Absorption Spectra of N-Acetyl-bis(1-pyrenylalanine)-methylester in the Excited and Ionic States

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ABSTRACT: Absorption spectra of the excited and ionic states of threo- and erythro-N-acetyl(1-pyrenylalanine)methylester were measured by ps and ns laser photolysis methods. Interchromophoric interaction affecting the absorption spectrum was observed only in the excited singlet state, while neither triplet excimer nor dimer cation was detected. The present results are quite different from those of other bichromophoric systems, which were ascribed to rather distant structures of relevant chromophores in dipeptides.
    KEY WORDS Laser Photolysis / Pyrenylalanine / Dipeptide / The Excited Singlet State / The Triplet State / Cation / Anion / Excimer / Conformation / Diastereoisomer /
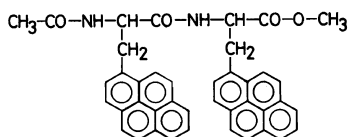
Studies on the electronic and geometrical structures of bichromophoric compounds are very important for understanding those of polymers having the same chromophores. While 1,3-diarylpropane has been a standard compound,[1,2] De Schryver et al. proposed recently that meso- and rac-2,4-diarylpentanes are more appropriate model compounds. Excellent examples are 2,4-diphenylpentane for polystyrene and 2,4-di(N-carbazolyl)-pentane for poly(N-vinylcarbazole) and their photophysical aspects have been studied in detail.[3] The influence of the conformational distribution on the dynamics of their excited singlet states has been elucidated by single photon counting measurement. On the other hand, the triplet, cationic, and anionic states can be studied with a laser photolysis

method, previously demonstrated in the systematic study on di(N-carbazolyl) compounds.[4] Bipyrenyl and binaphthyl compounds are being studied in detail as the next target systems,[5-7] since pyrene and naphthalene are molecules showing typically distinct intermolecular interactions in the excited singlet and cationic states. Excimer formation and decay dynamics of bis[1-(1-pyrenyl)ethyl]ethers as well as 2,4-di(1-pyrenyl)pentane, and N-acetyl-bis(1-pyrenylalanine)methylester are closely related to the conformational and configurational aspects of vinyl polymers and polypeptides. Recently, we succeeded in measuring for the first time absorption spectra of the triplet excimer of pyrene, examining bis[1-(1-pyrenyl)ethyl]ethers.[8] Intramolecular association of two pyrenyl chromophores in the

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cationic state was also confirmed by the N_2 gas laser photolysis method.[9] Their absorption spectra were similar to those of poly(1-vinylpyrene).[10] To explore the electronic structure and dynamics of pyrene-containing polymers with a specific geometry, polypeptides with this chromophore built in were studied. The results obtained in the study on the bichromophoric model compound, N-acetyl-bis(1-pyrenylalanine)methylester (Structure I,

$$CH_3-CO-NH-\underset{\underset{\text{(structure)}}{\overset{|}{CH_2}}}{CH}-CO-NH-\underset{\underset{\text{(structure)}}{\overset{|}{CH_2}}}{CH}-CO-O-CH_3$$

abbreviated as BlPyA) will be of later use in the interpretation of data related to the polymer system. In the present work, absorption spectra of this molecule in the excited and ionic states are reported.

EXPERIMENTAL

The samples are the same as used before.[6] N-acetyl-L-1-pyrenylalaninemethylester was used as a reference monomer. The solvent N,N-dimethylformamide (DMF) (Dotite Spectrosol) was purified by fractional distillation. The mean chromophore concentration of the pyrenyl group was adjusted to about $\sim 10^{-4}$ M. All the solutions were degassed or bubbled with N_2 gas. Transient absorption spectra were measured by a microcomputer-controlled ps Nd^{3+} : YAG laser photolysis system the details of which are published elsewhere.[11] The third harmonic (355 nm, ~ 22 ps fwhm, ~ 2 mJ) was used as an excitation pulse. The origin of the time axis corresponds to the time when both exciting and monitoring pulses take the maximum temporal overlap. Excimer laser (351 nm) photolysis was performed to obtain the spectra in the μs time region.[12]

RESULTS AND DISCUSSION

The time-resolved absorption spectra of the excited singlet state of threo- and erythro-BlPyA are shown in Figures 1 and 2, respectively. An absorption spectrum at 0 ps is assigned to the monomer excited singlet state, since the latter state has an absorption maximum at 475 nm.[13a] This band is a little more distinct in erythro-BlPyA than in threo-BlPyA. The relatively high absorbance in the short wavelength region can be ascribed to difference in the arrival time of the monitoring ps continuum.[13] A spectral change was induced rapidly up to a few ns. The spectral shape at 5 ns is similar to a superposition of the absorption bands of the monomer excited singlet state (475 nm) and excimer (495 nm).[14] Around 100 ps a similar peak was observed at 495 nm, however, this is more distinct compared to the spectrum observed at 5 ns. It is rather difficult to assign this band to the pyrene excimer, which is supported by its temporal characteristics. The formation time-constant of these bands in both BlPyA was estimated to be less than 100 ps and smaller than that of excimer formation.[15] No distinct excitation intensity effect upon the transient spectra was observed at any delay time.

Absorption spectrum of the triplet state was measured, using an excimer laser (351 nm). The spectral shape of threo-BlPyA was independent of the delay time and almost identical with that of the 1-substituted pyrene up to 10 μs,[8] as shown in Figure 3. No specific interchromophoric interaction was detected. An examination of erythro-BlPyA was impossible, since its solubility is so low that an excimer laser (351 nm) photolysis could not be applied. Intermolecular formation of the triplet excimer has never been confirmed in solution phase.

Cation and anion radicals of threo-BlPyA were produced by quenching its excited singlet state by ₌ 0.069 M 1,4-dicyanobenzene and 1.0 M 1,4-diazabicyclo[2,2,2]octane (Dabco),
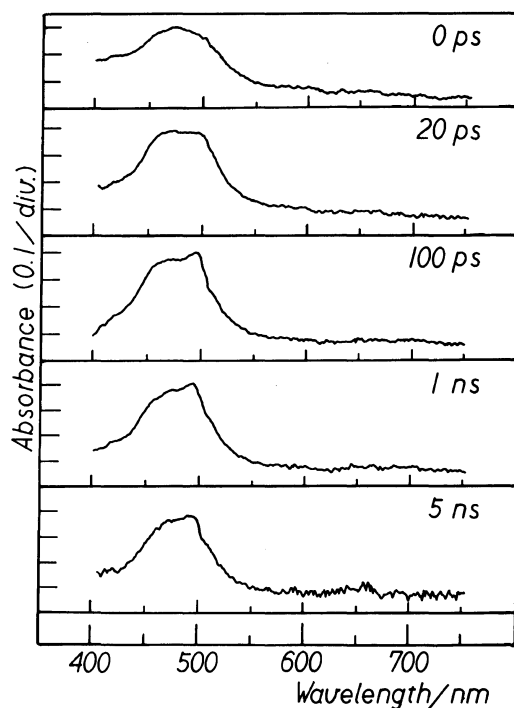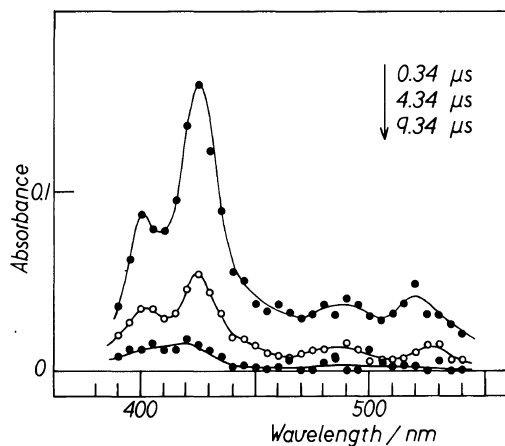
Figure 1. Time-resolved absorption spectra of *threo*-B1PyA in DMF.
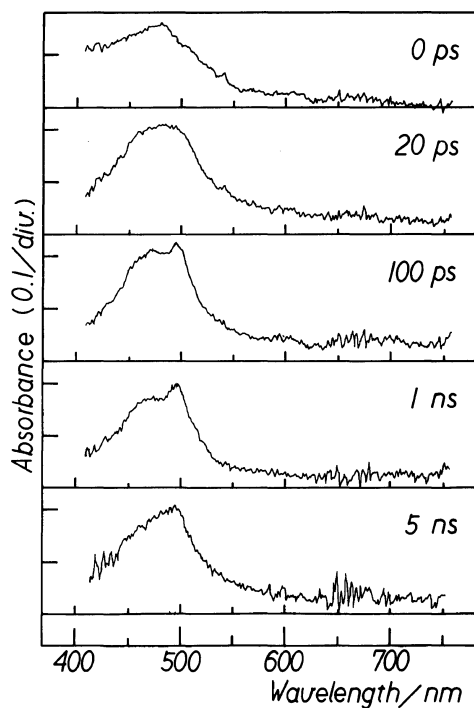
Figure 2. Time-resolved absorption spectra of *erythro*-B1PyA in DMF.

respectively. The absorption spectral change of the former case is clearly demonstrated in Figure 4(a). The absorption bands at early stages were replaced by the sharp absorption band of the pyrene cation at 460 nm. A shoulder at 430 nm may be ascribed to 1,4-dicyanobenzene anion. Since intramolecular association of a pyrene cation and a neutral one of bis[1-(1-pyrenyl)ethyl]ethers, resulting in dimer cation, occurred in sub μs time region,[8] time-resolved absorption spectra up to 9 μs were measured. The results are shown in Figure 4(b), where the absorption band of the triplet pyrene rises at 420 nm. This triplet state is considered to be produced by recombination of pyrene cation and the counter anion. However, the bands at 390 nm and 510 nm, indicating dimer cation formation,[16] were not detected.
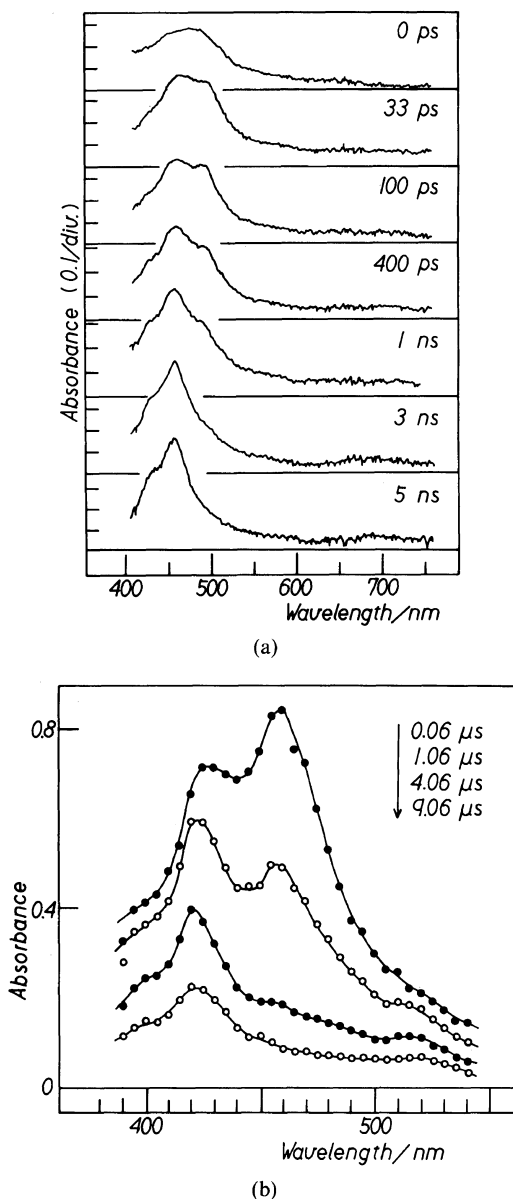
In the case of the quencher Dabco, a spectral change was observed as shown in Figure 5.

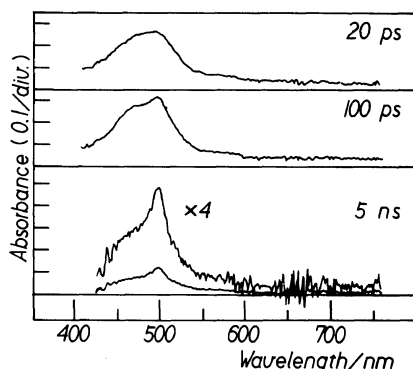**Figure 3.** Time-resolved absorption spectra of *threo*-B1PyA in benzene.

The band at 495 nm is quite similar to that of the monomer anion radical, indicating no interchromophoric interaction.

Summarizing the present results, it is con-

(a)

(b)

Figure 4. Time-resolved absorption spectra of *threo*-B1PyA quenched by 0.069 M 1.4-dicyanobenzene in DMF.

Figure 5. Time-resolved absorption spectra of *threo*-B1PyA quenched by 1.0 M Dabco in DMF.

cluded that intramolecular interaction between two pyrenyl groups is appreciable only in the excited singlet state. No absorption spectroscopic data indicating interchromophoric interactions in the triplet and ionic states was obtained. This is quite in contrast to other pyrene systems. Not only the singlet excimer but also the dimer cation is observed in intermolecular systems, and it was confirmed that the formation enthalpy of the latter was almost equal to that of the former.[16] In addition, intramolecular triplet excimer was observed in the compact geometry of bis[1-(1-pyrenyl)ethyl]ethers.[8] The differences between the present and other systems may be ascribed to geometrical structure of dipeptides.

According to recent detailed fluorescence studies,[15] an excimer common to *threo*- and *erythro*-B1PyA is formed from two conformers in the ground state. One is a folded and allows a transition of the side chains to an excimer-like geometry during the fluorescence lifetime of the pyrene. The other is extended and does not form the excimer structure of two pyrenyl groups rapidly and is in equilibrium with the folded conformer. The fluorescence intensity ratio of the excimer over the monomer excited singlet state (ϕ_{exc}/ϕ_{py}) is very sensitive to solvent, which was due to competitive intramolecular and solute-solvent hydrogen-bonding interactions. Since polarity and chemical structure of DMF are close to those of *N,N*-dimethylacetamide, fluorescence data in the former solvent may be similar to those in the latter. The value ϕ_{exc}/ϕ_{py} of both B1PyA is lower in *N,N*-dimethylacetamide compared to in other solvents, so that an extended form is

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relatively favored in the present DMF solutions.

Therefore it is suggested that a loose structure of relevant chromophores in dipeptides results in characteristic interchromophoric interactions in the excited and ionic states. Interchromophoric interaction in the triplet state is very small and that in the anionic one negligible in general,[4] so that the results on dipeptides in these states are acceptable. However, no intramolecular formation of dimer cation of pyrenyl chromophores was observed, although absorption bands of the singlet excimer were detected. A looser structure is considered to be possible in the case of dimer cation compared to the excimer, and actually we have confirmed that various geometrical structures of dimer cation are possible in carbazole systems.[4] We consider that a special formation process of the singlet excimers is involved in dipeptides. In a loose structure of two pyrenyl chromophores, electron transfer is first induced, being not overcome by excimer interaction. An attractive coulomb force in the produced ion-pairs accelerate a conformational change from an extended to a folded form, resulting in the singlet excimer. This mechanism can explain the diffence of temporal behavior between ps transient absorption and single photon counting measurements. Although the present spectral change occurs in the time range of 100 ps, the rise-time of excimer emission was in ns time scale.[15] Actually, the band near 500 nm observed at 100 ps can be partly ascribed to the anion radical of pyrenyl chromophores. This interpretation is the same as that given for [2,2] (1,3)pyrenophane[17] and dianthrylethanes[18] and being examined more detail in the present dipeptides.

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