

SHORT COMMUNICATIONS

## Absorption Spectra and Dynamics of the Triplet State of Bis[1-(1-pyrenyl)ethyl]ethers

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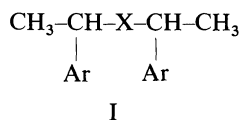
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The excimer formation in polymers with pendant aromatic chromophores has been actively investigated.<sup>1</sup> The configurational and conformational aspects have been found important in excimer dynamics.<sup>2-5</sup> The use of diastereoisomeric model compounds of structure I has been quite helpful in understanding the relation between the structure and dynamics of excimers in polyvinyl aromatic compounds.



Ar: phenyl, naphthyl,  
9-anthroyl, or  
N-carbazolyl

X : CH<sub>2</sub> or O

The *meso* and *racemic* isomers of 2,4-di(*N*-carbazolyl)pentane give the sandwich excimer and second excimer, respectively; the latter has a higher energy than the former.<sup>2</sup> From a configurational viewpoint, it was concluded that the sandwich and second excimers have full and partial overlap between two carbazolyl groups, respectively. In the case of the other substituents, the *meso* isomer always had a larger intensity ratio of the excimer over the monomer fluorescence, compared to the *racemic* isomer. The *meso* isomer of bis[1-(1-

naphthyl)ethyl]ether has two spectrally different excimers, due to strong steric interaction between the H<sub>8</sub> *peri*-hydrogen and the methyl groups.<sup>6</sup> This interaction is also important in bis[1-(9-anthryl)ethyl]ether.<sup>7</sup>

Compared to the above study on singlet excimers, the relation among absorption spectra, dynamics, and geometrical structures of the triplet excimer is still less understood. One method for elucidating this relation is estimating the stabilization and transition energies by an MO calculation and to relate them to geometrical structure.<sup>8</sup> Another approach is measuring the transient absorption spectra of the triplet diastereoisomers. We applied the ns laser photolysis method to carbazolyl and phenanthryl dimer model compounds.<sup>9,10</sup> Similar investigations were made for the intramolecular triplet excimers of the naphthalene and phenanthrene systems.<sup>11</sup> These transient absorption spectral measurements showed that electronic structure and dynamics depend on geometrical structure.

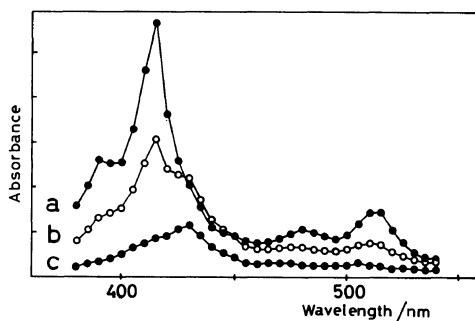
In the present work, the transient absorption spectral measurement was extended to dipyrenyl compounds, because pyrene is the most representative aromatic hydrocarbon showing intermolecular singlet excimer formation.<sup>12</sup> The synthesis and purification of *meso*- and *racemic*-bis[1-(1-pyrenyl)ethyl]ether (abbreviated as *m*-B1PyEE and *r*-B1PyEE, respectively) will be published elsewhere.<sup>13</sup> 1-Ethylpyrene (EtPy), a monomer model

compound, was purified by sublimation. *n*-Hexane and *N,N*-dimethylformamide (DMF) (Dotite Spectrosol) were used without further purification. The mean concentration of the pyrenyl group was  $\sim 5 \times 10^{-4}$  M. All solutions were flushed with  $N_2$  gas.

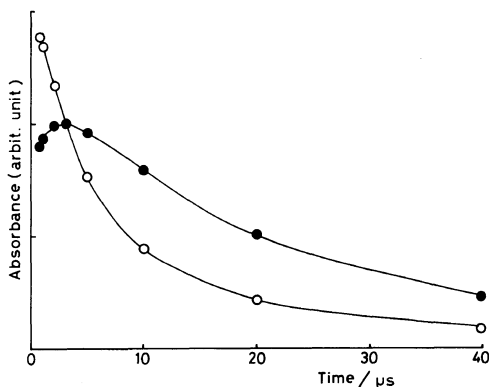
The transient absorption spectra were measured by a microcomputer-controlled  $N_2$  gas laser photolysis system.<sup>14</sup> The results on *r*-B1PyEE in *n*-hexane are shown in Figure 1. At an early delay time, peaks could be observed at 390 nm and 415 nm, and other bands were situated about 500 nm. This spectrum was similar to the  $T_n \leftarrow T_1$  spectrum of EtPy, which is quite insensitive to the particular solvent used, but quenched by oxygen. This behavior indicated that the triplet pyrenyl group of *r*-B1PyEE does not associate with the other neutral pyrenyl group at this delay time. At a later stage, however, the spectrum tended to be broad and structureless, and absorbance above 430 nm was enhanced. These spectral changes are more evident in *n*-hexane than in DMF.

The time-profiles of these absorptions are shown in Figure 2. The absorbance at 415 nm decayed rapidly, while that at 430 nm showed a rise at an early stage, followed by a rather slow decay. This suggests that the broad spectrum at the late stages is due to some species formed from the monomer triplet state. EtPy decayed monotonously without such a spectral change, although its concentration was twice that of the B1PyEE system. This may indicate that the intramolecular interaction accompanied by conformational change is responsible for the present behavior. Furthermore, it should be pointed out that no chemical reaction occurred under the present experimental condition. The present results indicate that the spectrum observed at 20  $\mu$ s is due to the intramolecular triplet excimer of pyrene. Similar absorption spectra were obtained for *m*-B1PyEE, suggesting some resemblance in dynamics.

The fluorescence spectra of the diastereoisomers indicate an appreciable contribution from the intramolecular excimer at 298 K, and its conformation and dynamics are also studied at the present stage of investigation.<sup>13</sup> If the conformation of the singlet excimer is also suitable for the triplet excimer, the spectrum measured immediately following intersystem crossing should be different from that for the monomer triplet state. The present



**Figure 1.** Time-resolved absorption spectra of *r*-B1PyEE in *n*-hexane. The delay times are 700 ns (a), 5  $\mu$ s (b), and 20  $\mu$ s (c).



**Figure 2.** Time-profiles of the transient absorbance of *r*-B1PyEE in *n*-hexane. Decay curves for peaks at 415 nm (○) and 430 nm (●).

result suggests, however, that the triplet excimer was formed in a few tens  $\mu$ s, indicating that the triplet excimer in the same conformation as that of the singlet excimer is unstable and dissociates into the monomer triplet state immediately after intersystem crossing. A conformational change then followed, leading to formation of the triplet excimer with a different geometrical structure.

This interpretation is consistent with the probable conformations for the  $\pi$ - $\pi$  interaction as was demonstrated on using the Büchi Dreiding model. The sandwich and partial overlap structures may be possible in both the *r*-B1PyEE and *m*-B1PyEE systems. There should be several excimer conformations for each structure, depending on the position of the ether bridge. Details of the conformational distribution and the change in the triplet B1PyEE will be reported in the near future.

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