J. Phys. Chem. 1991, 95, 5797-5802

Kinetics. The value for the overall rate of the self-reaction of $HOCH_2CH_2O_2$ radicals of $k_3 = 7.7\ (\pm 1.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} is the average obtained from the two chemical systems and is the first direct measurement of this rate constant. The value is considerably higher than the corresponding reactions for alkylperoxy radicals given in Table III, but similar to the value of $k_{30} = 6.1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} reported by Veyret et al.[29,30] for hydroxymethyl peroxy radicals:

$$2HOCH_2O_2 \rightarrow 2HOCH_2O + O_2 \qquad (30a)$$

$$\rightarrow HOCH_2OH + HOCHO + O_2 \qquad (30b)$$

The higher rate constants for hydroxyalkyl radicals helps confirm the different reactivity between the two classes of radicals suggested by previous work.[4,5,12]

The estimated branching ratio for the self-reaction of $HOCH_2CH_2O_2$ radicals of $k_{3a}/k_{3a+3b} = 0.75\ (\pm 0.1)$ favors the termination route and is considerably higher than for both the $CH_3CH_2O_2$ and $HOCH_2O_2$ radicals (Table III). A third route for reaction 3 involves the formation of a symmetrical peroxide:

$$2HOCH_2CH_2O_2 \rightarrow (HOCH_2CH_2O)_2 + O_2 \qquad (3c)$$

Reaction 3c is a very minor route for other small organic peroxy radicals, and it may be assumed that the same is true here, although the importance of this route cannot be measured in this study. Reactions 3a and 3c are both terminating pathways, and the branching ratio obtained in the kinetic analysis of k_{3a}/k_{3a+3b} may be more accurately represented as $k_{3a+3c}/k_{3a+3b+3c}$. Mechanistic details of the pathways for reaction 3 must await further studies and product analysis in particular.

Acknowledgment. We thank Mrs. J. Munk of Riso National Laboratories for her valuable assistance in conducting the experiments.

Laser Photolysis Studies on the Intramolecular Dimer Radical Cations Formed in 1,3-Dipyrenylpropanes

Akira Tsuchida, Yoshinobu Tsujii, Masataka Ohoka, and Masahide Yamamoto*

Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606, Japan *(Received: October 12, 1990)*

The structure and stabilization energy of dimer radical cations of intramolecular and intermolecular pyrenyl compounds were estimated by nanosecond laser photolysis in visible and near-IR regions. Electron-transfer quenching of three intramolecular dipyrenyl compounds, 1,3-di(1-pyrenyl)propane (1Py1Py), 1-(1-pyrenyl)-3-(2-pyrenyl)propane (1Py2Py), and 1,3-di(2-pyrenyl)propane (2Py2Py), produced the intramolecular dimer radical cation in an acetonitrile solution. The charge resonance (CR) band of dimer radical cations of 1Py1Py and 2Py2Py was located at 1600 nm, and this structure was ascribed to the full-overlap conformation of two pyrenyl groups. On the other hand, 1Py2Py formed a partial-overlap dimer cation radical whose CR band appeared at >2200 nm, which indicates a stability of ca. 2.4 kcal mol^{-1} less than that of the full-overlap type. The intermolecular pyrene (Py) dimer radical cation had a CR band at 1450-nm peak and was ca. 0.9 kcal mol^{-1} more stable than the full-overlap structure of 1Py1Py and 2Py2Py dimer radical cations. This conformation of intermolecular Py dimer radical cation was ascribed to a distorted conformation.

Introduction

Many studies have been made on photophysical and photochemical properties of intramolecular diaryl compounds such as 1,3-diarylpropanes, bis(1-arylmethyl) ethers, 2,4-diarylpentanes, and bis(1-arylethyl) ethers.[1,2] These compounds have two aromatic chromophores separated by a three-carbon and/or oxygen flexible chain which satisfies Hirayama's $n = 3$ rule.[3,4] At this chain length, two aromatic chromophores can take a sandwich conformation where the overlap of two π-orbitals of both chromophores is maximized, and hence when two chromophores are identical, the intramolecular excimer is readily formed by photoexcitation. The analysis of the intramolecular excimer emission spectra and decays of these bichromophoric compounds such as *N*-carbazolyl,[5] phenyl,[3,6] 1-naphthyl,[4,7] 2-naphthyl,[4,8] 9-anthryl,[9] biphenyl,[10] 9-phenanthryl,[11] 1-pyrenyl,[12] and 2-pyrenyl[13] moieties

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have given valuable information concerning the excimer formation in aromatic vinyl polymers. It is noteworthy that the assignment of two types of excimer emission, one of which is a full-overlap type and the other a partial-overlap type (known as "second excimer"), of poly(*N*-vinylcarbazole) was attained by the study of *meso*- and *rac*-2,4-di(*N*-carbazolyl)pentanes.[1e,5]

Intramolecular bichromophoric compounds are also used to study the conformations of dimer radical cations.[2,14,15] Irie et al.[14] studied the geometrical structure of intramolecular dimer radical cation of polymers and dimer model compounds having naphthalene chromophores by γ-ray irradiation[16] and the pulse radiolysis method. Masuhara et al.[15] studied the dimer radical cation formation of dicarbazolyl compounds by the laser photolysis method. Recently, we studied the dimer radical cation formation of dinaphthyl compounds by laser photolysis and have reported the overlap structure of two naphthyl groups in the dimer radical cation state.[2]

The structure of aromatic dimer radical cations is an important subject in radiation chemistry and photochemistry. Badger and Brocklehurst[17] proposed the distorted conformation of the naphthalene dimer radical cation. Kira et al.[18] studied the formation of dimer radical cations of polynuclear aromatic hydrocarbons in low-temperature rigid matrices. They measured the charge resonance (CR) band[17] of dimer radical cations in the near-IR region for the determination of dimer conformation. To clarify the overlap structure of dimer radical cations, intramolecular bichromophoric compounds are useful since the conformations of the two chromophores are restricted by the short chain. Previously,[2] we determined the naphthalene dimer radical cation structure by laser photolysis measurement in the visible region and assigned the absorption bands of two different dimer radical cation conformations. We report herein the findings we obtained on the dimer radical cation of pyrene chromophore by laser photolysis in visible and near-IR regions. Three intramolecular dipyrenyl compounds of 1,3-di(1-pyrenyl)propane (1Py1Py), 1-(1-pyrenyl)-3-(2-pyrenyl)propane (1Py2Py), and 1,3-di(2-pyrenyl)propane (2Py2Py) were measured in solutions at 298 K, and the conformations of the dimer radical cations were determined by the position of the CR band.

Experimental Section

Chemicals. Figure 1 shows the molecular structures of the compounds used along with their abbreviations. All materials used were purified by recrystallization and/or column chromatography. The purity of intramolecular dipyrenyl compounds was checked by liquid chromatography, and no trace of monomeric impurity was found.

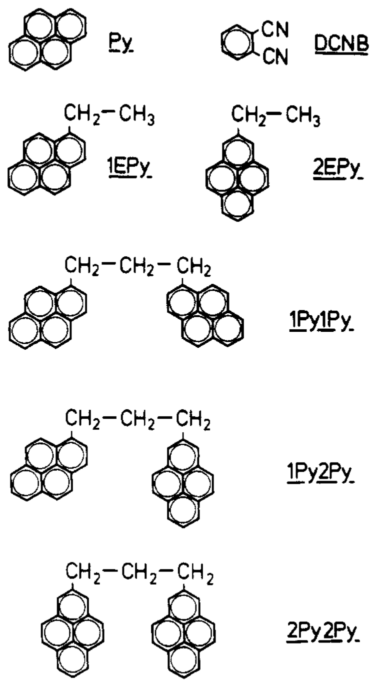

Figure 1. Molecular structures used in this study with their abbreviations: Py, pyrene; DCNB, 1,2-dicyanobenzene; 1EPy, 1-ethylpyrene; 2EPy, 2-ethylpyrene; 1Py1Py, 1,3-di(1-pyrenyl)propane; 1Py2Py, 1-(1-pyrenyl)-3-(2-pyrenyl)propane; 2Py2Py, 1,3-di(2-pyrenyl)propane.

Pyrene (Py, Tokyo Kasei Kogyo) was purified by recrystallization from ethanol two times and by silica gel flash column chromatography with benzene as the eluent.

1-Ethylpyrene (1EPy) was obtained by the hydrogenation of 1-vinylpyrene, which was prepared from 1-pyrenecarboxaldehyde (Aldrich) by the Wittig reaction,[19] using Pd/C as a catalyst in tetrahydrofuran. Recrystallization from hexane gave colorless leaflets, mp 100–101 °C: ^{1}H NMR ($CDCl_3$, 90 MHz, Me_4Si) δ 1.36–1.60 (3 H, t, CH_3), 3.22–3.56 (2 H, q, CH_2), 7.84–8.40 (9 H, m, aromatic).

2-Ethylpyrene (2EPy) was synthesized in the same manner as reported[13a] for 2-acetylpyrene[20,21] by a reduction with hydrazine hydrate in diethylene glycol. Recrystallization from methanol gave colorless crystals: mp 77–78 °C; ^{1}H NMR ($CDCl_3$, 90 MHz, Me_4Si) δ 1.36–1.60 (3 H, t, CH_3), 2.94–3.28 (2 H, q, CH_2), 7.84–8.42 (9 H, m aromatic).

1,3-Di(1-pyrenyl)propane (1Py1Py, Dojindo Lab. Co.) was purified by silica gel column chromatography and liquid chromatography.

1-(1-Pyrenyl)-3-(2-pyrenyl)propane (1Py2Py) was prepared from 1-pyrenecarboxaldehyde (Aldrich) and 2-acetylpyrene by the method of Chandross and Dempster.[4] 1-Pyrenecarboxaldehyde (6.6 g) and 2-acetylpyrene (6.2 g) were stirred in 600 mL of ethanol containing 2.0 g of NaOH (dissolved in 10 mL of water) at 40 °C for 22 h. The precipitated chalcone was 1-(2-pyrenoyl)-2-(1-pyrenyl)ethylene: 11.5 g, 93%; mp 280–282 °C. The chalcone (10.5 g) was hydrogenated by H_2 in 100 mL of tetrahydrofuran, using 0.5 g of 5% Pd/C at 40 °C for 16 h. The solution was filtered and evaporated. The residue was washed with acetone to give almost pure ketone, 1-(2-pyrenoyl)-2-(1-pyrenyl)ethane: 8.7 g, 75%; mp 224–225 °C. The ketone was reduced by the reflux of diethylene glycol solution (200 mL) containing the ketone (4.0 g), hydrazine hydrate (5 mL), and NaOH (5.0 g) for 2 h. After treatment with active charcoal and

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recrystallization from ethyl acetate three times, pure material of 1Py2Py, whose purity checked by liquid chromatography was more than 99.99%, was obtained as colorless needles: 0.60 g, 16%; mp 180–181 °C; ^{1}H NMR ($CDCl_3$, 90 MHz, Me_4Si) δ 2.24–2.64 (2 H, m, CH_2), 3.12–3.60 (4 H, m, CH_2), 7.86–8.32 (18 H, m, aromatic); IR (KBr) 3030 w, 2930 w, 2850 w, 1910 w, 1770 w, 1600 m, 1460 m, 1240 m, 1180 m, 870 s, 840 s, 820 s, 750 s, 710 s, and 680 m cm^{-1}.

Anal. Calcd for $C_{35}H_{24}$: C, 94.56; H, 5.44. Found: C, 94,70; H, 5.24.

1,3-Di(2-pyrenyl)propane (2Py2Py) was synthesized from 2-pyrenecarboxaldehyde[20,21] and 2-acetylpyrene following a method in the literature.[13a,c] Recrystallization from acetone gave colorless needles: mp 225–226 °C; ^{1}H NMR ($CDCl_3$, 90 MHz, Me_4Si) δ 2.24–2.64 (2 H, m, CH_2), 3.10–3.32 (4 H, t, CH_2), 7.88–8.40 (18 H, m, aromatic).

1,2-Dicyanobenzene (DCNB, Wako Pure Chem. Ind.), used as an electron acceptor for pyrenyl chromophore, was purified by recrystallization three times. The spectroscopic measurements were made in acetonitrile (MeCN, Wako) solvent which was dried by P_2O_5 and purified by repeated distillation.

Laser Photolysis Measurements. Samples for laser photolysis measurements were degassed by six freeze–pump–thaw cycles in a Pyrex ampule fitted with a 1-cm quartz cell. To attain the homogeneous excitation and the same distribution of excited states in the sample cell, the absorbance at excitation wavelength (308 or 351 nm) was adjusted to less than unity. The exciting laser pulse was properly attenuated by filters to avoid the multiphoton excitation of chromophores. All samples contained 5.0×10^{-2} M DCNB as an electron acceptor (as a quencher). Pyrenyl chromophores were selectivity excited by a 308- or 351-nm laser pulse as DCNB has no absorption at these wavelengths. The measurements were carried out at 298 K.

The apparatus of nanosecond laser photolysis used was described elsewhere.[22] Photoexcitation of samples was done by a Lambda Physik EMG101MSC excimer laser. The duration of 308- or 351-nm light pulse was ca. 17 ns. Absorption spectra in the visible and near-IR regions were measured with a photomultiplier (Hamamatsu, R928) and with an InAs photodiode (Hamamatsu, P838), respectively.[22b,c]

Results

Photoexcited Py is quenched by DCNB at the rate constant of 1.5×10^{10} M^{-1} s^{-1}, which was determined by the Stern–Volmer plots, in MeCN at 298 K. This electron-transfer quenching in polar MeCN solvent produces a radical cation of Py ($Py^{\bullet+}$) and a radical anion of DCNB ($DCNB^{\bullet-}$).

Figure 2a shows the transient absorption spectrum of Py with DCNB obtained at 500 ns after photoexcitation in MeCN solvent at 298 K. The excitation wavelength was 308 nm, and the concentration of Py was 8.1×10^{-5} M. At this concentration, almost no Py excimer emission could be found and therefore excited singlet Py ($^1Py^*$) is mainly quenched within 1.3 ns at the concentration of 5×10^{-2} M DCNB. In Figure 2a two large absorption peaks are recognized at 415 and 445 nm. The 415-nm band is the T–T absorption of Py triplet[23] ($^3Py^*$), and the 445-nm band is assigned to $Py^{\bullet+}$.[23,24] In the near-IR region of the spectrum, no noticeable absorption can be found. As for the absorption of $DCNB^{\bullet-}$, which has a band peak at 373 nm, the contribution of $DCNB^{\bullet-}$ is negligible in the visible and near-IR region.[2]

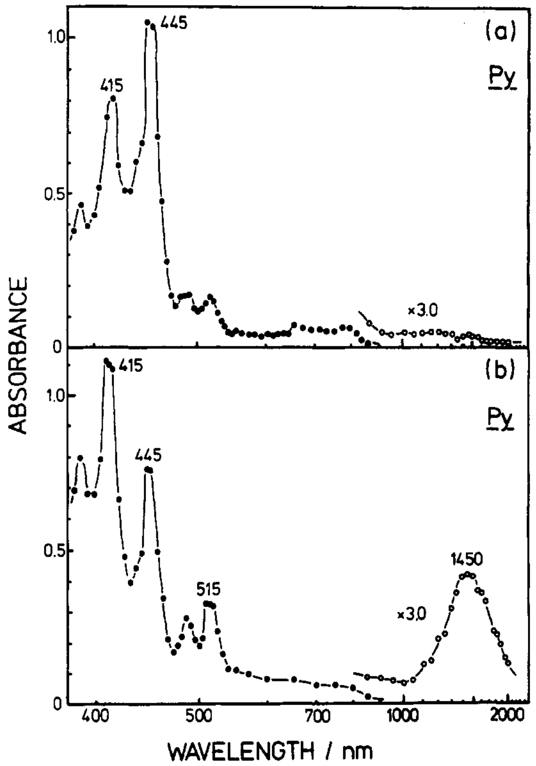

Figure 2. Transient absorption spectra of Py with DCNB obtained at 500 ns after laser excitation in acetonitrile (MeCN) solvent at 298 K. Spectra in the UV and visible region (filled circles) were obtained by a photomultiplier detector, and those in the near-IR region (open circles) were obtained by an InAs photodiode detector: ordinates of the latter spectra were tripled in the figure. (a) Py (8.1×10^{-5} M) was excited at 308 nm in the presence of DCNB (5.0×10^{-2} M). (b) Py (1.3×10^{-3} M) was excited at 351 nm in the presence of DCNB (5.0×10^{-2} M).

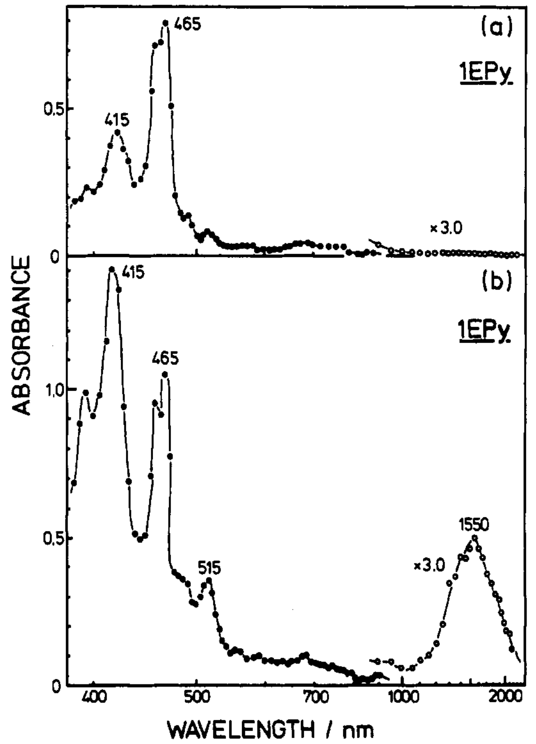

Figure 3. Transient absorption spectra of 1EPy with DCNB obtained at 500 ns after laser excitation in MeCN solvent at 298 K. See also caption of Figure 2. (a) 1EPy (6.2×10^{-5} M) was excited at 308 nm in the presence of DCNB (5.0×10^{-2} M). (b) 1EPy (1.0×10^{-3} M) was excited at 351 nm in the presence of DCNB (5.0×10^{-2} M).

In Figure 2b, the excitation of sample was made with a 351-nm laser pulse. The molar extinction coefficient of Py at 351 nm is smaller than that at 308 nm, and hence the concentration of Py can be raised to 1.3×10^{-3} M, keeping the same optical homogeneity in the sample cell. In this figure, two new absorption bands

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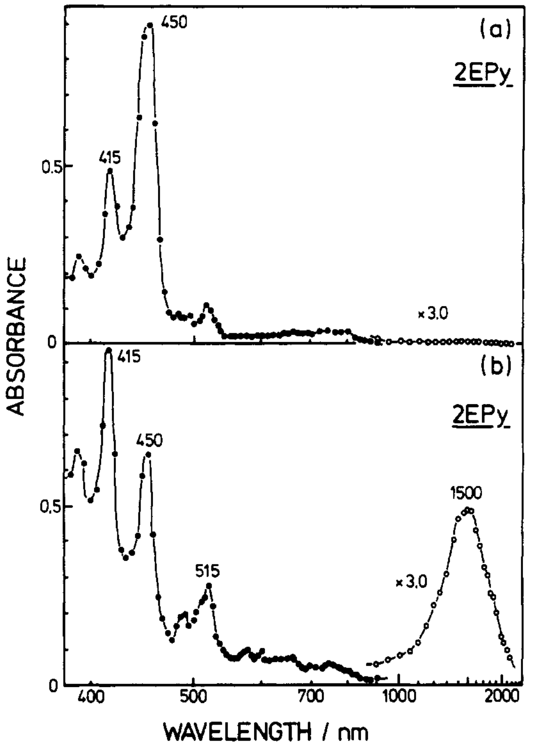

Figure 4. Transient absorption spectra of 2EPy with DCNB obtained at 500 ns after laser excitation in MeCN solvent at 298 K. See also caption of Figure 2. (a) 2EPy (3.9×10^{-5} M) was excited at 308 nm in the presence of DCNB (5.0×10^{-2} M). (b) 2EPy (1.0×10^{-3} M) was excited at 351 nm in the presence of DCNB (5.0×10^{-2} M).

can be seen at 515 and 1450 nm. These absorption bands are ascribed to the dimer radical cation of Py (Py$_2^{\bullet+}$).[18,25] The latter 1450-nm band in the near-IR region is the charge resonance (CR) band.[17] At this concentration of Py, equilibrium of monomer Py$^{\bullet+}$ and dimer Py$_2^{\bullet+}$ is established[25] and the Py$^{\bullet+}$ band still can be seen at 445 nm.

Figure 3a shows the transient absorption spectrum of 1EPy quenched by DCNB. Substitution by an ethyl group at the unsymmetrical 1-position changed the shape of the visible 1EPy$^{\bullet+}$ band a little from that of Py$^{\bullet+}$ which is shown in Figure 2a. The absorption peak shifts to 465 nm, and the band becomes rather broad. The band at 415 nm is ascribed to ^{3}1EPy*. In this concentration of 1EPy of 6.2×10^{-5} M, no CR band can be seen in the near-IR region. By raising the 1EPy concentration to 1.0×10^{-3} M, the CR band appeared at 1550 nm as shown in Figure 3b. The peak shifts ca. 100 nm to longer wavelengths compared with that of Figure 2b. The peak of the visible band of 1EPy$_2^{\bullet+}$ was at the same position, 515 nm, as that of Py$_2^{\bullet+}$.

Figure 4a shows the transient absorption spectrum of 2EPy (3.9×10^{-5} M) quenched by DCNB. The 2EPy$^{\bullet+}$ band is located at the 450-nm peak, and at this concentration of 2EPy, no CR band is observed in the near-IR region. At a higher concentration of 1.0×10^{-3} M, the CR band of 2EPy$_2^{\bullet+}$ appeared at the 1500-nm peak as shown in Figure 4b. The visible 2EPy$_2^{\bullet+}$ band can be seen at 515 nm, whose position and band shape are almost the same as those of Py$_2^{\bullet+}$ and 1EPy$_2^{\bullet+}$.

The dimer radical cation formed intermolecularly may take the most stabilized conformation. However, the allowed conformation of dimer radical cation of intramolecular dipyrenyl compounds of 1Py1Py, 1Py2Py, and 2Py2Py is limited by the conformational restriction of the methylene chain.

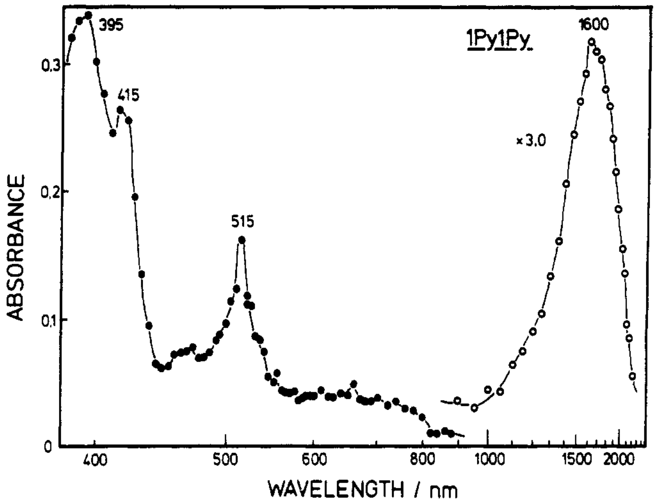

Figure 5. Transient absorption spectra of 1Py1Py (3.7×10^{-5} M) with DCNB (5.0×10^{-2} M) in MeCN solvent at 298 K. See also caption of Figure 2. 1Py1Py was excited by a 308-nm laser pulse.

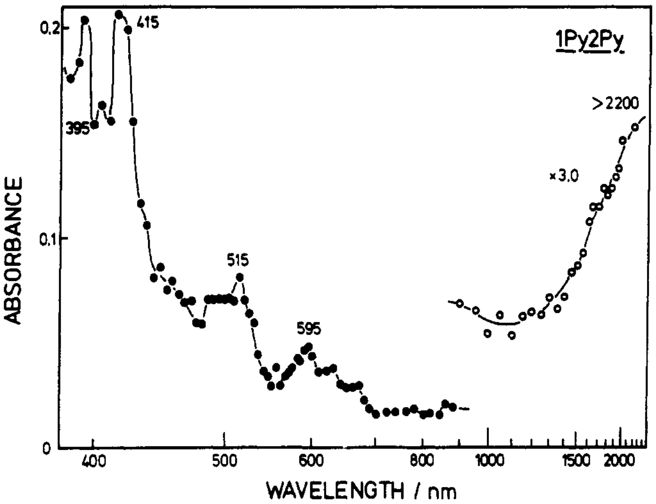

Figure 6. Transient absorption spectra of 1Py2Py (3.3×10^{-5} M) with DCNB (5.0×10^{-2} M) in MeCN solvent at 298 K. See also caption of Figure 2. 1Py2Py was excited by 308-nm laser pulse.

Figure 5 shows the transient absorption spectrum of the intramolecular bichromophoric compound 1Py1Py quenched by DCNB. The excitation was made by a 308-nm laser pulse, and hence the concentration of 1Py1Py was as low as 3.7×10^{-5} M. At this concentration, the contribution of intermolecular interaction, such as excimer and dimer radical cation formation, of 1Py1Py is negligible in consideration of the results for Py, 1EPy, and 2EPy described as before. In this figure, four absorption peaks are recognized. There is a CR band of 1Py1Py$^{\bullet+}$ whose peak appears at 1600 nm. The absorption bands at 515 and 415 nm are ascribed to 1Py1Py$^{\bullet+}$ and ^{3}1Py1Py*, respectively. The absorption at 395 nm is probably another visible band of the 1Py1Py$^{\bullet+}$[25a] dimer radical cation. In this system, no appreciable absorption of Py$^{\bullet+}$ whose positive charge is localized to one pyrene moiety could be seen. Two pyrenyl groups at the C$_3$ position are favorable to a sandwich conformation,[3] and this displaces the equilibrium to the dimer radical cation formation.

Figure 6 shows the transient absorption spectrum of 1Py2Py quenched by DCNB. This 1Py2Py has two pyrenyl groups substituted at different positions. It is noteworthy that the peak position of the CR band of 1Py2Py$^{\bullet+}$ shifts beyond a wavelength of 2200 nm, which is beyond the wavelength limit of our apparatus. The CR band position reflects the degree of interaction of two chromophores,[18c] and this is discussed in a later section. The bands appearing at ca. 595, 515, and 395 nm are ascribed to intramolecular 1Py2Py$^{\bullet+}$ dimer radical cation because 1EPy$^{\bullet+}$ and 2EPy$^{\bullet+}$ monomer radical cations have no absorption at these positions. The band at 415 nm is the T–T absorption of ^{3}1Py2Py*. Similarly to 1Py1Py$^{\bullet+}$, no appreciable absorption of localized Py$^{\bullet+}$ could be found.

Figure 7 shows the absorption spectrum of 2Py2Py quenched by DCNB. Two pyrenyl groups of 2Py2Py are linked by a

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(25) (a) Kira, A.; Arai, S.; Imamura, M. *J. Chem. Phys.* **1971**, *54*, 4890. (b) Arai, S.; Kira, A.; Imamura, M. *J. Chem. Phys.* **1972**, *56*, 1777.

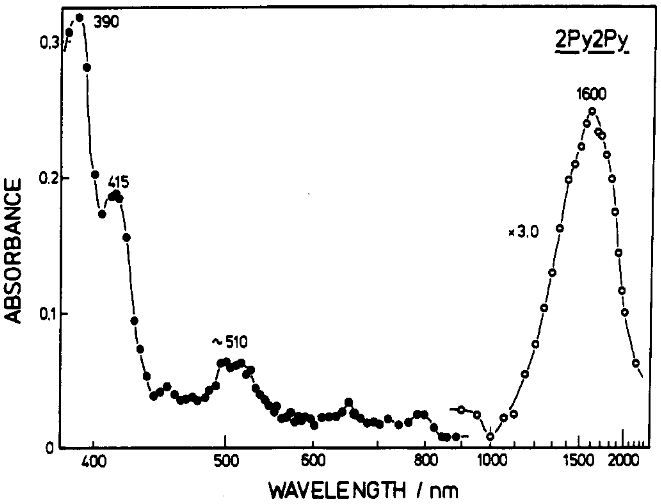

Figure 7. Transient absorption spectra of 2Py2Py (3.5×10^{-5} M) with DCNB (5.0×10^{-2} M) in MeCN solvent at 298 K. See also caption of Figure 2. 2Py2Py was excited by a 308-nm laser pulse.

methylene chain at a symmetrical 2-position, and the substitution at this position forms no rotamer of pyrenyl chromophore. The CR band of this 2Py2Py$^{\bullet+}$ appears at 1600 nm, which is the same position as that of 1Py1Py$^{\bullet+}$. In a series of measurements at a fixed excitation wavelength, the absorbance of samples and the laser intensity were kept constant. Therefore, the ordinates of the transient absorption spectra are comparable for all figures. The magnitude of the 2Py2Py$^{\bullet+}$ CR band seems to be somewhat smaller than that of 1Py1Py$^{\bullet+}$. The bands at ca. 510 and 390 nm are assigned to the 2Py2Py$^{\bullet+}$ dimer band. The positions of these bands are in good agreement with those reported by Masuhara[26] for bis(1-pyrenylethyl) ether. The band at 415 nm, which can be seen in all spectra, is ascribed to that of ^{3}2Py2Py*.

Discussion

Conformations of Intramolecular Dimer Radical Cations. The dimer radical cation is expected to have a sandwich structure.[17] Two intermolecular pyrenyl chromophores may take various sandwich conformations, whereas the allowed conformations for intramolecular dipyrenyl compounds are limited by the restriction of the C_3 methylene chain.

Figure 8 shows all possible sandwich conformations of three dipyrenyl compounds of this study. The substitution of a pyrenyl chromophore at an unsymmetrical 1-position forms rotamers. Therefore, two conformations are allowed for the sandwich conformation of 1Py1Py. One is the full-overlap and the other is the partial-overlap structure as shown in the figure. On the other hand, substitution of Py at a symmetrical 2-position forms no rotamer. Accordingly, the possible sandwich conformations for 1Py2Py and 2Py2Py are only one for each compound. The numbers of overlapped benzene rings for these conformations of 1Py1Py full, 1Py1Py partial, 1Py2Py, and 2Py2Py are four, one, two, and four, respectively.

The position of the CR band indicates the degree of interaction of two pyrenyl chromophrores of the dimer radical cation.[17,18c,22b] The laser photolysis measurements showed the CR band peak of 1Py1Py$^{\bullet+}$, 1Py2Py$^{\bullet+}$, and 2Py2Py$^{\bullet+}$ as 1600, >2200, and 1600 nm, respectively. There is only one possible sandwich structure of the 2Py2Py$^{\bullet+}$ dimer radical cation as shown in Figure 8. Therefore, we ascribed the CR band at 1600 nm in Figure 7 to this structure. The situation is analogous for the 1Py2Py$^{\bullet+}$ dimer radical cation. The only possible sandwich structure of 1Py2Py$^{\bullet+}$ is the one shown in Figure 8, and this structure has the CR band at >2200 nm as shown in Figure 6. As for 1Py1Py, two overlap conformations are possible by the rotation of pyrenyl chromophore as shown in Figure 8. The observed CR band absorption for 1Py1Py$^{\bullet+}$, as shown in Figure 5, was almost the same in shape and peak position as that of 2Py2Py$^{\bullet+}$. Therefore, this band is ascribed to the full-overlap conformation of the 1Py1Py$^{\bullet+}$ dimer radical cation. Our present findings show no positive evidence of the existence of the 1Py1Py$^{\bullet+}$ partial-overlap form. The CR band of the partial-overlap form may be located at too long a wavelength to be measured or the partial-overlap form may be minor. The reason seems to be the latter because the magnitude of the CR band of 1Py1Py$^{\bullet+}$ as shown in Figure 5 is not less than that of 2Py2Py$^{\bullet+}$ in Figure 7.

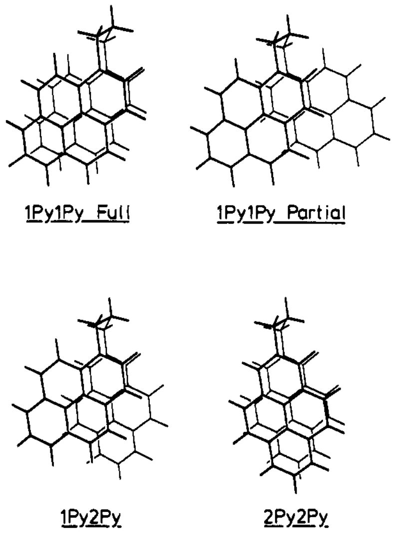

Figure 8. Allowed sandwich conformations of intramolecular pyrene dimer radical cations for 1Py1Py, 1Py2Py, and 2Py2Py dimer compounds.

Quenching Process by DCNB. Extensive investigations have been made on the excimer formation and decay of 1Py1Py. Zachariasse et al.[12d,h] proposed a three-state model for the interpretation of 1Py1Py fluorescence. Siemiarczuk and Ware[12g,i] claimed the existence of the ground-state conformers. Schryver et al.[1e] proposed the existence of preequilibrium of tt and tg$^\pm$ conformers in the ground state. In this study we focused our attention on the conformation of the dimer radical cation, which is the final product of every quenching route. The electron acceptor DCNB can quench both locally excited and excimer states of 1Py1Py, both of which produce 1Py1Py$^{\bullet+}$ dimer radical cations. In the ground state, 1,3-disubstituted propane can take a tt and a tg$^\pm$ chain conformation.[1e] On the other hand, the sandwich excimer and dimer radical cation take a g$^+$g$^-$ or g$^-$g$^+$ (same overlap) conformation, and this conformational change takes a few nanoseconds. At 5.0×10^{-2} M DCNB concentration, it takes 1.3 ns to quench the pyrenyl chromophore as mentioned before. Therefore, in this experimental condition, the intramolecular excimer formation and the quenching by DCNB are competing. This makes the processes complicated, though the latter occurs somewhat preferentially. In our previous study on dinaphthyl compounds,[2] the ground-state conformations were less reflected to the dimer radical cation structures; the ratios of two rotamers of eclipsed type to staggered type were almost the same for 1,3-di(2-naphthyl)propane and *meso*- and *rac*-2,4-di(2-naphthyl)pentane. However, for 1Py1Py, the full-overlap conformation of 1Py1Py$^{\bullet+}$ was found to be major as mentioned before. This may be because the overlap of only one benzene ring of pyrenyl chromophore is not sufficient to produce a partial-overlap 1Py1Py$^{\bullet+}$ dimer radical cation.

Stabilization Energy of Dimer Radical Cation. The charge resonance between two chromophores of dimer radical cation splits the energy levels of constituent molecules. If the splitting is symmetrical, the stabilization energy is equal to half the energy of the observed transition.[18,27]

Table I summarizes the visible and near-IR bands of dimer radical cations observed in this work. The stabilization energies were calculated from the peak positions of the CR bands. These

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(26) Masuhara, H. *J. Mol. Struct.* **1985**, *126*, 145.

(27) Badger, B.; Brocklehurst, B. *Nature* **1968**, *219*, 263.

TABLE I: Absorption Maxima and Stabilization Energies of Dimer Radical Cations of Pyrenyl Compounds Observed in This Study

compd	abs max/nm		stabilizn energy[a]/ kcal mol^{-1}
	vis	near-IR	
Py	515	1450	9.86
1EPy	515	1550	9.23
2EPy	515	1500	9.54
1Py1Py	515	1600	8.94
1Py2Py	515, 595	>2200	<6.50
2Py2Py	ca. 510	1600	8.94

[a] Stabilization energies were calculated from the absorption peak of charge resonance (CR) bands. See also text.

values obtained by their peaks are probably overestimated;[27] Arai et al.[25b] reported the stabilization energy of Py$_2^{\bullet+}$ as 7.1 ± 1.5 kcal mol^{-1}. In this report, we tentatively use the values shown in Table I because our interest here is on the relative values and the order of stabilization energy for different overlap structures.

As shown in the table, the stabilization energy of Py$_2^{\bullet+}$ is the largest. Full-overlap conformation of 1Py1Py$^{\bullet+}$ and 2Py2Py$^{\bullet+}$ is about 0.9 kcal mol^{-1} less stable than Py$_2^{\bullet+}$. The stabilization energy of 1Py2Py$^{\bullet+}$ is the smallest, more than 3.3 kcal mol^{-1} less stable than Py$_2^{\bullet+}$. According to Kira et al.,[18c] the increase in molecular size of polynuclear aromatic hydrocarbons causes a decrease in the attractive force by the repulsion between filled orbitals of constituent molecules. In the present study, molecular size is fixed to that of the pyrenyl chromophore, whereas the overlap is changed. The full-overlap conformation of intramolecular 1Py1Py$^{\bullet+}$ and 2Py2Py$^{\bullet+}$ dimer radical cations has the strongest attractive resonance, but the repulsive force is also maximum. The stronger interaction for intermolecular Py$_2^{\bullet+}$ is explained by assuming the distorted dimer radical cation structure. 1EPy$_2^{\bullet+}$ and 2EPy$_2^{\bullet+}$ are also expected to have distorted forms. However, the stabilization energy is not so large as that of Py$_2^{\bullet+}$. This may be due to the steric hindrance of ethyl group or slight change of the electronic state of pyrene chromophore by ethyl substitution.

The CR band of intramolecular 1Py2Py$^{\bullet+}$ appeared at >2200 nm, and hence the stabilization energy was the smallest. As shown in Figure 8, only two benzene rings overlap in this compound. The attractive charge resonance at this conformation is considered to be weaker than that at the full-overlap conformation.

Conclusion

The conformation and the stabilization energy of pyrenyl dimer radical cation were studied for three intramolecular dipyrenyl propanes. 1Py1Py$^{\bullet+}$ and 2Py2Py$^{\bullet+}$ form full-overlap dimer radical cations which have a CR band peak at ca. 1600 nm. The overlap structure by only two benzene rings of 1Py2Py$^{\bullet+}$ decreased the stabilization energy more than 2.4 kcal mol^{-1} from that of the full-overlap type. The dimer radical cation of intermolecular Py$_2^{\bullet+}$ took a distorted conformation, and this form was ca. 0.9 kcal mol^{-1} more stable than the perfect sandwich overlap conformation.

Photocatalysis of Oligo(*p*-phenylenes). Photoreductive Production of Hydrogen and Ethanol in Aqueous Triethylamine

Shinjiro Matsuoka, Hiroyuki Fujii, Taisuke Yamada, Chyongjin Pac, Akito Ishida,[†] Setsuo Takamuku,[†] Mitsuhiro Kusaba,[‡] Nobuaki Nakashima,[‡] Shozo Yanagida,[*]

Chemical Process Engineering, Faculty of Engineering, Institute of Scientific and Industrial Research, and Institute of Laser Engineering, Osaka University, Suita, Osaka 565, Japan

Kazuhito Hashimoto,[§] and Tadayoshi Sakata[∥]

Institute for Molecular Science, Myoudaiji, Okazaki 444, Japan *(Received: November 13, 1990; In Final Form: March 19, 1991)*

Oligo(*p*-phenylenes) (OPP-*n*), *p*-terphenyl (OPP-3) to *p*-sexiphenyl (OPP-6), catalyze water-reductive H$_2$ formation and reduction of concomitantly formed acetaldehyde to ethanol upon irradiation of heterogeneous suspensions in aqueous organic solution in the presence of triethylamine (TEA) and RuCl$_3$. Colloidal Ru^0 is photoformed in situ to work as an electron relay. The activity of OPP-*n* increases with the number of phenylene units except for the cases of OPP-3 and of the alkylated derivatives, where the net photocatalytic activities are higher, mainly due to the effective homogeneous catalysis, since their solubilities in the solvents employed are significantly larger. The homogeneous photocatalysis of OPP-3 leads not only to H$_2$ evolution but also to effective formation of ethanol in the absence of colloidal Ru^0, being accompanied by photo-Birch reduction of OPP-3. Dynamics studies of OPP-3 reveal that photocatalysis should be initiated by formation of the excited singlet state of OPP-3 (^{1}OPP-3*), which is reductively quenched by TEA at a rate controlled by diffusion to produce the OPP-3 radical anion (OPP-3$^{\bullet-}$) and the TEA radical cation (TEA$^{\bullet+}$). From laser flash photolysis and pulse radiolysis experiments, it is concluded that electron transfer from OPP-3$^{\bullet-}$ leads to effective reduction of water to H$_2$ catalyzed by Ru^0 colloid. Furthermore, it is confirmed that OPP-3$^{\bullet-}$ gives electrons directly to acetaldehyde without any electron relays like colloidal metals, resulting in the formation of ethanol. During photocatalysis, OPP-3 itself undergoes photo-Birch reduction to some extent.

Introduction

We previously reported that under visible light, poly(*p*-phenylene) (PPP) prepared by Yamamoto's method shows heterogeneous photocatalysis for cis–trans photoisomerization of simple olefins[1] and for photoreductions of water, ketones, and olefins to respective H$_2$, alcohol, and dihydro compounds in the presence of triethylamine (TEA) as a sacrificial electron donor.[2] Although colloidal Ru metal formed by the concurrent photolysis

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[†] Institute of Scientific and Industrial Research.

[‡] Institute of Laser Engineering.

[§] Present address: Department of Synthetic Chemistry, Faculty of Engineering, Tokyo University, Hongo, Bunkyo-ku, Tokyo 113, Japan.

[∥] Present address: Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta, Midori-ku, Yokohama 227, Japan.

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(2) (a) Yanagida, S.; Kabumoto, A.; Mizumoto, K.; Pac, C.; Yoshino, K. *J. Chem. Soc., Chem. Commun.* **1985**, 474. (b) Shibata, T.; Kabumoto, A.; Shiragami, T.; Ishitani, O.; Pac, C.; Yanagida, S. *J. Phys. Chem.* **1990**, *94*, 2068.

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