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Correlation of Exciplex Formation with Ground State Conformations in Flexible Bichromophoric Esters: 2-(1-Pyrenyl)ethyl *p*-Cyanobenzoate and Its Model Compounds

Jun Kawakami,† Toshiaki Furuta, Junko Nakamura,†† Akira Uchida, and Michiko Iwamura*

Department of Biomolecular Science, Faculty of Science, Toho University, 2-2-1 Miyama, Funabashi, Chiba 274-8510

†Department of Materials Science and Technology, Faculty of Science and Technology, Hirosaki University, Hirosaki, Aomori 036-8561

††Institute of Physical and Chemical Research, Wako, Saitama 350-01

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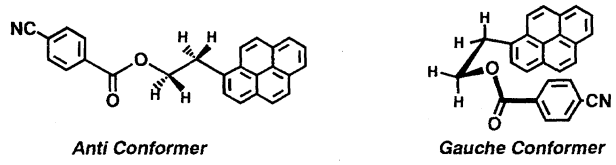
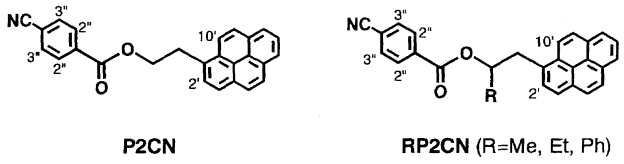
Two kinds of model compounds for a bichromophoric ester, 2-(1-pyrenyl)ethyl *p*-cyanobenzoate (**P2CN**), were synthesized: 1-substituted 2-(1-pyrenyl)ethyl *p*-cyanobenzoates (**RP2CN**, R = Me, Et, and Ph) as flexible model compounds and *trans*-2-(1-pyrenyl)cyclohexyl *p*-cyanobenzoate (**cyclo-P2CN**) as a rigid model compound. **P2CN** and all the model compounds had an intramolecular exciplex emission ($\phi_{EX} \approx 0.010$) and efficient quenching of fluorescence from the locally excited pyrene part ($\phi_{LE} \approx 0.001$). The decay lifetimes of the locally excited pyrene were 365 ps for **P2CN** and 66 ps for **cyclo-P2CN**, which were respectively identical with the risetime for the exciplex formation. The ^{1}H NMR of both **P2CN** and **RP2CN** showed the shifts of H_2'' and H_3'' of the *p*-cyanobenzoyl to the higher and H_{10}' of 1-pyrenyl signals to the lower magnetic field compared with those of the reference compounds, approaching towards those of **cyclo-P2CN**. NOE was observed between H_{10}' and H_2'' of **cyclo-P2CN**, and, although very weak, between H_2' and H_3'' of **MeP2CN**. In the solid state, **P2CN** adopts a folded conformation, which is roughly close to the gauche conformation, with the dihedral angle of 57.5° between *p*-cyanophenyl ring and pyrenyl ring based on X-ray crystallographic analysis on a leaflet monoclinic crystal, suggesting the exciplex formation from this conformation in **P2CN**.

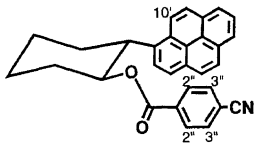
Intramolecular excimer or exciplex formation has been studied extensively using bichromophoric molecules of general structure D–$(CH_2)_n$–A, where D and A denote donor and acceptor chromophores, respectively. Of particular interest is the role of geometric effects, i.e., the relative orientations of the two chromophores in the ground state that give rise to an excimer or an exciplex.[1—6] For example, Zachariasse and co-workers reported, on the basis of the conformational analysis of α,ω-di(1-pyrenyl)alkane by ^{1}H NMR, that one of the emissive excimers was derived from a sandwich-like conformer in which the two chromophores are in a face-to-face disposition.[3,4] As for the correlation of an intramolecular exciplex formation with ground-state conformation, De Shryver and his group reported that the intramolecular exciplex of *N,N*-dimethyl-3-(1-pyrenyl)-1-propylamine was derived from two distinct ground state conformers, which were correlated with the orientation of the C–N bond.[5c] Eisenthal and co-workers reported, based on the time-resolved fluorescence analysis, that two ground state conformers of 9-{3-[4-(dimethylamino)phenyl]propyl}anthracene gave two kinds of exciplexes, one with an emission maxima at ca. 500 nm and a lifetime of 1.9 ns, and the other with ca. 600 nm and 2.6 ns, respectively.[6] However, their exact conformation has not been mentioned.

Previously, we studied the effects of the substituents upon fluorescence quenching and exciplex formation in ω-(1-pyrenyl)alkyl *p*-substituted benzoates **P*n*X**. Among these flexible bichromophoric esters, those with n = 1 or 2 and **X** = CN show strong fluorescence quenching and exciplex formation in solvents of various polarity.[7] Large negative values of the free energy change in electron transfer between methyl *p*-cyanobenzoates and methyl 2-(1-pyrenyl)-ethyl ether obtained electrochemically ($\Delta G_{ET} = -0.41$ eV) indicate that efficient photoinduced electron transfer from the pyrene part to the benzoate part is responsible for the strong fluorescence quenching as well as the exciplex formation.[7] We studied spectroscopic properties of 2-(1-pyrenyl)ethyl *p*-cyanobenzoate (**P2CN**) in detail, because they showed the most outstanding effects among those examined.[8] Single photon counting measurements on an ethyl acetate solution of **P2CN** showed a decay lifetime of 365 ps for the locally excited pyrene emission, which is exceptionally short for an isolated pyrene chromophore and identical with the rise time of the exciplex emission. The observation of ^{1}H NMR NOE between the pyrene and *p*-cyanobenzoate ring protons of **P2CN** suggested the presence of a considerable amount of the folded conformers in the ground state in which the *p*-cyanobenzoate part is situated roughly gauche to the pyrene part with respect to the C_1–C_2 bond. We therefore presumed that the exciplex with a very short risetime of 365 ps might be derived from the folded conformers (Scheme 1). However, a possibility of the exciplex formation from the extended con-



Scheme 1.





Scheme 2.

formers (i.e., the *p*-cyanobenzoate part is situated anti with respect to the pyrene ring) via the rotation of the C_1–C_2 bond cannot be excluded if the rate of the interconversion between the folded and extended conformers in the excited state is comparable to the rate of decay of the photo-excited state. We therefore became interested in using conformationally restricted model compounds to discuss the correlation of the exciplex formation with the ground state conformation in our system. *trans*-2-(1-Pyrenyl)cyclohexyl *p*-cyanobenzoate (**cyclo-P2CN**) has a *gauche* conformation for the two chromophores with respect to the C_1–C_2 bond of the cyclohexane ring, and it can be used as a rigid model compound for the *gauche* conformer of **P2CN** (Scheme 2). 1-Substituted 2-(1-pyrenyl)ethyl *p*-cyanobenzoates (**RP2CN**, R = Me, Et, Ph) are flexible molecules, although the *gauche* conformation for the two chromophores with respect to the C_1–C_2 bond might be more favorable than the anti one because a bulkier alkyl or phenyl on C_1 has to be in the *anti*-position with respect to the pyrene on C_2. ^{1}H NMR of **RP2CN** clearly showed that this is the case. The fluorescence spectra and the decay lifetimes were also studied in detail. X-Ray crystallographic analysis of **P2CN** showed a preference for a folded conformation in the solid state which is roughly close to the *gauche* conformation.

Experimental

General. ^{1}H NMR spectra were recorded on a JEOL GSX 270 or JEOL α-500 spectrometer with TMS as an internal standard. UV-visible absorption spectra were taken on a Hitachi 330 spectrometer. Three-dimensional intensity data were collected by a Rigaku AFC-6 diffractometer. Fluorescence spectra and its temperature dependency were taken on a Hitachi 850 fluorophotometer. Fluorescence quantum yields were measured at room temperature relative to those of pyrene (ϕ_f = 0.53)[9] for solutions of matched absorbance (0.1) at the excitation wavelength (313 nm). Fluorescence lifetimes were measured with a photon-counting apparatus with a hydrogen arc lamp (Hamamatsu Photophysics, time resolution ca. 1 ns). The measurements of fluorescence lifetimes in the picosecond range were done with a mode-locked Nd-YAG laser using its second harmonic emission of R6G and DCM (310—327 nm) as a picosecond excitation light source.

Materials. Spectrograde solvents (Fluorosol, supplied by Cica-Merck) were used without further purification. For measurements of absorption and emission spectra and lifetimes, all of the compounds were purified by repeated column chromatography on silica gel and recrystallization. Their purity was confirmed by HPLC with UV absorption and fluorescence emission detectors. In the case where impurities were detected even after repeated chromatography and recrystallization, the sample solution was collected directly from HPLC. The concentration of the solutions for spectroscopic studies was adjusted to less than 10^{-5} M (1 M = 1 mol dm^{-3}) where no intermolecular interaction was found and the absorbance at the excited wavelength was less than 0.1. The samples were degassed by freeze-pump-thaw cycles on a high vacuum line (at ca.10^{-5} Torr, 1 Torr = 133.322 Pa) and sealed under vacuum.

Synthesis. The preparation and the material data of 2-(1-pyrenyl)ethyl *p*-cyanobenzoate (**P2CN**) were reported in Ref. 7.

***trans*-2-(1-Pyrenyl)cyclohexanol:** To a stirred solution of 1.43 g (5.09 mmol) of 1-bromopyrene in dry THF (10 mL) at −72 °C was added 3.6 mL (5.1 mmol) of a solution of BuLi in hexane (1.43 M), and this mixture was stirred for an additional 20 min under argon. To the 1-pyrenyl lithium solution was added 0.63 mL (5.1 mmol) of borontrifluoride etherate via a syringe within 20 s, and then 0.57 mL (5.6 mmol) of cyclohexene oxide was added via a syringe within 10 s. The mixture was gradually warmed to room temperature over 16 h with stirring. The reaction was quenched by adding saturated sodium bicarbonate. The mixture was then diluted with chloroform and washed with 1 M HCl and saturated brine. Drying over anhydrous magnesium sulfate and concentration under vacuum yielded a crude product. The crude product was chromatographed on a column (70 g of Wako Gel C-200, 9% ethyl acetate/hexane) to yield 895 mg (2.98 mmol, 58% yield) of *trans*-2-(1-pyrenyl)cyclohexan-1-ol: Mp 138—140 °C; ^{1}H NMR (270 MHz; $CDCl_3$; Me_4Si) δ = 8.45 (1H, d, J = 9.0 Hz), 8.2—8.0 (8H, m), 4.10 (1H, m), 3.69 (1H, m), 2.28 (1H, m), and 2.1—1.6 (8H, m).

***trans*-2-(1-Pyrenyl)cyclohexyl *p*-Cyanobenzoate (cyclo-P2CN):** To a stirred solution of 24.7 mg (0.0822 mmol) of *trans*-2-(1-pyrenyl)cyclohexanol, 12.8 mg (0.087 mmol) of *p*-cyanobenzoic acid and 0.5 mg (0.004 mmol) of 4-dimethylaminopyridine (DMAP) in dichloromethane (1 mL), 11.6 mg (0.056 mmol) of dicyclohexylcarbodiimide at 0 °C was added. The stirring was continued for 1 h at 0 °C and then overnight at room temperature. White precipitates were filtered off and the filtrate was washed with 1 M HCl and saturated sodium bicarbonate. Drying over anhydrous magnesium sulfate and concentration under vacuum yielded a crude product. After flash column chromatography (10 g of Wako Gel C-300, 6.2% ethyl acetate/hexane), 25.7 mg (0.060 mmol, 73% yield) of **cyclo-P2CN** was isolated: Mp 85—86 °C; ^{1}H NMR (270 MHz; $CDCl_3$; Me_4Si) δ = 8.51 (1H, d, J = 9.5 Hz), 8.20—7.98 (8H, m), 7.57 (2H, d, J = 8.0 Hz), 7.30 (2H, d, J = 8.0 Hz), 5.55 (1H, ddd, J = 10, 10, and 8 Hz), 4.10 (1H, ddd, J = 10, 10, and 8 Hz), 2.47 (1H, m) 2.22 (1H, m), and 2.06—1.61 (6H, m). HRMS Calcd for $C_{30}H_{23}NO_2$: M^+, 429.1729. Found : m/z 429.1717 (M^+).

1-(1-Pyrenyl)-2-propanol: To a stirred solution of 1.410 g (5.015 mmol) of 1-bromopyrene in dry THF (22 mL) at −78 °C was added 3.6 mL (5.1 mmol) of a solution of BuLi in hexane (1.43 M), and stirring was continued at this temperature for an additional 20

min under argon. To the 1-pyrenyl lithium solution was added 0.7 mL (10 mmol) of 1,2-epoxypropane via a syringe, and the mixture was gradually warmed to room temperature over 16 h with stirring. The reaction was quenched by adding saturated ammonium chloride. After evaporation of the excess THF, the mixture was extracted with chloroform. Washing with saturated brine, drying over anhydrous magnesium sulfate and concentration under vacuum yielded 1.82 g of crude product. The crude product was chromatographed on a column (50 g of Wako Gel C-200, 20% ethyl acetate/hexane) to give 735 mg (2.82 mmol, 56% yield) of 1-(1-pyrenyl)-2-propanol and 51 mg (0.20 mmol, 4% yield) of its regio isomer: Mp. 110 °C; ^{1}H NMR (270 MHz; $CDCl_3$; Me_4Si) δ = 8.31 (1H, d, J = 9.0 Hz), 8.20—8.0 (7H, m), 7.91 (1H, d, J = 8.0 Hz), 4.32 (1H, m), 3.54 (1H, dd, J = 5.0 and 13.5 Hz), 3.46 (1H, dd, J = 8.0 and 13.5 Hz), 1.53 (1H, d, J = 3.5 Hz), and 1.39 (3H, d, J = 6.0 Hz). Found: C, 87.86; H, 5.89%. Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19 %.

1- Methyl- 2- (1- pyrenyl)ethyl *p*- Cyanobenzoate (MeP2-CN): This reaction was done as described for the preparation of **cyclo-P2CN**, except that 131 mg (0.503 mmol) of 1-(1-pyrenyl)-2-propanol was used. After column chromatography (15 g of Wako Gel C-200, 6.2% ethyl acetate/hexane), 44.2 mg (0.113 mmol, 23% yield) of **MeP2CN** was isolated: Mp 197 °C; ^{1}H NMR (270 MHz; $CDCl_3$; Me_4Si) δ = 8.46 (1H, d, J = 9.0 Hz), 8.22—7.95 (7H, m), 8.06 (2H, d, J = 8.5 Hz), 7.92 (1H, d, J = 8.0 Hz), 7.67 (2H, d, J = 8.5 Hz), 5.66 (1H, ddq, J = 7.2, 6.5, and 6.0 Hz), 3.94 (1H, dd, J = 6.5 and 13.5 Hz), 3.56 (1H, dd, J = 7.2 and 13.5 Hz), and 1.45 (3H, d, J = 6.0 Hz). HRMS Calcd for $C_{27}H_{19}NO_2$: M^+, 389.1416. Found: m/z 389.1412 (M^+).

1- Ethyl- 2- (1- pyrenyl)ethyl *p*- Cyanobenzoate (EtP2-CN): This reaction was done as described for the preparation of **cyclo-P2CN** except that 1,2-epoxybutane was used instead of cyclohexene oxide: Mp 174 °C; ^{1}H NMR (270 MHz; $CDCl_3$; Me_4Si) δ = 8.48 (1H, d, J = 9.0 Hz), 8.23—7.95 (7H, m), 8.06 (2H, d, J = 9.0 Hz), 7.90 (1H, d, J = 8.0 Hz), 7.68 (2H, d, J = 9.0 Hz), 5.54 (1H, dd, J = 5.0 and 7.0 Hz), 3.89 (1H, dd, J = 7.0 and 14.5 Hz), 3.58 (1H, dd, J = 5.0 and 14.5 Hz), 1.83 (2H, m), and 1.02 (3H, t, J = 7.5 Hz). Found: C, 83.10; H, 5.44; N, 3.66%. Calcd for $C_{28}H_{21}NO_2$: C, 83.37; H, 5.21; N, 3.47%.

1-Phenyl-2-(1-pyrenyl)ethanol: This reaction was done as described for the preparation of **PhP2CN**, except that 0.722 g (6.01 mmol) of styrene oxide was used instead of cyclohexene oxide. After column chromatography (50 g of Wako Gel C-200, 14% ethyl acetate/hexane), 245 mg (0.761 mmol, 15% yield) of 1-phenyl-2-(1-pyrenyl)ethanol was isolated: Mp 135 °C; ^{1}H NMR (270 MHz; $CDCl_3$; Me_4Si) δ = 8.24—7.78 (9H, m,), 7.45—7.30 (5H, m), 5.17 (1H, dd, J = 6.0 and 7.5 Hz), 3.76 (1H, dd, J = 7.5 and 14.0 Hz), 3.73 (1H, dd, J = 6.0 and 14.0 Hz), and 1.60 (1H, s). HRMS Calcd for $C_{24}H_{18}O$: M^+, 322.1358. Found: m/z 322.1352 (M^+).

1- Phenyl- 2- (1- pyrenyl)ethyl *p*- Cyanobenzoate (PhP2-CN): This reaction was done as described for the preparation of **cyclo-P2CN**, except that 100 mg (0.311 mmol) of 1-phenyl-2-(1-pyrenyl)ethanol was used. After recrystallization from benzene, 137 mg (0.304 mmol, 98% yield) of **PhP2CN** was isolated: Mp 239 °C; ^{1}H NMR (270 MHz; $CDCl_3$; Me_4Si) δ = 8.43 (1H, d, J = 9.5 Hz), 8.20—7.98 (8H, m), 8.06 (2H, d, J = 9.0 Hz), 7.68 (2H, d, J = 8.0 Hz), 7.67 (2H, d, J = 9.0 Hz), 7.40—7.28 (5H, m), 6.45 (1H, dd, J = 6.5 and 7.5 Hz), 4.18 (1H, dd, J = 7.5 and 14.0 Hz), and 3.85 (1H, dd, J = 6.5 and 14.0 Hz). Found: C, 85.45; H, 4.76; N, 3.08%. Calcd for $C_{32}H_{21}NO_2$: C, 85.14; H, 4.66; N, 3.10%.

Results

Synthesis. As summarized in Fig. 1, **RP2CN** (R = Me, Et, and Ph) were obtained by esterification of *p*-cyanobenzoic acid with the corresponding 1-substituted 2-(1-pyrenyl)ethanol, which was prepared by the reaction of 1-bromopyrene with butyl lithium followed by the addition of 2-substituted oxirane (substituents: methyl, ethyl, and phenyl) in the presence of boron trifluoride etherate. **Cyclo-P2CN** was prepared similarly from the reaction of 1-bromopyrene with cyclohexene oxide via 2-(1-pyrenyl)cyclohexanol. The crude compounds were purified by repeated column chromatography and recrystallization until they satisfied the degree of purity required for emission spectrum measurements. The structures were analyzed by ^{1}H NMR as well as by the elemental analysis and MS spectra.

NMR Studies. In **P2CN**, an exciplex emission was observed in several solvents with a range of the dielectric constants (ε) of 1.94—36.2 including chloroform (ε = 4.70). The ^{1}H NMR spectra (7.0—8.6 ppm) of **P2CN**, **RP2CN** (R = Me, Et, and Ph), and **cyclo-P2CN** in deuteriochloroform obtained at 270 MHz are shown in Fig. 2, where the chemical shifts of the reference compounds, (H_2'' and H_3'' for those of methyl *p*-cyanobenzoate, and H_{10}' for that of **P2M**), are indicated. Table 1 shows the chemical shifts and their shifts from the reference compounds ($\Delta\delta$). While the chemical shifts of H_{10}' of all these compounds are to the lower magnetic field, those of H_2'' and H_3'' shifted to a higher magnetic field

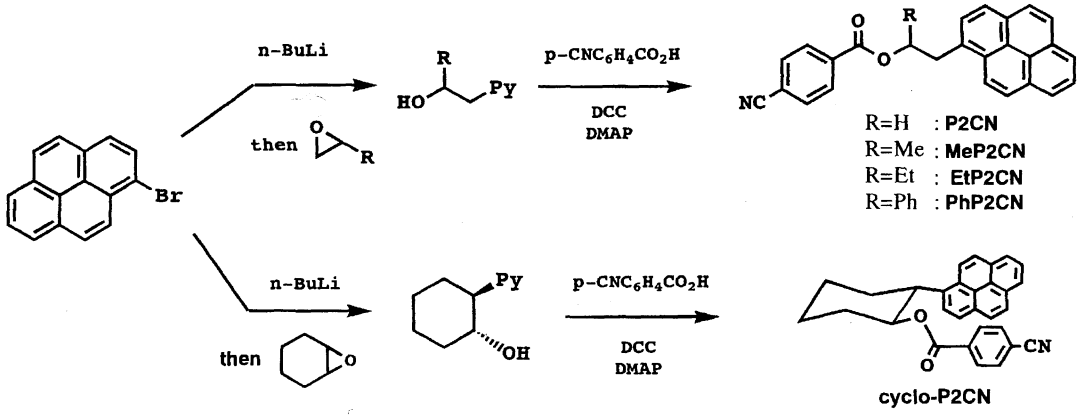


Fig. 1. Sythesis of **RP2CN** (R = Me, Et, and Ph) and **cyclo-P2CN**.

Table 1. Chemical Shifts (δ) and Displacements ($\Delta\delta$) from the References

	H'_{10}		H''_2		H''_3	
	δ/ppm	$\Delta\delta$[a)]	δ/ppm	$\Delta\delta$[b)]	δ/ppm	$\Delta\delta$[c)]
P2CN	8.38	+0.05	8.03	−0.11	7.65	−0.11
MeP2CN	8.46	+0.13	8.06	−0.08	7.67	−0.09
EtP2CN	8.48	+0.15	8.06	−0.08	7.68	−0.08
PhP2CN	8.43	+0.10	8.06	−0.08	7.67	−0.09
cyclo-P2CN	8.51	+0.18	7.57	−0.57	7.30	−0.46

a) $\Delta\delta$ are the displacements of chemical shifts from H'_{10} of 2-(1-pyrenyl)ethyl acetate. b) $\Delta\delta$ are the displacements of chemical shifts from H''_2 of methyl *p*-cyanobenzoate. c) $\Delta\delta$ are the displacements of chemical shifts from H''_3 of methyl *p*-cyanobenzoate.

Table 2. Crystal Data of **P2CN**

Formula	$C_{26}H_{17}NO_2$
Formular weight	375.41
Color of crystal	Colorless
Crystal system	Monoclinic
Space group	$P2_1/a$
Unit cell parameters	a = 11.837(2) Å
	b = 5.261(1) Å
	c = 30.714(4) Å
	β = 98.36(1)°
	V = 1892.4(6) Å^3
Z	4
Residuals $R(F)$; $wR(F^2)$	0.069; 0.147
GOF on F^2	1.07

Table 3. Bond Lengths, Angles, and Torsion Angles of **P2CN**

O(1)–C(18)	1.445(7)
O(1)–C(19)	1.335(6)
O(2)–C(19)	1.183(6)
C(1)–C(17)	1.502(9)
C(17)–C(18)	1.520(8)
C(19)–C(20)	1.508(8)
C(19)–O(1)–C(18)	116.3(5)
C(1)–C(17)–C(18)	113.1(6)
O(1)–C(18)–C(17)	107.6(5)
O(1)–C(19)–O(2)	123.9(6)
O(1)–C(19)–C(20)	111.9(5)
O(2)–C(19)–C(20)	124.2(6)
C(2)–C(1)–C(17)–C(18)	−93.6(7)
C(19)–O(1)–C(18)–C(17)	169.2(5)
C(1)–C(17)–C(18)–O(1)	71.6(7)
C(18)–O(1)–C(19)–C(20)	−174.7(5)
C(1)–C(19)–C(20)–C(21)	−1.8(8)

compared to those of the reference compounds. ^{1}H NMR 1D NOE and 2D NOE (NOESY) measurements were done to estimate the ground state conformations. The 1D NOE was observed between the H''_2 and H'_{10} protons of **cyclo-P2CN** in deuteriochloroform (Fig. 3a). Although 1D NOE was not observed, **MeP2CN** showed weak but distinct 2D NOE (NOESY) between the H'_2 and H''_3 (Fig. 3b).

X-Ray Crystal Structure Analysis. A leaflet crystal of **P2CN** was obtained from a mixture of benzene and hexane and used for X-ray crystal structure analysis. An ORTEP drawing is given in Fig. 4 and crystal data are shown in Table 2. Selected bond lengths, angles, and torsion angles are listed in Table 3. As shown in the ORTEP drawing in Fig. 4, the molecule adopts a folded conformation with

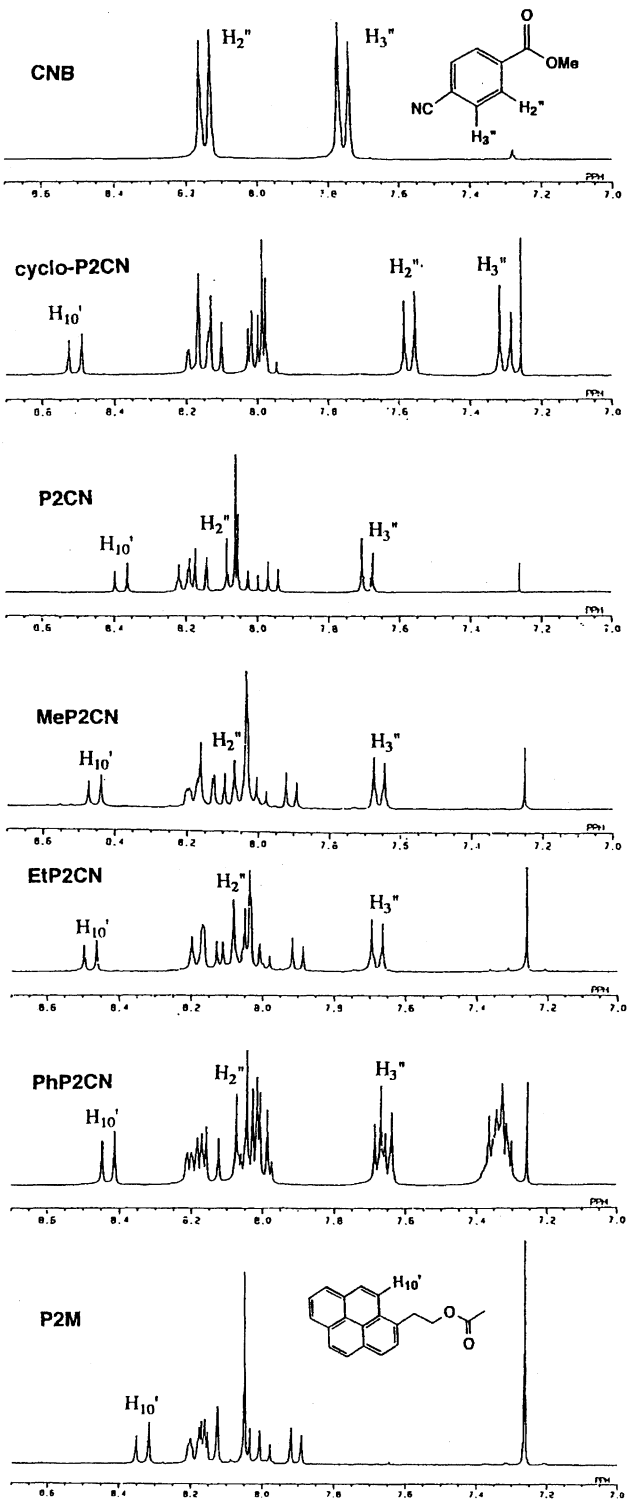


Fig. 2. ^{1}H NMR spectra of **CNB**, **cyclo-P2CN**, **P2CN**, **RP2CN** (R = Me, Et, and Ph) and **P2M**.

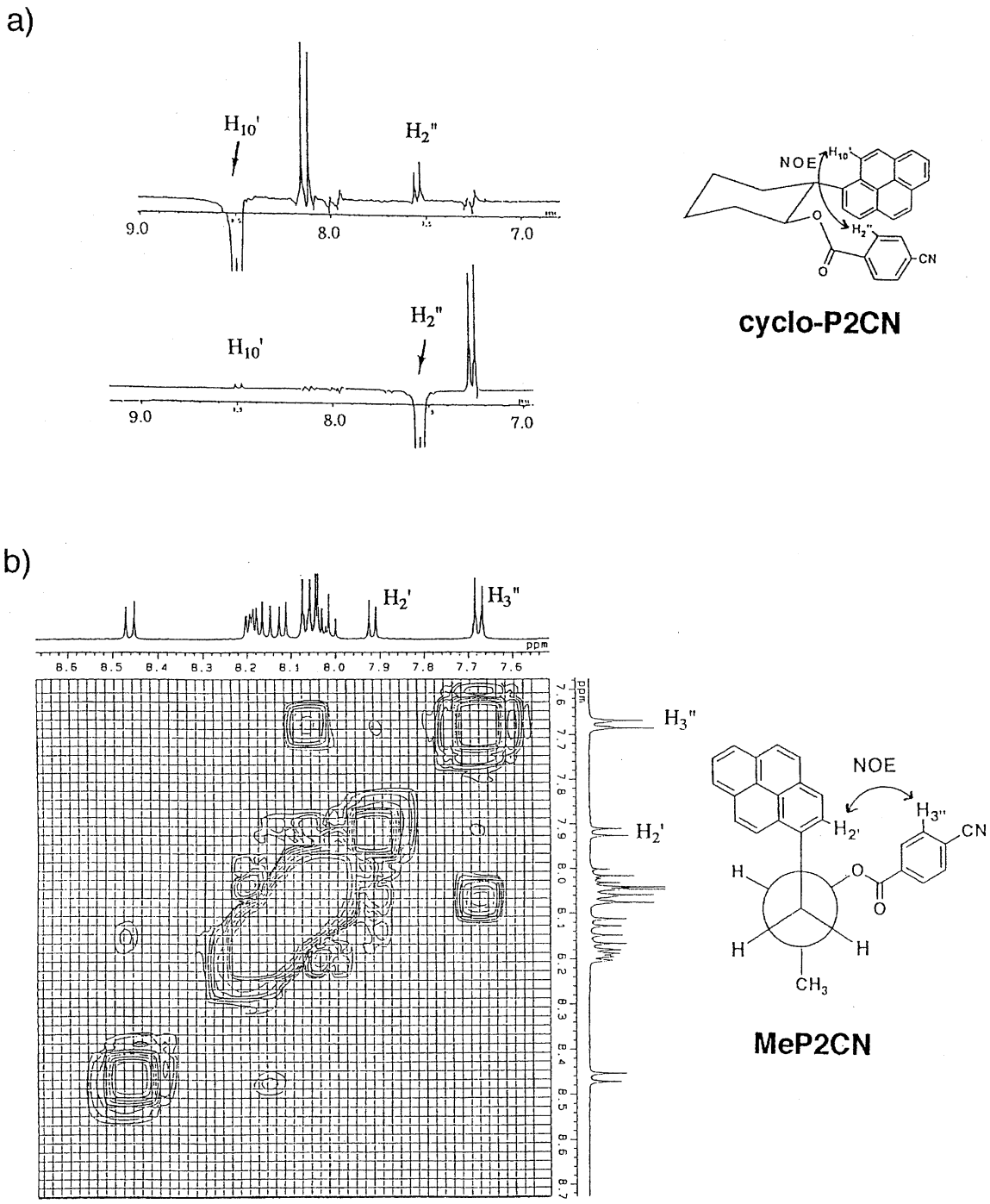


Fig. 3. ^{1}H NMR NOE spectra in $CDCl_3$ at room temperature. a) NOE difference spectrum of **cyclo-P2CN** (270 MHz). b) 2D NOESY spectrum of **MeP2CN** (500 MHz).

the angle of 57.5° between the *p*-cyanophenyl and pyrenyl rings, in which the dihedral angle of C(1)–C(17)–C(18)–O(1) is 71.6°, and roughly close to the *gauche* orientation.

Absorption Spectra and Emission Spectra. The UV absorption spectra of **P2CN**, **RP2CN** (R = Me, Et, and Ph), and **cyclo-P2CN** were superimposable on the corresponding equimolar mixture of the reference compounds 2-(1-pyrenyl)ethyl acetate (**P2M**) and methyl *p*-cyanobenzoate (**CNB**). The absorption spectra of these compounds above 300 nm is similar to that of pyrene, and no new absorption at longer wavelengths was observed. Therefore, the strong intramolecular interactions, such as charge transfer between the pyrenyl and the *p*-cyanobenzoyl chromophores, are absent in the ground states of these compounds.

P2CN, **RP2CN**, and **cyclo-P2CN** had strong exciplex emissions along with very weak locally excited emissions from the pyrenyl part in solvents of low to medium polarity such as isooctane or ethyl acetate. Figure 5 shows the emission spectra of these compounds in ethyl acetate. Fluorescence quantum yields (Φ) in ethyl acetate obtained relative

Table 4. Exciplex Emission Maxima (λ_{max}), Fluorescence Quantum Yields (Φ),[a] and Fluorescence Lifetimes (τ_f)[b] in Ethyl Acetate

	λ_{max}/nm	Φ_{total}[c]	Φ_{LE}[c]	Φ_{EX}[c]	Φ_{EX}/Φ_{total}	τ_f/ns
P2CN	505	0.011	0.001	0.010	0.91	0.365
MeP2CN	496	0.010	0.001	0.009	0.90	<1
EtP2CN	501	0.010	0.001	0.009	0.90	<1
PhP2CN	503	0.010	0.001	0.009	0.90	<1
cyclo-P2CN	484	0.009	0.0002	0.0088	0.98	0.066

a) Relative to pyrene (Φ = 0.53). b) Monitored at 377 nm. c) $\Phi_{total} = \Phi_{LE} + \Phi_{EX}$, where Φ_{LE} is the emission from the pyrene part and Φ_{EX} is the exciplex emission.

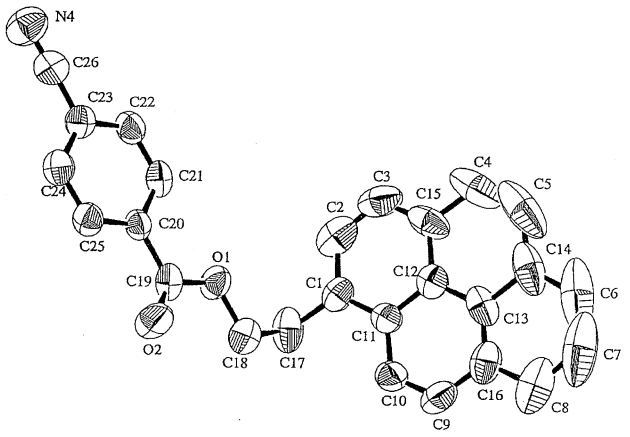


Fig. 4. An ORTEP drawing of 2-(1-pyrenyl)ethyl *p*-cyanobenzoate (**P2CN**).

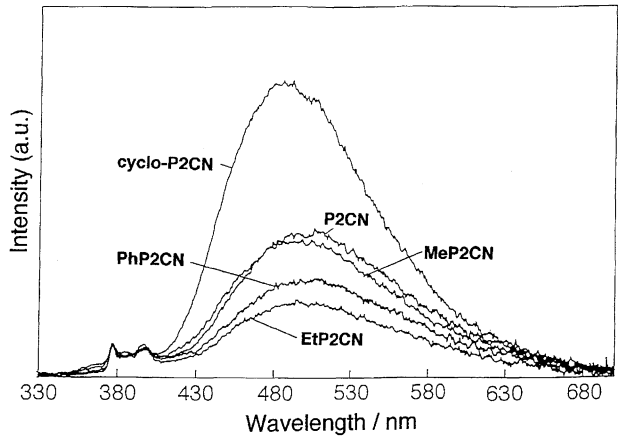


Fig. 5. Fluorescence spectra excited at 313 nm in ethyl acetate at room temperature, normarized at 377 nm.

to that of pyrene are reported in Table 4, in which Φ_{total} is the quantum yield for total emission, Φ_{LE} is that of a locally excited emission, and Φ_{EX} is that of the exciplex emission. The Φ_{total} values of **P2CN**, **RP2CN**, and **cyclo-P2CN** are almost the same (ca. 0.01) and are far smaller than those of pyrene itself (Φ = 0.53 in a polar solvent), indicating that fluorescence quenching by photo-induced electron transfer is efficient. The ratio of Φ_{EX}/Φ_{total} is largest in **cyclo-P2CN** in which the two chromophores are fixed in the *gauche* position so that an exciplex is formed most readily. As far as the ratios of Φ_{EX}/Φ_{total} are concerned, the bulkiness of the substituents in **RP2CN** did not have any particular effect on exciplex formation.

The temperature dependency of **P2CN**, **RP2CN** (R = Me, Et, and Ph), and **cyclo-P2CN** fluorescence in ethyl acetate was examined in the temperature range of -80 to 20 °C (Fig. 6). The intensity of the exciplex emission of these compounds were decreased more sharply than that of the locally excited emission as the temperature was lowered. At the same time, the exciplex emission maxima were shifted to a longer wavelength by the increase of the solvent polarity at the lower temperature.

Time-Resolved Single Photon Counting Measurements. The fluorescence lifetimes monitored at 377 nm, which correspond to the decay lifetimes of the locally excited pyrenyl group in ethyl acetate, are given in Table 4. The time-resolved single photon counting measurement on **cyclo-P2CN** gave 66 ps for a rise time of the exciplex formation and the lifetime of the locally excited pyrene, which is considerably shorter than that of 365 ps observed for **P2CN**.[7,8] The decay lifetimes of **RP2CN** (R = Me, Et, and Ph) in the nanosecond time scale were found to be less than 1 ns. Although their lifetimes have not been measured in the picosecond time scale, they are expected to be between 365 and 66 ps, judging from the similarities in their other spectral properties to those of **P2CN** and **cyclo-P2CN**.

Discussion

While bond rotation in simple alkanes such as butane takes place within 100 ps, computer simulations have demonstrated that the bond rotation in a system with two bulky substituents in the anti orientation, such as 1,4-diarylsubstituted butane, requires more time.[10] Eisenthal et al. showed that their observations on 9-anthracene-$(CH_2)_3$-*p*-*N*,*N*-dimethylaniline is consistent with this prediction: The exciplex formation occured on the nanosecond time scale because the bond rotation must drag large moieties through the solvent.[6] Therefore, the exciplex formation in **P2CN** with the excited state lifetime of 365 ps would be more likely from the ground state conformers in which the two chromophores are situated closely so that a drastic change of conformation is not necessary; the exciplex formation from the *anti* conformer is unlikely. To obtain more information on the ground state conformers producing the exciplex, we synthesized two kinds of model compounds that correspond to the *gauche* conformers of **P2CN**: **cyclo-P2CN** as a rigid model

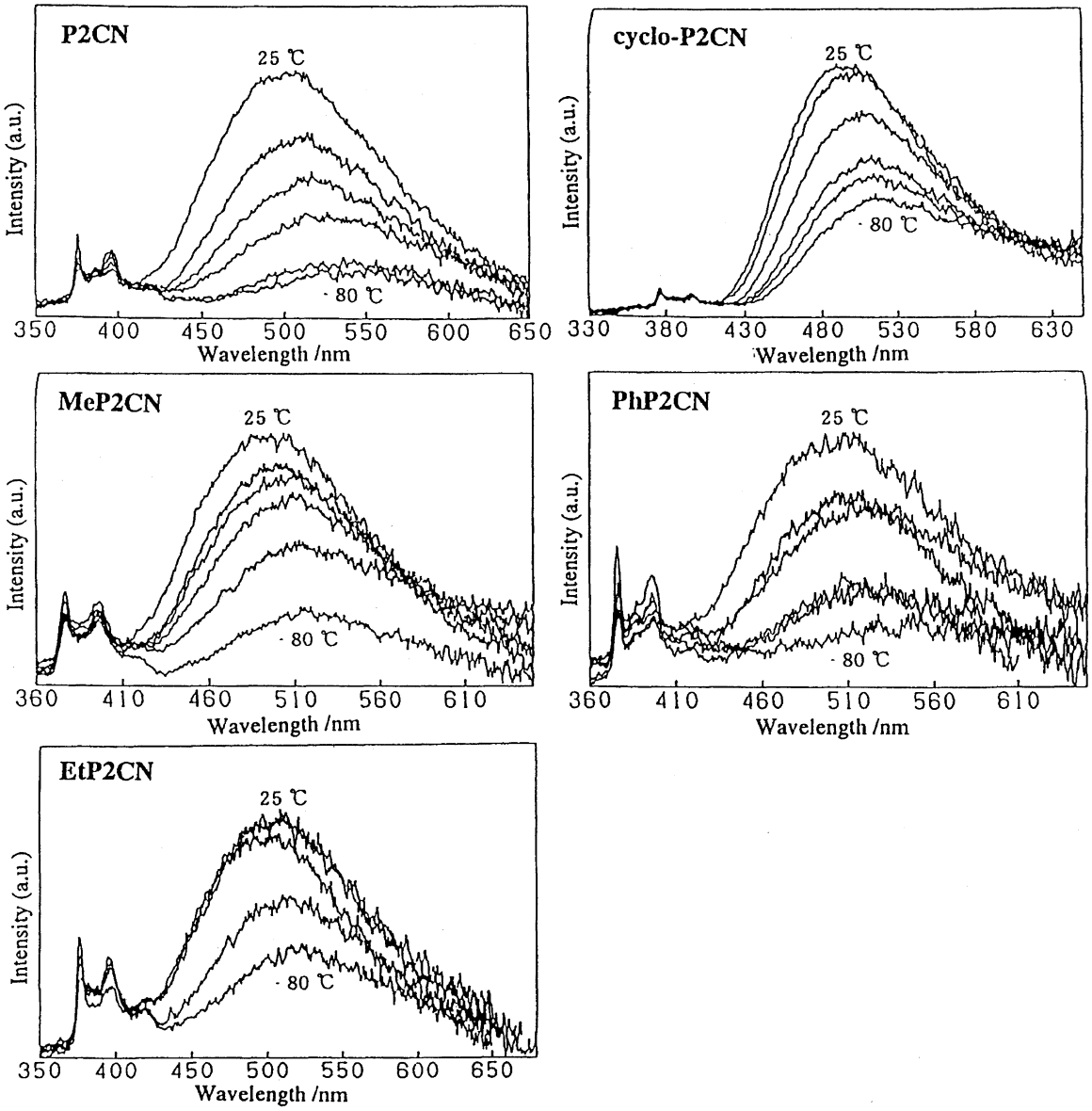


Fig. 6. Fluorescence spectra of **P2CN**, **RP2CN** (R = Me, Et, and Ph) and **cyclo-P2CN** in the temperature range of −80 to 25 °C in EtOAc.

and **RP2CNs** as flexible models.

For the ground state conformers of **P2CN**, we could obtain some information from the analysis of ^{1}HNMR. The chemical shifts of H_2'', H_3'' of the *p*-cyanobenzoate ring and H_{10}' of the pyrene ring (as shown in Fig. 2) signals show the relative orientation of these two aromatic rings particularly clearly. Table 1 shows the chemical shifts of these protons and their shifts ($\Delta\delta$) from those of the reference compounds (methyl *p*-cyanobenzoate for H_2'' and H_3'', and 2-(1-pyrenyl)-ethyl acetate for H_{10}', respectively). Judging from the largest shifts of −0.57 (H_2''), −0.46 (H_3''), and +0.18 ppm (H_{10}') in **cyclo-P2CN**, the *p*-cyanobenzoyl group of **cyclo-P2CN** is magnetically shielded most strongly by the pyrene ring current, and, at the same time, the H_{10}' part of the pyrene ring is most strongly de-shielded by the benzene ring current of the *p*-cyanobenzoyl group. Therefore, the cyanobenzoyl of **cyclo-P2CN** is most likely to be situated above the pyrene ring in a face to face orientation. In **P2CN** and **RP2CN**, the shifts of H_2'' and H_3'' are −0.11 to −0.08 ppm, respectively, which is not apparently influenced by the size of the substituents on C_1. On the other hand, the shifts of H_{10}' show some effect of the substituents; the smallest shift of +0.05 for **P2CN** and the largest shift of +0.15 ppm for **EtP2CN**. Because the shifts of these three kinds of protons are in the same direction, although to a lesser extent, as these of **cyclo-P2CN**, more contribution of the *gauche* conformers than that of the *anti* conformers is presumed. The observation of 1D NOE between H_{10}' and H_2'' of **cyclo-P2CN** shows clearly that the two chromophores are situated very close to each other. In contrast, the observation of weak 2D NOE but not 1D NOE in **MeP2CN** between H_2' and H_3'' indicates that this open-chain flexible ester is in a folded shape to make the two chromophores closely situated, but to an lesser extent than in **cyclo-P2CN**.

X-Ray crystallographic analysis indicates that **P2CN** adopts a folded conformation in the solid state. The dihedral angle of 71.6° along C(1)(of pyrene)–C(17)–C(18)–O(1) in Fig. 4 is roughly close to the *gauche* orientation. It is of note that the CFF91 calculation for **P2CN** which included the effects of solvation, also gave the preference to the folded conformation, although the dihedral angle was somewhat different.[11] Therefore, the *anti* or extended disposition of the pyrenyl and *p*-cyanobenzoyl are proved to be energetically less stable than the *gauche* (or folded) conformation.

As shown in Table 4, the fluorescence quantum yields, Φ_{total}, Φ_{LE}, Φ_{EX} are almost the same for **P2CN** and **RP2CN**. **Cyclo-P2CN** also shows similar, but slightly smaller values, suggesting that neither substituent nor conformational effect on fluorescence quenching is important compared to the very efficient photoinduced electron transfer from the pyrenyl to *p*-cyanobenzoyl groups through 4 bonds, i.e. pyrene–C–C–O–*p*-cyanobenzoyl. Judging from the observation that the emission maxima of the exciplex are almost the same for all of these compounds, as shown in Fig. 5, we assume that the geometrical disposition of the two chromophores in the exciplex is similar throughout this series. As the temperature was gradually lowered, the intensity of the exciplex emission of all the compounds was decreased more drastically than that of the locally excited emission (Fig. 6), which suggests that photoinduced electron transfer is efficient even at the low temperature.[12] However, the temperature dependence of the exciplex emission differs from compound to compound. For example, while **cyclo-P2CN** has relatively strong exciplex emission even at −80 °C, the exciplex emission of **P2CN** was drastically decreased. Ratios of the intensities at the emission maxima at −80 °C vs. those at 20 °C are roughly 1/2 for **cyclo-P2CN**, 1/10 for **P2CN**, 1/5 for **MeP2CN**, 2/5 for **EtP2CN**, and 3/10 for **PhP2CN**. These values suggest that the formation of the exciplex would become more and more difficult as the two chromophores concerned are farther apart in the ground state: The largest value for **cyclo-P2CN**, with the most closely situated two chromophores in nearly an exact gauche conformation along C_1–C_2, and the smallest value for **P2CN** with the two chromophores which are supposed to be the farthest apart. The rise times of the exciplex formation, 365 ps for P2CN and 66 ps for **cyclo-P2CN**, also indicates that it would take more time for **P2CN** than for **cyclo-P2CN** to attain a conformation suitable to the exciplex formation.

In this way, we studied the ground state and excited state conformations of **P2CN** in which two chromophores are combined by a spacer including an ester bond and its rigid and flexible model compounds, using NMR, X-ray crystallographic analysis, absorption and emission spectra, and the decay analysis. All these compounds showed similarities in the properties such as the efficient intramolecular photoinduced electron transfer, the shielding effect on ^{1}H NMR chemical shifts caused by the aromatic ring currents, and the temperature dependence of the emission spectra. We conclude that in this series of compounds, the donor and the acceptor groups are situated roughly in gauche position, from which the exciplex is derived.

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12) For a donor and an acceptor system connected by polymethylene chains, the temperature dependency of Φ_{LE} (fluorescence quantum yield for locally excited emission), Φ_{EX} (fluorescence quantum yield for exciplex emission) is often related to activation energy and enthalpy for fomation of an exciplex. However, we sustained to use this correlation because we observed two components for the exciplex decay which varied their ratio depending on the monitored wavelength.