}} = 20$ $\mathrm{mol^{-1}\,dm^3}$ (correlation coefficient: $r=0.998$) was obtained, while for the intramolecular excimer band (480 nm) $k_{\mathrm{qe}}\tau_{\mathrm{e}}=216$ $\mathrm{mol^{-1}\,dm^3}$ ($r=0.999$) was obtained. Similar quenching experiments based on the quantum yield of **6** were performed. From the linear correlation between the quantum yield of **6** and the concentration of oxygen, the $k_{\mathrm{q}}\tau$ value (here k_{q} is an oxygen quenching rate constant for formation of a product and τ is the lifetime of the excited species giving a product) was obtained as 231 ($r=0.991$). The value of **6** was in agreement with the $k_{\mathrm{qe}}\tau_{\mathrm{e}}$ value obtained from quenching experiments of the intramolecular excimer emission. Therefore, the formation of **6** probably proceeds through *ipso*-coupling from the intramolecular excimer. Product **7** may be produced by electrophilic attack of a 4-methoxy-1-naphthyl cation formed by heterolytic cleavage of the PO–C bond to another 4-methoxy-1-naphthyl group. Intermediate **9** may be in equilibrium with **9′** by migration of a 4-methoxy-1-naphthyl group through σ-bridged carbonium intermediate **10** (Scheme 3).[25] The presence of this intermediate is also supported by the formation of ethoxy derivative **7′** on photolysis of **1e** in ethanol.

The quantum yields of these products were affected by temperature; Table 1 summarizes the quantum yields of **6**, **7**, and **8** from **1e** at several temperatures.

Table 1. Temperature Dependence of Quantum Yields of **6**, **7**, and **8**[a)]

Temp	$\phi/10^{-3}$		
K	**6**	**7**	**8**
268	1.8	4.0	10.7
278	2.8	4.2	10.0
288	3.1	4.4	9.8
298	3.4	4.6	9.6
308	3.6	3.8	8.5
318	3.7	3.1	8.4

a) Conditions; in MeOH, 1.0×10^{-3} $\mathrm{mol\,dm^{-3}}$.

With decreasing temperature, the quantum yield of **6** decreased, but the quantum yield of **8** increased. The quantum yield of **7** had a maximum at 298 K. The complicating feature in the quantum yield by temperature may result from the successive reaction paths contained in the formation of products.

Photolyses of Tri-9-anthryl Phosphate 11a and Di-9-anthryl Methylphosphonate 11b. Upon irradiation with 365 nm monochromatic light in tetrahydrofuran (1.0×10^{-3} $\mathrm{mol\,dm^{-3}}$, irradiation for 5 min), **11a** underwent intramolecular (4+4) photocycloaddition between two anthryl groups to afford photocycloisomer **12a** (ϕ=2.5×10^{-2}) quantitatively.

Upon irradiation with 365 nm monochromatic light in acetonitrile (1.0×10^{-3} $\mathrm{mol\,dm^{-3}}$, irradiation for 5 min), **11b** gave photocycloisomer **12b** (ϕ=1.5×10^{-1}) quantitatively in the same manner as above (Scheme 4). Product **12b** was restored to **11b** upon irradiation with 254 nm monochromatic light.

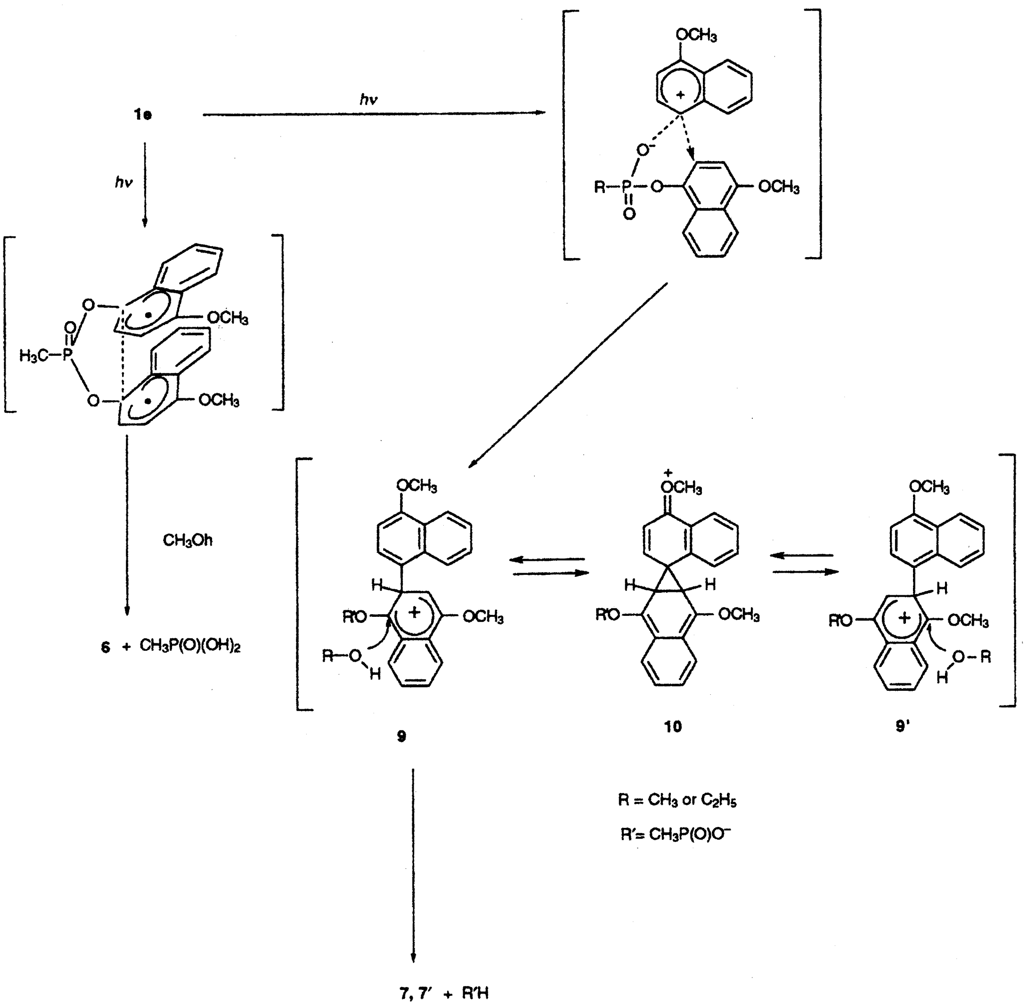
The quantum yields of **12a** and **12b** in acetonitrile, tetrahydrofuran, and benzene are shown in Table 2. The quantum yields of photocycloaddition were little affected by the polarity of the solvent. Bouas-Laurent and co-workers have reported that the quantum yields of the intramolecular photocycloaddition of bis(9-anthryloxy)methane and 1,3-di-(9-anthryl)propane in methylcyclohexane were 0.36 and 0.14, respectively.[22)] and the later value adequately approximates our results. No differences between O–P–O and methylene spacers were detected. These photochemical behaviors differ from those of phenyl or naphthyl derivatives.

Fluorescence Spectra of Anthryl Derivatives. The fluorescence spectra of **11a**, **11b**, and dimethyl 9-anthryl phosphate **11c** are shown in Fig. 4. Compound

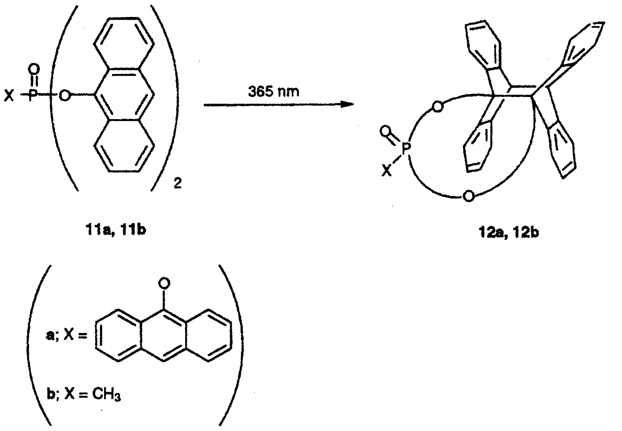
Table 2. Reaction Quantum Yields of **12a** and **12b** in Some Solvents[a)]

Solvent	$\phi_{\mathbf{12a}}/10^{-2}$	$\phi_{\mathbf{12b}}/10^{-1}$
Acetonitrile	—	1.5
Tetrahydrofuran	2.5	1.1
Benzene	2.4	1.1

a) Conditions; 1.0×10^{-3} $\mathrm{mol\,dm^{-3}}$, irradiated with 365 nm monochromatic light at room temperature.



Scheme 3.



Scheme 4.

11c was used as a reference for the monomer models of **11a** and **11b**. The fluorescence spectra of **11a** and **11b** were similar to the spectrum of **11c**, and consisted of only one component as in the results of the quenching analysis of the spectra by oxygen (described below). The intramolecular excimer emission was not observed at room temperature.

The fluorescence quantum yields of **11a**, **11b**, and

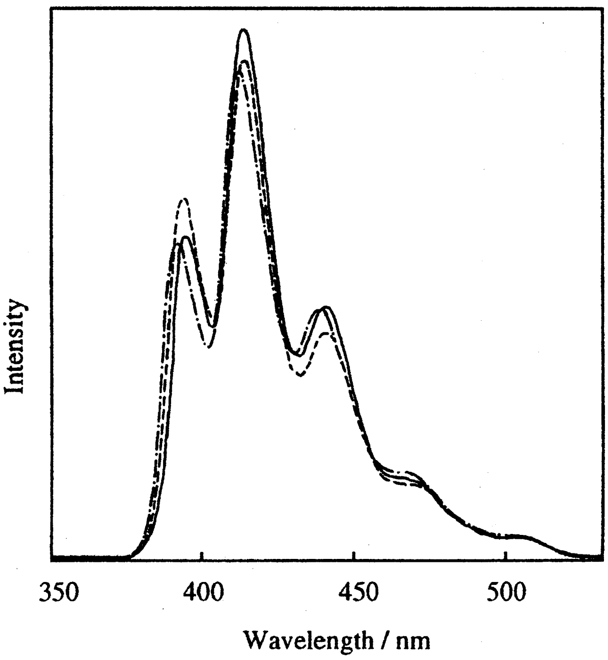


Fig. 4. Fluorescence spectra of **11a** (solid), **11b** (one dot broken), and **11c** (broken) in THF (1.0×10^{-4} mol dm^{-3}, $\lambda_{\mathrm{ex}}=365$ nm).

11c were determined to be 0.17, 0.21, and 0.47, respectively, by comparison with the fluorescence quantum yield of quinine sulfate.

Quenching of Anthryl Derivatives. The fluorescence spectra of **11a** and **11b** were quenched by dissolved oxygen. The quenching of both fluorescence spectra occurred in only one manner, similar to the quenching of **11c**. The $k_{\mathrm{qm}}\tau_{\mathrm{m}}$ values **11a**, **11b**, and **11c** were estimated by simple Stern–Volmer calculations as 12 (correlation coefficient: $r=0.996$), 14 ($r=0.999$), and 17 $\mathrm{mol^{-1}\,dm^{3}}$ ($r=0.997$), respectively. A similar quenching experiment on the quantum yield of **12b** was performed. From a linear correlation between the quantum yield of **12b** and the concentration of oxygen, $k_{\mathrm{q}}\tau=17$ $\mathrm{mol^{-1}\,dm^{3}}$ ($r=0.991$) was obtained. It is well-known that the intramolecular (4+4) photocycloaddition of bianthrylalkanes proceeds through an intramolecular excimer. However, when the intramolecular excimer is nonemissive, the rate constants of the cycloaddition and the non-radiative decay of the intramolecular excimer are much larger than those of the emission and the back reaction of the intramolecular excimer to the monomer.[28] It seems that the cycloisomer forms directly from the monomer. In our system, the intramolecular (4+4) photocycloaddition of **11b** probably occurs in the monomer directly, because the intramolecular excimer is nonemissive and $k_{\mathrm{q}}\tau$ of **12b** nearly agrees with $k_{\mathrm{qm}}\tau_{\mathrm{m}}$ of the monomer emission of **11b**.

Experimental

Apparatus. Melting points were obtained with a Yanagimoto micro point apparatus. CHN microanalyses were obtained with a Perkin–Elmer Model 240 analyzer. UV-visible spectra were recorded on a Hitachi 150-20 spectrometer. Steady-state fluorescence spectra were recorded on a Hitachi 850 type fluorescence spectrometer. The temperature effects of the fluorescence spectra were determined using an Oxford DN704 cryostat with a DTC-2 digital temperature controller. ^{1}H and ^{13}C NMR spectra were determined in $\mathrm{CDCl_3}$ with tetramethylsilane as an internal standard on a Bruker-AM600 spectrometer. GLC analyses were carried out by use of a 2% Silicone OV-17 column. GC-MS spectra were recorded with a JMS-DX 300 instrument and high-resolution mass spectra were obtained on a JMS-01SG-2 instrument. HPLC analyses were carried out on a Shimadzu LC-10AS instrument with a Shiseido Capcell Pak C18 AG 120 column. Photolysis was carried out with a 300 W high-pressure mercury lamp EHBW-300 (Eikosha Co., Ltd.), a 60 W low-pressure mercury lamp or an ultra-high-pressure mercury lamp using a monochromator.

Materials. Tri-1-naphthyl phosphate **1a** was prepared by the reaction of 1-naphthol with phosphorus pentachloride in carbon tetrachloride.[29] Mp 149—150 °C, λ_{max} (MeCN) 271.2 ($\varepsilon=1.6\times10^{4}$), and 280.4 ($1.9\times10^{4}$).

Di-1-naphthyl methylphosphonate **1b** was prepared by the following reaction. Methylphosphonic dichloride was added to an ether solution of 1-naphthol at the presence of triethylamine. Mp 77—78 °C, λ_{max} (MeOH) 271.2 ($\varepsilon=1.5\times10^{4}$) and 280.0 ($1.6\times10^{4}$).

Tri-2-naphthyl phosphate **1c** was prepared in a manner similar to **1a**.[29] Mp 96—97 °C, λ_{max} (MeCN) 273.6 ($\varepsilon=1.5\times10^{4}$).

Tris(4-methoxy-1-naphthyl) phosphate **1d** was prepared in a manner similar to **1a**.[29] Mp 110—111 °C, λ_{max} (MeCN) 298.4 ($\varepsilon=2.0\times10^{4}$) and 320.8 ($1.2\times10^{4}$).

Bis(4-methoxy-1-naphthyl) methylphosphonate **1e** was prepared in a manner similar to **1b**. Mp 106—107 °C, λ_{max} (MeCN) 298.0 ($\varepsilon=1.3\times10^{4}$).

Dimethyl 1-naphthyl phosphate **4a** was prepared by the reaction of 1-naphthol with dimethyl phosphorochloridate in the presence of triethylamine in ether. Bp 180—185 °C/0.1 mmHg (1 mmHg=133.322 Pa), λ_{max} (MeCN) 271.0 ($\varepsilon=7.4\times10^{3}$) and 279.0 ($9.5\times10^{3}$).

4-Methoxy-1-naphthyl dimethyl phosphate **4d** was prepared in a manner similar to that described above. Bp 187—193 °C/0.1 mmHg, λ_{max} (MeCN) 298.0 ($\varepsilon=1.2\times10^{4}$) and 320.8 ($7.6\times10^{3}$).

Tri-9-anthryl phosphate **11a** was prepared by the following reaction. A mixture of anthrone and triethylamine in ether was added dropwise into an ether solution of a one-third molar amount of phosphoryl trichloride. Mp 205—208 °C (Found: C, 80.33; H, 4.03; P, 5.17%. Calcd for $\mathrm{C_{42}H_{27}O_4P_1}$: C, 80.50; H, 4.34; P, 4.94%). MS *m/z* 626 ($\mathrm{M^+}$; 25), 610 (45), 417 (25), 239 (100), 223 (70), 193 (85), 165 (20), etc. UV λ_{max} (THF) 337.2 ($\varepsilon=8.9\times10^{3}$), 354.0 ($1.8\times10^{4}$), 372.8 ($2.8\times10^{4}$), and 393.6 ($2.6\times10^{4}$). ^{1}H NMR ($\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$) $\delta=8.28$ (6H, d, $J=8.6$ Hz), 8.19 (3H, s), 7.96 (6H, d, $J=8.6$ Hz), 7.37 (6H, dd, $J=8.6$ and 7.6 Hz), and 7.16 (6H, dd, $J=8.6$ and 7.6 Hz).

Di-9-anthryl methylphosphonate **11b** was prepared by the following reaction. A mixture of anthrone and triethylamine in ether was added dropwise into an ether solution of a one-half molar amount of methylphosphonic dichloride. Mp 233—234 °C (Found: C, 77.55; H, 4.56; P, 6.69%. Calcd for $\mathrm{C_{29}H_{21}O_3P_1}$: C, 77.67; H, 4.72; P, 6.91%). MS *m/z* 448 ($\mathrm{M^+}$; 100), 370 (10), 255 (55), 224 (10), 193 (45), 176 (10), 165 (15), etc. UV λ_{max} (THF) 333.2 ($\varepsilon=3.5\times10^{3}$), 349.6 ($7.2\times10^{3}$), 368.0 ($1.2\times10^{4}$), and 388.8 ($1.2\times10^{4}$). ^{1}H NMR ($\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$) $\delta=8.43$ (4H, d, $J=6.6$ Hz), 8.34 (2H, s), 8.00 (4H, d, $J=6.3$ Hz), 7.47 (8H), and 1.87 (3H, d, $J_{\mathrm{HP}}=16.9$ Hz).

Dimethyl 9-anthryl phosphate **11c** was prepared by the reaction of anthrone with dimethyl phosphorochloridate at the presence of triethylamine in ether. Mp 70—72 °C (Found: C, 63.71; H, 5.18; P, 10.16%. Calcd for $\mathrm{C_{16}H_{15}O_4P_1}$: C, 63.58; H, 5.00; P, 10.25%). MS *m/z* 302 ($\mathrm{M^+}$; 100), 288 (25), 274 (30), 194 (60), and 165 (25). UV λ_{max} (THF) 330.8 ($\varepsilon=2.6\times10^{3}$), 346.8 ($5.2\times10^{3}$), 364.8 ($7.9\times10^{3}$), and 384.8 ($7.2\times10^{3}$). ^{1}H NMR ($\mathrm{CDCl_3}$, $\mathrm{Me_4Si}$) $\delta=8.42$ (2H, d, $J=8.9$ Hz), 8.31 (1H, s), 7.98 (2H, d, $J=7.9$ Hz), 7.53 (2H, dd, $J=6.7$ and 8.9 Hz), 7.51 (2H, dd, $J=6.7$ and 7.9 Hz), and 3.98 (6H, s).

General Photolysis Procedure for Identification and Isolation of Products. A 250 $\mathrm{cm^3}$ solution of substrate (1.0×10^{-3} $\mathrm{mol\,dm^{-3}}$) was charged in a 10 mm thick doughnut-type cell (quartz or Pyrex) and argon was bubbled through the solution to purge dissolved air. After irradiation with a high-pressure mercury lamp (300 W) under cooling with water (20—25 °C) for 1 h, the reaction mixture was analyzed by HPLC and compared with authentic samples prepared by other methods. In some cases, the reaction products were isolated by column chromatography on silica gel, and the isolated products were identified by element analysis and ^{1}H and ^{13}C NMR spectroscopy. In addition, after methylation with diazomethane, the products were analyzed by GLC or GC-MS.

Product Analysis. After refluxing the photolyzed mixtures **1a** and **1b** in excess methanol, the same two products were isolated by a silica-gel column chromatography. Each component was identified as follows.

1,2′-Binaphthalen-1′-ol 2: MS *m/z* 270 (M$^+$; 100), 239 (10), 120 (10), etc. ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ=148.61, 134.54, 134.30, 134.25, 132.14, 128.94, 128.59, 128.57, 128.34, 127.57, 126.88, 126.58, 126.49, 126.25, 125.87, 125.57, 124.34, 122.58, 119.92, and 119.53. ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ=8.32 (1H, dd, J=9.0 and 2.3 Hz), 7.95 (1H, d, J=8.0 Hz), 7.96 (1H, d, J=7.0 Hz), 7.88 (1H, dd, J=8.8 and 2.3 Hz), 7.68 (1H, d, J=7.4 Hz), 7.61 (1H, dd, J=9.0 and 8.9 Hz), 7.56 (1H, dd, J=7.0 and 8.0 Hz), 7.55 (1H, d, J=6.9 Hz), 7.54 (1H, dd, J=7.0 and 8.0 Hz), 7.54 (1H, d, J=7.4 Hz), 7.53 (1H, dd, J=6.9 and 7.0 Hz), 7.42 (1H, dd, J=9.0 and 8.8 Hz), and 7.35 (1H, d, J=8.2 Hz).

1,1′-Binaphthalene 3: Mp 152—153 °C, **3** was identified by comparison with an authentic sample prepared by the method described below.

By methylation of **2** with diazomethane in methanol, 1-methoxy-1′,2-binaphthalene **2′** (MS *m/z* 284 (M$^+$; 100), 269 (70), 239 (20), 134 (10), etc.) was obtained. In the case of **1b**, methylation with diazomethane before methanolysis gave methyl 1′,2-binaphthalen-1′-yl methylphosphonate (**4b**) (MS *m/z* 362 (M$^+$; 20), 270 (70), 253 (100), etc.), **3**, and dimethyl methylphosphonate (**5b**).

Photolysis of **1c** was carried out in a manner similar to that described above. Phosphate **1c** was recovered and no product was detected by HPLC.

In both photolyses of tris(4-methoxy-1-naphthyl) phosphate **1d** and bis(4-methoxy-1-naphthyl) methylphosphonate **1e**, the same three components were isolated by silica-gel column chromatography, and each component was identified by ^{1}H and ^{13}C NMR spectroscopy.

4,4′-Dimethoxy-1,1′-binaphthalene 6: MS *m/z* 314 (M$^+$; 100), 299 (40), 268 (20), 239 (20), 284 (10), etc. ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ=155.07, 134.09, 130.80, 127.98, 126.45, 126.34, 125.50, 125.02, 122.03, 103.40, and 55.58. ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ=8.26 (1H, d, J=8.4 Hz), 7.35 (1H, dd, J=8.0 and 8.4 Hz), 7.27 (1H, d, J=7.7 Hz), 7.19 (1H, dd, J=8.0 and 8.4 Hz), 7.26 (d, J=8.4 Hz), 6.82 (1H, d, J=7.8 Hz), and 3.98 (3H, s).

1′,4,4′-Trimethoxy-1,2′-binaphthalene 7: MS *m/z* 344 (M$^+$; 100), 329 (70), 301 (30), 215 (10), etc. ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ=155.32, 147.63, 142.37, 135.18, 133.80, 130.37, 129.37, 129.11, 127.85, 126.72, 126.58, 126.31, 126.01, 125.50, 125.18, 123.99, 122.13, 121.45, 117.54, 103.31, 61.25, 56.90, and 55.65. ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ=8.37 (1H, d, J=8.5 Hz), 8.21 (1H, d, J=8.5 Hz), 7.45 (1H, dd, J=7.1 and 8.7 Hz), 7.33 (1H, d, J=8.3 Hz), 7.30 (1H, s), 7.47 (1H, dd, J=7.0 and 8.3 Hz), 7.35 (1H, dd, J=7.1 and 8.7 Hz), 7.32 (1H, d, J=8.2 Hz), 7.15 (1H, dd, J=6.9 and 8.2 Hz), 6.93 (1H, d, J=7.8 Hz), 7.39 (1H, d, J=7.8 Hz), 4.09 (3H, s), 3.98 (3H, s), and 3.97 (3H, s).

2,4,4′-Trimethoxy-1,1′-binaphthalene 8: MS *m/z* 344 (M$^+$; 100), 329 (70), 301 (30), 215 (10), etc. ^{13}C NMR (CDCl$_3$; Me$_4$Si) δ=155.32, 147.63, 142.37, 135.18, 133.80, 130.37, 129.37, 129.11, 127.85, 126.72, 126.58, 126.31, 126.01, 125.50, 125.18, 123.99, 122.13, 121.45, 117.54, 103.31, 61.25, 56.90, and 55.65. ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ=8.37 (1H, d, J=8.5 Hz), 8.21 (1H, d, J=8.5 Hz), 7.47 (1H, dd, J=7.0 and 8.3 Hz), 7.45 (1H, dd, J=7.1 and 8.7 Hz), 7.39 (1H, d, J=7.8 Hz), 7.35 (1H, dd, J=7.1 and 8.7 Hz), 7.33 (1H, d, J=8.3 Hz), 7.32 (1H, d, J=8.2 Hz), 7.30 (1H, s), 7.15 (1H, dd, J=6.9 and 8.2 Hz), 6.93 (1H, d, J=7.8 Hz), 4.09 (3H, s), 3.98 (3H, s), and 3.97 (3H, s).

By methylation of a photolyzed mixture of **1d** with diazomethane in methanol, **4d**, **6**, **7**, and **8** were obtained. In the case of **1e**, **4b**, **6**, **7**, and **8** were obtained.

In the photolysis of **1e** in ethanol, three components were isolated. One was **6**. The other two components were as follows;

1′,4′-Diethoxy-4-methoxy-1,2′-binaphthalene 7′: MS *m/z* 372 (M$^+$; 100), 343 (45), 330 (30), 315 (95), 287 (40), 255 (10), 215 (15), etc. ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ=155.07, 150.35, 146.56, 132.81, 129.54, 129.52, 128.23, 127.70, 126.49, 126.48, 126.23, 126.13, 125.62, 125.39, 125.04, 122.53, 122.20, 122.03, 103.40, 101.87, 69.59, 63.97, 55.59, 15.54, and 14.90. ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ=8.34 (1H, d, J=9.2 Hz), 8.33 (1H, d, J=9.0 Hz), 8.20 (1H, d, J=8.3 Hz), 7.72 (1H, d, J=8.4 Hz), 7.56 (1H, dd, J=7.0 and 8.3 Hz), 7.53 (1H, dd, J=8.3 and 9.2 Hz), 7.48 (1H, dd, J=8.1 and 9.3 Hz), 7.48 (1H, d, J=7.7 Hz), 7.42 (1H, dd, J=7.0 and 8.5 Hz), 6.90 (1H, d, J=7.8 Hz), 6.73 (1H, s), 4.14 (2H, q, J=6.9 Hz), 4.07 (3H, s), 3.54 (2H, q, J=7.0 Hz), 1.50 (3H, t, J=6.9 Hz), and 0.95 (3H, t, J=7.1 Hz)

2,4-Diethoxy-4′-methoxy-1,1′-binaphthalene 8′: MS *m/z* 372 (M$^+$; 100), 358 (30), 343 (98), 315 (70), 299 (20), 255 (10), 215 (10), etc. ^{13}C NMR (CDCl$_3$, Me$_4$Si) δ=155.25, 146.88, 142.02, 134.64, 133.82, 130.45, 129.73, 129.46, 127.85, 126.58, 126.54, 126.35, 125.75, 125.49, 125.14, 123.95, 122.09, 121.83, 119.20, 103.31, 69.34, 65.48, 55.63, 15.99, and 15.31. ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ=8.36 (1H, d, J=8.4 Hz), 8.24 (1H, d, J=8.3 Hz), 7.46 (1H, dd, J=6.9 and 8.3 Hz), 7.43 (1H, dd, J=7.1 and 8.7 Hz), 7.38 (1H, d, J=7.8 Hz), 7.35 (1H, d, J=8.3 Hz), 7.33 (1H, dd, J=7.0 and 8.3 Hz), 7.32 (1H, d, J=8.3 Hz), 7.27 (1H, s), 7.14 (1H, dd, J=7.0 and 8.3 Hz), 6.92 (1H, d, J=7.8 Hz), 4.33 (2H, q, J=7.0 Hz), 4.20 (2H, q, J=7.0 Hz), 4.08 (3H, s), 1.54 (3H, t, J=7.0 Hz), and 1.41 (3H, t, J=7.0 Hz).

The photocycloisomer of tri-9-anthryl phosphate **11a** was obtained as follows. A 250 cm^3 tetrahydrofuran solution of **11a** (1.0×10^{-3} mol dm^{-3}) was charged in a doughnut-type Pyrex cell and argon was bubbled through the solution to purge dissolved air. After irradiation with a 300 W high-pressure mercury lamp under water cooling with water (20—25 °C) for 1 h, the solution was concentrated and the photoproduct was purified by silica-gel column chromatography (eluent: chloroform/hexane=1 : 3). Mp>260°C decomp (Found: C, 80.39; H, 4.06; P, 5.11%. Calcd for $C_{42}H_{27}O_4P_1$: C, 80.50; H, 4.34; P, 4.94%). MS *m/z* 626 (M$^+$; 100), 610 (10), 370 (15), 239 (25), 223 (15), 194 (85), 178 (35), 165 (50), etc. ^{1}H NMR (CDCl$_3$, Me$_4$Si) δ=8.29 (2H, d, J=8.6 Hz), 8.19 (1H, s), 7.95 (2H, d, J=8.6 Hz), 7.83 (4H, d, J=7.3 Hz), 7.63 (4H, d, J=6.6 Hz), 7.37 (2H, dd, J=8.6 and 7.6 Hz), 7.16 (2H, dd, J=8.6 and 7.6 Hz), 7.05 (4H, dd, J=8.3 and 7.3 Hz), 6.97 (4H, dd, J=8.3 and 6.6 Hz), and 4.79 (2H, s).

The photocycloisomer of di-9-anthryl methylphosphonate

12b was obtained by a manner similar to that for **12a**. Mp >260°C decomp (Found: C, 77.43; H, 4.78; P, 6.83%. Calcd for $C_{29}H_{21}O_3P_1$: C, 77.67; H, 4.72; P, 6.91%). MS *m/z* 448 (M^+; 100), 370 (10), 255 (50), 240 (10), 193 (40), 176 (10), 165 (15), etc. ^{13}C NMR ($CDCl_3$, Me_4Si) δ=140.99, 140.23, 139.60, 127.36, 127.23, 125.93, 123.54, 52.80, and 12.54. ^1H NMR ($CDCl_3$, Me_4Si) δ=7.53 (4H, d, J=7.5 Hz), 7.13 (4H, d, J=8.8 Hz), 6.95 (4H, dd, J=8.8 and 6.1 Hz), 6.93 (4H, dd, J=6.1 and 7.5 Hz), 4.68 (2H, s), 2.35 (3H, d, J_{HP}=17.5 Hz).

Preparation of Authentic Samples. 1,1′-Binaphthalene **3** was prepared by following reaction. 1-Bromonaphthalene was heated with copper and iodine at 280 °C for 4 h to give **3**.[30] Mp 152—153 °C, bp 220—224 °C. ^{13}C NMR ($CDCl_3$, Me_4Si) δ=138.56, 133.64, 132.96, 128.17, 127.92, 127.87, 126.61, 125.99, 125.82, and 125.38. ^1H NMR ($CDCl_3$, Me_4Si) δ=7.94 (1H, d, J=6.9 Hz), 7.93 (1H, d, J=6.9 Hz), 7.58 (1H, dd, J=7.0, 6.9 Hz), 7.48 (1H, d, J=8.0 Hz), 7.46 (1H, dd, J=7.0 and 6.9 Hz), 7.39 (1H, d, J=8.4 Hz), and 7.26 (1H, dd, J=7.7 and 8.0 Hz).

4,4′-Dimethoxy-1,1′-binaphthalene **6** was prepared by the following reaction. To a solution of 1-methoxynaphthalene in 98% formic acid, one molar amount of hydrogen peroxide was added dropwise at 40 °C for 12 h. The red precipitate formed was recrystallized from ethyl acetate to give a pure product, mp 262—263 °C.

Benzophenone Sensitization. A benzophenone sensitization experiment was carried out under the following conditions; a methanol solution of **1e** (1.0×10^{-3} mol dm^{-3}) containing benzophenone (2.0×10^{-2} mol dm^{-3}) was irradiated with a high-pressure Hg lamp through a $BiCl_3/HCl$ solution filter.

Temperature Effect of Fluorescence Spectra. Fluorescence spectra were observed using a quartz cell (10 mm×10 mm) filled with a methanol solution of **1d** or **1e** (1.0×10^{-4} mol dm^{-3}). The temperature was controlled by a cryostat with a digital temperature controller. The emission spectra were recorded on a fluorescence spectrometer.

Measurement of Product Quantum Yields. The quantum yields of product formation were measured as follows: A 3-cm^3 methanol solution of the substrate (1.0×10^{-3} mol dm^{-3}) saturated with argon gas in a quartz cell (10 mm×10 mm) was irradiated using a low-pressure mercury lamp. Photolysis was stopped within 10% conversion. Actinometry was carried out using a potassium trioxalatoferrate(III) solution.[31] The product yield was determined by GLC using biphenyl as a standard.

Temperature Effect of Product Quantum Yields on the Photolysis of 1e. The quantum yields of the formation of **6**, **7**, and **8** were measured as described above. A quartz cell (10 mm×10 mm) filled with a methanol solution of **1e** (1.0×10^{-3} mol dm^{-3}) was dipped in a transparent quartz Dewar flask. The temperature of the samples was kept constant by circulating methanol or water.

Measurement of the Quantum Yields of Photocycloisomer 12a and 12b Formation. The quantum yields of the formation of **12a** and **12b** were measured as follows: A 3-cm^3 solution of substrate (1.0×10^{-3} mol dm^{-3}) saturated with argon gas in a quartz cell (10 mm×10 mm) was irradiated with 365 nm monochromatic light using a ultra-high-pressure mercury lamp with a monochromator. Actinometry was carried out using a potassium trioxalatoferrate(III) solution.[31] The product yield was determined by HPLC using naphthalene as a standard.

Measurement of Fluorescence Spectra Quantum Yields. The fluorescence quantum yields at 298 K were determined as relative quantum yields to that of quinine sulfate (1.0×10^{-4} mol dm^{-3}) in 0.5 mol dm^{-3} sulfuric acid (ϕ=0.55) as a reference.[32]

Quenching of Fluorescence by Oxygen. Six 3-cm^3 solutions of the substrate (1.0×10^{-4} mol dm^{-3}) were charged in six separate quartz cells (10 mm×10 mm). Argon, air, 40, 60, 80% oxygen/nitrogen or pure oxygen gas was bubbled into the solutions until saturated at 20 °C for 10 min. The concentrations of oxygen in these solutions were evaluated from their solubilities in the solvent. The emission spectra were recorded on a fluorescence spectrometer.

Quenching of Product Quantum Yields by Oxygen. Six 3-cm^3 solutions of the substrate (1.0×10^{-3} mol dm^{-3}) saturated with the prescribed concentration of oxygen were prepared, and their quantum yields were measured in a manner similar to that described above.

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