Excimer Fluorescence and Photodimerization of Anthracenophanes and 1,2-Dianthrylethanes

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Abstract: Anthracenophanes and 1,2-dianthrylethanes were studied as models of excimers. It was found that (1) there are natively various structures of excimer, (2) the so-called "$n = 3$ rule" is not valid in the case of dianthrylalkanes, (3) the excimers of 1,2-dianthrylethanes show two different kinds of structures, and (4) excimer fluorescence lifetimes are reduced due to the photodimerization in the case of *syn*-[2.2](1,4)anthracenophane, [2.2](1,4)(9,10)anthracenophane, and 1,2-dianthrylethane (type 2).

Introduction

It is very difficult to clarify the detailed excimer structure formed in solution through the diffusion-controlled reaction.

There have been studies of excimers in crystals[2] and intramolecular excimers[3,4] to clarify this point. A study of the pyrene crystal indicated that the excimer has a displaced parallel-pair configuration of two pyrene molecules.[2] On the other hand, in the case of intramolecular excimer formation of α,ω-diphenylalkanes (Ph-$(CH_2)_n$-Ph) and α,ω-dinaphthylalkanes, for example, it was found that an excimer can be formed when $n = 3$, that is the so-called $n = 3$ rule.[3] Ferguson et al.[5] found that the excimer-type emission cannot be observed in the case of the stable anthracene dimer, which does not have the parallel sandwich-pair structure. This result was supported by the theoretical calculation of Morris.[6]

Above results indicate that it is necessary for the excimer to have the parallel sandwich-pair structure. But the possibility remains that other forms of excimer exist; in the case of the intramolecular excimer, the "$n = 3$ rule" may not be held so rigorously, at least in the dianthrylethanes investigated here. In other words, it may be possible, contrary to theoretical calculations, that it is not necessary for the excimer to have some definite structure, although there may be the most stable structure as predicted by those calculations.

Ferguson et al. reported that the excimer state is an intermediate of the photodimerization reaction of anthracene,[7] so it is necessary to investigate the photodimerization for discussion of the excimer fluorescence lifetime.

The points mentioned above could be investigated satisfactorily by dealing with the anthracenophanes and 1,2-dianthrylethanes whose structures are given in Figure 1.

Experimental Section

Materials. [2.2](9,10)Anthracenophane was prepared by the same method as given in the literature.[8] Details of the syntheses of other anthracenophanes were reported elsewhere.[9] 1,2-Di(9-anthryl)ethane was synthesized according to the same method given in the literature.[10] 1,2-Di(1-anthryl)ethane was first synthesized in the present work by the following procedure. To a stirred solution of freshly prepared phenyllithium (18 mmol) in ether was added 5.0 g (18 mmol) of 1-bromomethylanthracene[11] in benzene (50 ml) at room temperature over a period of 45 min under a nitrogen atmosphere. The mixture was then heated and refluxed for 13 h. After cooling the reaction mixture, water was added slowly. The organic layer was separated, washed successively with aqueous sodium bicarbonate and water, and concentrated. The crude product was chromatographed over neutral alumina (Woelm, activity 1) and the eluate with a mixture of petroleum ether-benzene (1:4) was concentrated under reduced pressure. The solid residue was recrystallized from benzene to give 0.75 g (22%) of pale yellow leaflets, mp 238.0-238.5 °C: NMR ($AsCl_3$) δ 3.74 (s, 4 H), 7.3-8.2 (m, 14 H), 8.46 (s, 2 H), and 8.65 (s, 2 H). Anal. Calcd for $C_{30}H_{22}$: C, 94.20; H, 5.8%; mol wt, 382.48. Found: C, 93.92; H, 6.08%; mol wt, 382 (MS). 1,2-Di[1-(4-methylanthryl)]ethane was prepared in 97% yield from 1-methyl-4-bromomethylanthracene[9a] and magnesium by a procedure similar to that given in the literature.[10] The product was recrystallized from benzene to give pale yellow needles, mp 225-226 °C: NMR ($CDCl_3$) δ 2.80 (s, 6 H), 3.68 (s, 4 H), 7.25 (s, 4 H), 7.3-7.6 (m, 4 H), 7.9-8.2 (m, 4 H), 8.59 (s, 2 H), and 8.67 (s, 2 H). Anal. Calcd for $C_{32}H_{26}$: C, 93.62; H, 6.38. Found: C, 93.42; H, 6.33. Spectrograde methyltetrahydrofuran (MTHF) and methylcyclohexane (MCH) were used without further purification. Decalin was passed through a column of activated alumina in order to remove trace quantities of naphthalene.

Apparatus. Fluorescence spectra were measured on an Aminco-Bowman spectrophotofluorometer which has been calibrated to give correct quantum spectra. Fluorescence lifetimes were determined by use of a pulsed nitrogen-gas laser as the exciting light source combined with a sampling oscilloscope and an *xy* recorder. The time resolution of this system was about 2.5 ns. Sample solutions were degassed by means of freeze-pump-thaw cycles. Preparation and degassing of sample solutions were conducted in a dark room. Fluorescence quantum yields were determined using anthracene in ethanol as a standard, whose fluorescence yield is equal to 0.28. For the measurements of the temperature dependence of the fluorescence lifetime, a cuvette was immersed in isopentane in a quartz Dewar and the temperature of isopentane was controlled by dropping liquid nitrogen. The temperature could be decreased to 120 K by this method. The relative yields of photochemical reactions were measured from the decrease of the absorbance after the irradiation with a xenon lamp.

Results

Excimer Emission. 1. *syn*-[2.2](1,4)Anthracenophane (I). Broad excimer emission with a peak at 630 nm was observed in MTHF rigid solution at 77 K. The excitation spectrum monitored at 600 nm was coincident with the absorption spectrum of I. The lifetime of the excimer fluorescence of I was 62 ns at 77 K. The fluorescence intensity of I was greatly diminished at room temperature owing to the photodimerization as well as the photoisomerization described later. We have confirmed that the observed fluorescence spectrum of I frequently involves the contribution from *anti*-[2.2](1,4)anthracenophane (IV) produced by the photoisomerization of I. IV shows a fluorescence band with a peak at 460 nm and its quantum yield is much larger than that of I. In order to obtain the correct fluorescence spectrum of I, one must excite the solution at sufficiently long wavelength where IV does not absorb, as indicated in Figure 2.

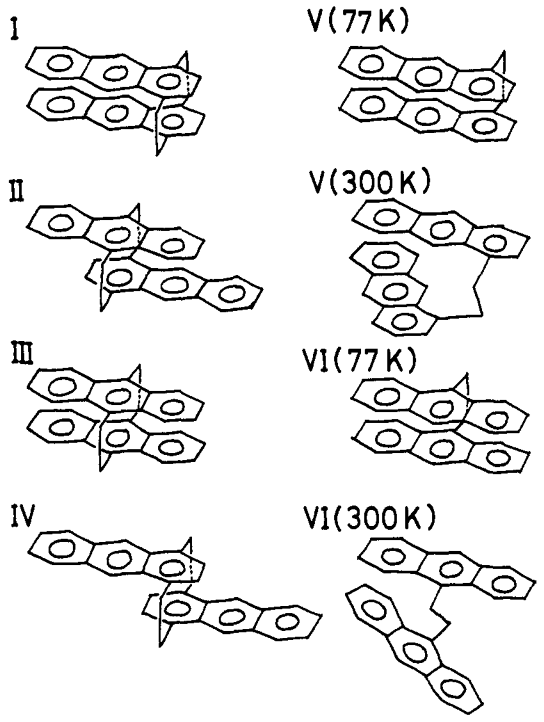

Figure 1.

Table I. Wavelengths of Band Maxima (λ_M) and Lifetimes (τ) of Various Types of Anthracene Excimers

	λ_M, nm	τ, ns
I	620[a]	62[a]
II	570[a]	150[a]
V (300 K)	460[b]	60[b]
V (77 K)	530[a]	70[a]
VI (300 K)	460[b]	
V (77 K)	530[a]	90[a]
DA	580[c]	105[d]

[a] At 77 K. [b] At 300 K. [c] At 10 K (from ref 13). [d] At 90 K (from ref 13).

2. [2.2](1,4)(9,10)Anthracenophane (II). Broad excimer fluorescence with a peak at 570 nm was observed in MTHF at 77 K, as shown in Figure 3. Its excitation spectrum was in accordance with the absorption spectrum and its lifetime was 150 ns in MTHF at 77 K. The fluorescence intensity at room temperature was much weaker compared with that at 77 K.

3. [2.2](9,10)Anthracenophane (III). No emission spectra due to the excimer state of III could be observed at room temperature as well as at 77 K, in agreement with the previous reports.[12] This result may be ascribed to the very effective intramolecular photodimerization. The distance between two anthracenes of III may be in the effective range of dimerization with no need of large structural change after excitation. This is a somewhat different situation from other anthracenophanes.

4. *anti*-[2.2](1,4)Anthracenophane (IV). The fluorescence band of IV shows a vibrational structure (Figure 4). The fluorescence quantum yield of IV in MTHF was 0.27 and its lifetime was 11 ns at room temperature. This value of the fluorescence lifetime is the same as that of 1,4-dimethylanthracene in ethanol at room temperature.

5. 1,2-Di(1-anthryl)ethane (V). The presence of two types of intramolecular excimers of V has been revealed by the present study (Figure 5). One is formed by the association of an excited anthracene with the ground-state partner at room temperature (type 1). The excimer fluorescence of type 1 shows a band maximum at 460 nm and its lifetime is 60 ns. The substitution of methyl groups for the 4,4′ positions of the anthracene nuclei of V does not affect the results obtained at room temperature as described above.

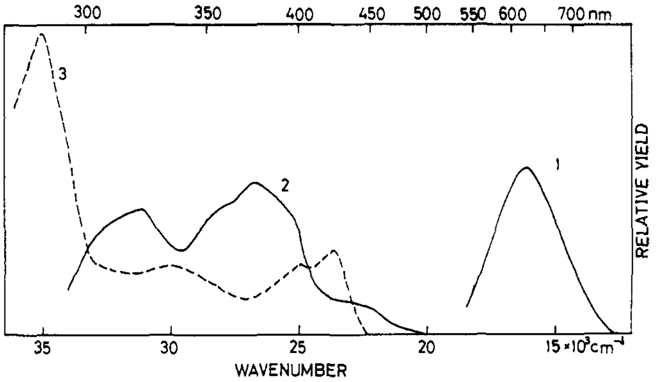

Figure 2. The fluorescence and excitation spectra of I at 77 K in MTHF: 1, excimer fluorescence; 2, excitation spectrum monitored at 600 nm; 3, excitation spectrum monitored at 520 nm.

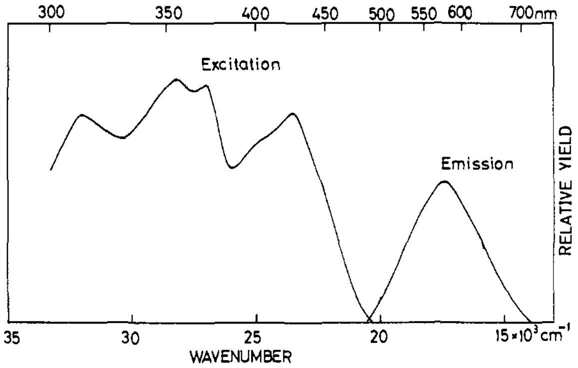

Figure 3. The fluorescence and excitation spectra of II at 77 K in MTHF.

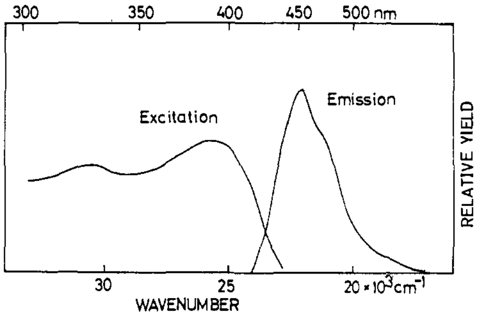

Figure 4. The fluorescence and excitation spectra of IV at room temperature in MTHF.

The other form of the intramolecular excimer (type 2) was obtained by photodecomposing the intramolecular photodimer of V at 77 K (Figure 6). Namely, when V dissolved in MCH–decalin 1:1 mixed solvent was irradiated with a 150-W xenon lamp through a Toshiba UV35 filter at room temperature, it was gradually converted into the intramolecular photodimer. After confirming by absorption spectral measurements that the dimerization was completed, the sample cell was dipped in liquid nitrogen and irradiated by a 20-W low-pressure mercury lamp; the sample gradually turned yellow-green in color due to the excimer fluorescence of type 2. This type of excimer fluorescence could not be observed at room temperature. Furthermore it is necessary to choose a sufficiently rigid solvent at 77 K. The intensity of the monomer emission is

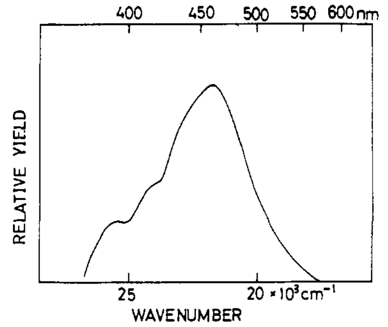

Figure 5. The fluorescence spectra of V at room temperature in acetonitrile.

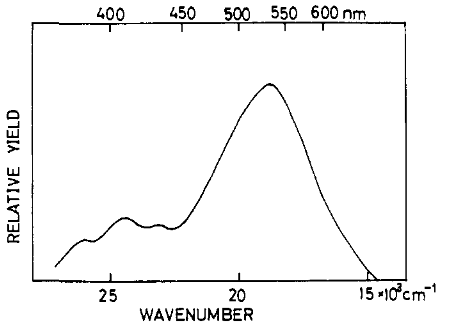

Figure 6. The fluorescence spectra of the photodecomposition product of the intramolecular photodimer of V at 77 K in MCH-decalin 1:1 mixed solvent.

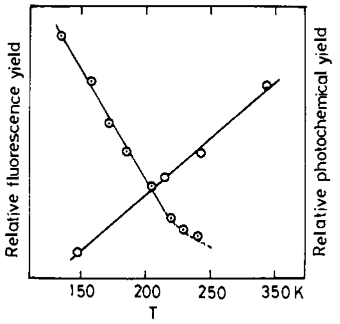

Figure 7. The observed relation between the fluorescence yield and the yield of the photochemical reaction of I: ⊙, fluorescence yield; ○, photochemical yield.

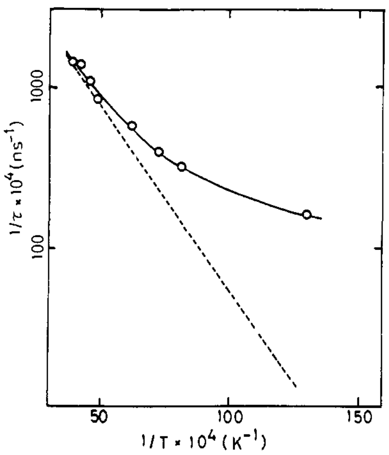

Figure 8. Temperature dependence of the lifetime of the excimer fluorescence of I in MTHF. Activation energy was estimated from the slope represented by the broken line.

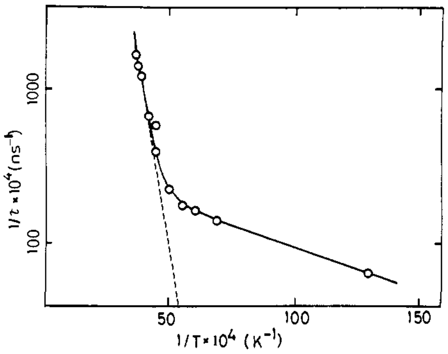

Figure 9. Temperature dependence of the lifetime of the excimer fluorescence of II in MTHF. Activation energy was estimated from the slope represented by the broken line.

stronger than that of the excimer emission in MTHF and the former is comparable with the latter in MCH. MCH-decalin 1:1 mixed solvent was the most satisfactory for our purpose.

6. 1,2-Di(9-anthryl)ethane (VI). The results of VI were analogous to those of V, except that the excimer formation yields are not as good as those of V.

Photodimerization. 1. Temperature dependences of the relative fluorescence yield and the photochemical reaction of I showed that the excimer fluorescence state was inactivated by the photochemical reaction (Figure 7). The activation energy for the photochemical reaction can be obtained from the Arrhenius plot of the inverse of the fluorescence lifetime vs. temperature (Figure 8), since the following expression is satisfied

$$1/\tau = 1/\tau_0 + Ae^{-\Delta E/RT}$$

where ΔE is the activation energy, τ is the lifetime at a given temperature, and τ_0 is the lifetime in the case of no photochemical reaction. The values of τ were 62 and 150 ns at 77 K in MTHF rigid glass for I and II, respectively. These values were considerably reduced to about 7 ns or below at 300 K for both compounds. The exact value of τ_0 cannot be estimated under present conditions because the photodimerization seems to take place even at 77 K. At room temperature the value of $1/\tau_0$ can be neglected compared with $1/\tau$ in the equation. The value of ΔE was obtained to be 1.1 kcal/mol.

2. The activation energy of the photochemical reaction of II was evaluated to be 3.3 kcal/mol by means of the method analogous to the case of I (Figure 9). This value is somewhat larger than the value of 1.7 kcal/mol for the anthracene sandwich-pair dimerization and is similar to the value for the anthracene-naphthalene intramolecular dimerization.[7,13]

3. Photodimerization of V seems to proceed not through the excimer of type 1, but through the type 2 excimer. Thus, the photodimerization seems to suppress almost completely the type 2 excimer fluorescence at room temperature.

Discussion

We have found that virtually there are various structures of excimer states of anthracenes. As one can see in the case of V or VI, two different structures of excimer are possible. Furthermore, V and VI can form excimer states in spite of the fact that they do not conform to the "n = 3 rule" proposed by Hirayama[3a] and confirmed by Chandross et al.[3b] in the studies of α,ω-diphenylalkanes and dinaphthylalkanes.

1. The lifetime of the excimer fluorescence of I at 77 K is shorter than those of usual excimers.[14] This may be due to the dimerization reaction, which inactivates the excimer state even in the rigid MTHF solution at 77 K. From the facts that the activation energy of the dimerization of I is smaller and the wavelength of the band maximum of its excimer fluorescence is longer, respectively, than those of the sandwich pair of anthracene molecules in dianthracene crystal (DA), it may be

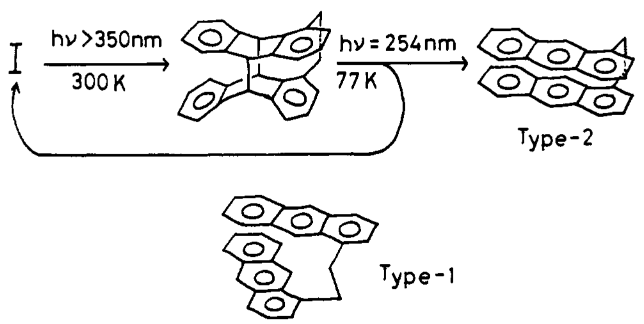

Figure 10. The formation of the type 2 excimer of V.

concluded that the more stable the excimer state becomes, the more efficiently the dimerization occurs in the case of the sandwich pair of anthracenes.

2. The lifetime of the excimer fluorescence of II is longer than that of I, since the photodimerization of II is considerably reduced due to its structure. Namely, this molecule has a displaced parallel-pair structure which does not appear favorable for the photodimerization. This structure was predicted for the excimers of naphthalene, fluorene, and dibenzofuran.[15]

3. As we have pointed out already, the dimerization seems to occur rapidly with no need of large structural change in the excited state of III, since III does not show the excimer fluorescence and its photodimerization yield is high.[12] The distance between the two anthracene moieties of III is considered to be about 3.0 Å.[16] This value is somewhat shorter than the value of the excimer (~3.5 Å) obtained from the theoretical calculations.[17] These results are in agreement with the above described fact that the distance between two moieties is in the effective range of photodimerization. It is clear that the change of the structure in the course of the dimerization in the excimer state is more extensive in the case of I than III, although the structure of the excimer state of I seems to be somewhat similar to III. There is a recent report[18] which describes the existence of the fluorescence of III. However, from our point of view, it must be ascribed to an impurity whose emission was observed at first in our study also, but its excitation spectrum was not coincident with the absorption spectrum.

4. The fact that the fluorescence band of IV has a vibrational structure in contrast to the structureless excimer fluorescence spectra of some other systems may reveal that the excited state of IV is natively not the excimer one.

5. As for the structure of the type 1 excimer of V (300 K), it may be reasonable to postulate the form shown in Figure 10, in view of the fact that the type 1 excimer fluorescence of the 4,4′-dimethyl-substituted compound (1,2-di[1-(4-methylanthryl)]ethane) is identical with that of V.

The excimer fluorescence spectra similar to the type 1 have been observed also in the following cases. Perkampus et al.[19] reported the fluorescence spectrum of the thin film of anthracene formed by sublimation under high vacuum at low temperature. Their spectrum is very similar to the type 1 excimer fluorescence spectrum reported here. Thus, the anthracene excimer observed by Perkampus et al. in the thin film at low temperature seems to have the structure as depicted in Figure 10. Another example of the excimer state analogous to the type 1 of V seems to be formed by exciting the photocleavage products of dianthracene in a rigid matrix of methylcyclohexane at 77 K (A·A).[20] The maximum wavelength (470 nm) of A·A is quite similar to that of the type 1 rather than the type 2 excimer of V. Although the lifetime of the type 1 excimer fluorescence is 60 ns at room temperature, it might become much longer at 77 K and approach that of A·A (~200 ns). The rather long lifetime of the excimer fluorescence of A·A seems to indicate the absence of the photodimerization reaction, which may be the case if the excimer of A·A takes the conformation indicated in Figure 10.

Type 1 excimer emissions of V or VI are the examples which probably do not have the structure predicted from the theoretical viewpoint for the excimer formed by diffusion-controlled encounter. Furthermore, the "$n = 3$ rule" is not so serious a condition, at least in the case of α,ω-dianthrylalkanes, which is different from the cases of diphenylalkanes and dinaphthylalkanes.[3]

The wavelengths of the excimer fluorescence band maxima are in the order: I > DA > II > V (type 2 at 77 K), VI (type 2 at 77 K) > V (type 1 at 300 K); VI (type 1 at 300 K) (Table I). This result may be explained in terms of the magnitude of the overlap between two anthracene nuclei, which seems to play an important role in the stabilization of the excimer state and also in the destabilization of the Franck-Condon ground state.

As for the fluorescence lifetime data, it may appear rather strange that the lifetimes of I, V (type 2), and VI (type 2) are shorter in comparison with those of II or DA. But this fact may be explained on the basis of intramolecular photodimerization. Excimer emission at longer wavelength means a larger overlap and stronger electronic interaction between two anthracene moieties. The anthracene excimer state with relatively longer wavelength emission is favorable for the intramolecular photodimerization, considering that the 9,10 positions of anthracene are the most reactive sites. In fact, I is much more liable to dimerize than II and the dimerization tendencies of V and VI are somewhat smaller than that of I.

More detailed studies on the assignment of the excited-state and excimer emissions of anthracenophanes, including fluorescence polarization[21] and the photochemical studies at lower temperatures,[22] will be reported in a separate paper.

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