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Absorption Spectra of Inter- and Intramolecular Exciplex Systems of Pyrene and *N,N*-Dimethylaniline in Alcoholic Solutions

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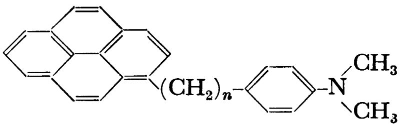
Absorption spectra of inter- and intramolecular exciplex systems of pyrene and *N,N*-dimethylaniline in alcoholic solution were obtained by means of ns laser photolysis. The spectra of intermolecular systems can be reproduced by the superposition of bands of the pyrene anion and the *N,N*-dimethylaniline cation. Similar results were obtained with intramolecular systems of P_1 and P_2, where P_n is (1-pyrenyl)-$(CH_2)_n$-(*p*-dimethylaminophenyl). The absorption band of P_3 exciplex is structureless and very broad, the position of the maximum remaining unchanged. From the relation between absorption spectra and conformation of intramolecular systems, it is concluded that the broad band is due to the sandwich type of structure of the donor cation and the acceptor anion. Anomalous behavior of intermolecular exciplexes in alcoholic solutions is discussed on the basis of their absorption spectra.

The measurement of the absorption spectra of excited molecules in solution has become possible by application of lasers. The absorption spectra of exciplex systems have been measured by several workers[1–5] and the following problems have been discussed: (a) The back CT transition from the anionic moiety to the cationic one. The absorption band due to this transition can be observed in addition to the absorption bands ascribed to the transitions localized in anion as well as cation. (b) Dependence of spectra upon solvent, which has its origin in fluorescence studies on exciplexes.[6] (c) The relation between absorption spectra of exciplexes and their geometrical conformation. We have examined these problems comparing the results of inter- and intramolecular exciplex systems in the same solvent.

The other subject of the present work is to study the exciplexes in alcohols by means of their absorption spectra. The behavior of exciplexes is very sensitive towards environments, some anomalies in alcohols being pointed out as follows. (i) According to the results on the intermolecular exciplex system composed of pyrene (Py) and *N,N*-dimethylaniline (DMA) in aprotic solvents,[7,8] quantum yield and lifetime of exciplex fluorescence decrease with increase in solvent polarity. When dielectric constant is *ca.* 12 the yield decreases sharply, ionic dissociation occurring in place of fluorescent exciplex formation.[9] However, the exciplex fluorescence in alcoholic solutions shows smaller red shift, higher quantum yield and longer lifetime as compared to the results in aprotic solvents with the same value of dielectric constant.[3,10] The experimental values in various alcohols show dependence upon solvent dielectric constant in a similar manner to that in the case of aprotic solvents. In other words, the results in protic solutions correspond to those in aprotic ones with lower value of dielectric constant. (ii) The ionic dissociation to free cation and anion was investigated in polar solvents and empirical equations representing the relationship between dissociation yield and the solvent dielectric constant were proposed.[11] Although the same type of equation is satisfied in both cases of alcohols and aprotic solvents, the parameters in the equation differ from each other.

In the present work absorption spectra of inter- and intramolecular exciplex systems of Py and DMA were observed in some alcohols by means of ns laser photolysis. The intramolecular systems of P_n, ($n=1$, 2, 3),



were examined in order to clarify the relation between spectra and geometrical conformation. Absorption spectra of intermolecular exciplex were observed in 1-pentanol, 2-propanol, and ethanol. The dynamics of exciplex in alcohols are discussed on the basis of these spectra.

Experimental

Laser Photolysis Apparatus. The details of our ns laser photolysis apparatus are essentially the same as those reported.[12] Improvement was made on the wiring of photomultiplier HTV 1P28 for improving *S*/*N* ratio.[13] Examined voltage larger than the standard value is supplied to 1—5 dynodes, the signal current being withdrawn from the 6th dynode with 50 Ω resistor. Negative value of 50 V was supplied to the remainder of dynodes in order to obtain correct time-response. The breeder current of the last two dynodes is 30 mA. A series of capacitors are set between successive dynodes. The linearity of an output signal was checked, the sum of intensity of fluorescence and monitoring flash lamp being confirmed to be measured correctly.

Improvement was also made by setting a simple and convenient monitoring device for exciting pulse intensity. The 347 nm pulse is partially reflected, scattered with MgO and lead to a pin photodiode HP 5082 4220. The signal is deformed to a pulse, whose height is a few volt and decay time is 10 ms, by use of a peak hold circuit.[14] Relative intensity of an exciting pulse is digitally given on solid state display, which holds the value until the next laser shot is given. This device was checked with an oscilloscope-photomultiplier system and also by a thermopile (HADRON 100).[15]

Linearity between the Intensity of an Exciting Laser Pulse and Measured Optical Density. Besides nonlinear effect due to high intensity laser excitation, geometrical correlation between exciting beam and monitoring light sometimes leads to a

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deviation from linearity between the intensity of an exciting pulse and measured optical density.[16] This can be ascribed to the contribution of stray light from an exciting pulse to monitoring light, or to inhomogeneous spatial distribution of an exciting pulse. The linearity was confirmed by measuring the T-T absorption spectra of anthracene in ethanol and the bands of anions produced through the ionic dissociation of Py–DMA and 1,2,4,5-tetracyanobenzene–toluene systems in acetonitrile.

Absorption spectra of the exciplex systems were obtained by use of oscillograms at various wavelength. The fluctuation of an excitation intensity was $\pm 6\%$.

Materials. Py, DMA, and P_n's are the same as used previously.[4,17] The GR grade 2-propanol, 1-pentanol and ethanol were used without purification. The concentration of solution was adjusted so that the optical density at 347 nm is about unity. This corresponds to the order of 10^{-3} and 10^{-5} M in the cases of inter- and intramolecular systems, respectively. The concentration of DMA in the former system was determined so as to quench the Py fluorescence more than 95%. All the solutions were degassed by the usual freeze-pump-thaw method.

Results

Since the exciplex consisting of aromatic hydrocarbon and amine has a large dipole moment, its electronic structure is considered to be an ion-pair of the donor cation and the acceptor anion. The absorption spectra may be similar to the sum of bands of the donor cation and the acceptor anion. The back CT transition from the anion to the cation is also expected to appear.[1,3,18] Usually the reference spectra used for the assignment of the exciplex absorption spectra are those of an anion produced by alkaline metal reduction of hydrocarbon and of a cation produced by γ-irradiation. The difference of measuring apparatus and of environments of ions lead to some ambiguity in discussing the spectral shape. The transient spectra of intermolecular Py–DMA system in acetonitrile are referred to, since their measurements can be made by the same laser photolysis apparatus and in the fluid solution. It is well known that the ionic dissociation to the Py anion and the DMA cation is the main deactivation process in acetonitrile, and its quantum yield is about 0.8.[19] Since no chemical species other than ions and triplet Py is detected, these spectra are the best reference for assigning the $S_n \leftarrow S_1$ spectra of exciplexes. The result is given in Fig. 1. The bands at about 24000 cm^{-1} and at 20100 cm^{-1} are ascribed to the triplet Py and to the Py anion, respectively. The shoulder at 22000 cm^{-1} is due to the superposition of bands of both ions. These bands are in agreement with those in literatue.[20] At a long delay the ion bands decrease and the triplet Py increases. The band shape in the region from 18000—23000 cm^{-1} is independent of delay time. Therefore, the bands in this region are mainly ascribed to the sum of the Py anion and the DMA cation, the concentration ratio of both ions being unity.

The time-resolved spectra of the intermolecular Py–DMA system in 2-propanol and 1-pentanol are given in Figs. 2 and 3. Since the decay of short-lived component agrees with that of exciplex fluorescence, the spectra obtained at the short delay is tentatively ascribed to the exciplex. These two spectra agree with those given in Fig. 1 except for the contribution of the triplet Py. As the bands at 20200 and 22200 cm^{-1} decrease, the triplet Py increases. Similar results were obtained also in ethanol.

Observed spectra of P_1 and P_2 in 2-propanol are given in Figs. 4 and 5. The rise of the short-lived components is too fast to be analyzed, their decays being identical with those of exciplex fluorescence. As

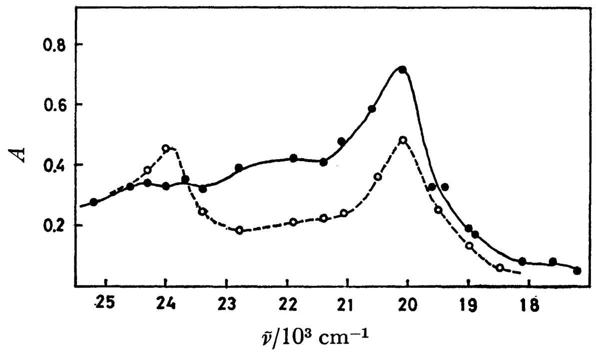

Fig. 1. Transient absorption spectra of intermolecular Py–DMA system in acetonitrile (See text).
-●- 30 ns after the beginning of laser oscillation. (In the present paper the delay time is given in this manner.), -○-150 ns.

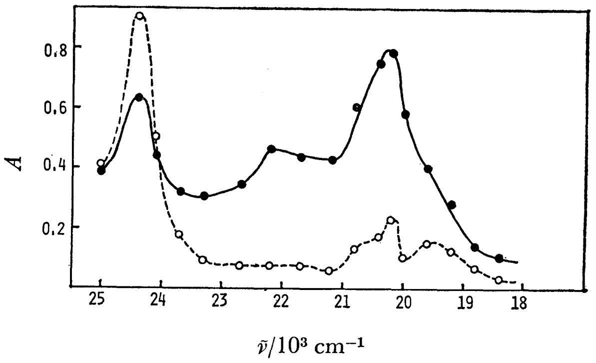

Fig. 2. Transient absorption spectra of intermolecular Py–DMA system in 2-propanol.
-●- 50 ns, -○- 400 ns.

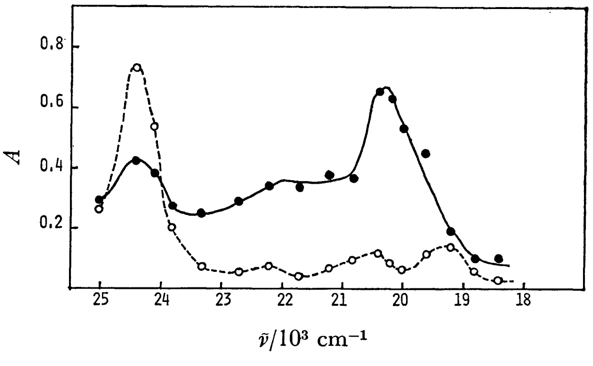

Fig. 3. Transient absorption spectra of intermolecular Py–DMA system in 1-pentanol.
-●- 50 ns, -○- 400 ns.

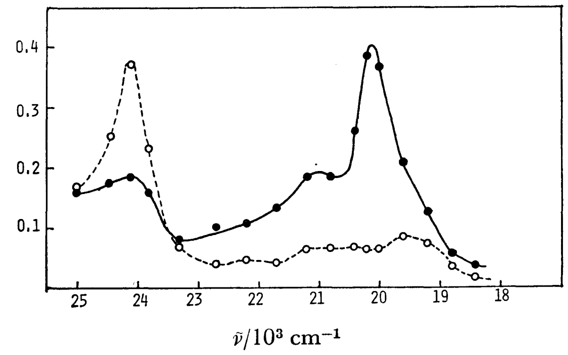

Fig. 4. Transient absorption spectra of P_1 in 2-propanol. -●- 15 ns, -○- 150 ns.

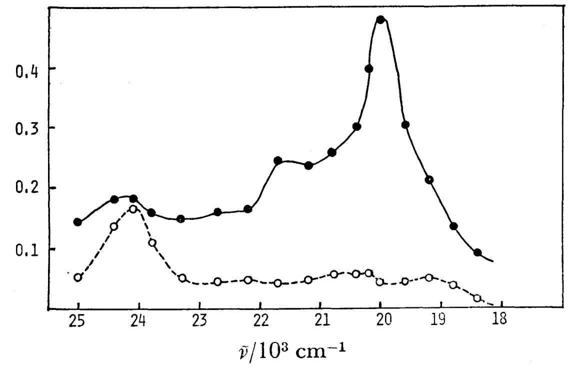

Fig. 5. Transient absorption spectra of P_2 in 2-propanol. -●- 25 ns, -○- 250 ns.

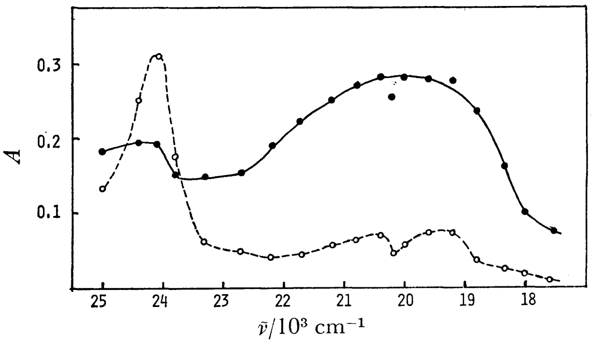

Fig. 6. Transient absorption spectra of P_3 in 2-propanol. -●- 35 ns, -○- 350 ns.

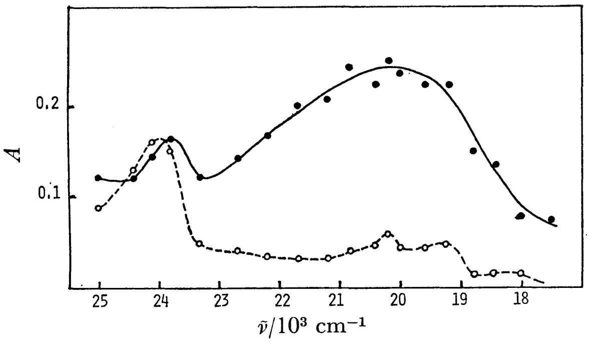

Fig. 7. Transient absorption spectra of P_3 in acetone. -●- 35 ns, -○- 350 ns.

compared with the bands of intermolecular systems the shoulder at the higher wave number side of the Py anion band is shifted to red, its intensity relative to that of the Py anion band (20000 cm^{-1}) increasing. At a long delay, only the triplet Py is identified, its characteristic peak being observed at 24100 cm^{-1}.

The absorption spectra of P_3 are very broad, the band maximum being almost at the same position as that of P_1 or P_2, as shown in Fig. 6. The half-width is about 4000 cm^{-1}. Since ionic dissociation is prohibited in the case of intramolecular compounds, exciplex is formed also in acetone in spite of its high polarity. The absorption spectra of P_3 in the latter solvent are similar to those in alcohol (Fig. 7). The absorption band due to the triplet Py of P_3 shows a peak at 24100 cm^{-1} just as in the case of P_1 and P_2.

The present results can be summarized as follows. (i) The spectra of intermolecular systems can be reproduced approximately by the superposition of bands of the acceptor anion and the donor cation. (ii) Although similar spectra are observed in the cases of P_1 and P_2, the shoulder at higher wave number side of the Py anion band is shifted to the red compared with the case of intermolecular system. (iii) P_3 exciplex shows a characteristic broad band. (iv) The T-T spectra of intramolecular systems are independent of the number of the methylene chain, the characteristic band lying at 24100 cm^{-1}. On the other hand, the triplet Py of intermolecular system shows an absorption peak at 24400 cm^{-1}.

Discussion

Absorption Spectra and Geometrical Conformation of Intramolecular Exciplex Systems. The relation between absorption spectra and geometrical conformation has been studied in detail in the case of 1,2,4,5-tetracyanobenzene complexes in the excited state.[18] However, information on exciplex is scarce.[4] Compounds P_1 and P_2 cannot take the structure of sandwich type, the distance between donor and acceptor moieties being rather long. On the other hand, both stretched and stacked forms are possible for P_3. The dipole moment of all these exciplexes is quite large.[7,8] Exciplexes can be considered approximately to be a kind of ion-pair consisting of donor cation and acceptor anion. In the cases of P_1 and P_2, the interaction between both ions seems to be rather small and the absorption spectra can be reproduced by the superposition of bands of their component ions. Similar spectra can be expected if the exciplex of P_3 is of stretched form. However, a quite broad band is observed, so that P_3 exciplex seems to take the geometry, which is impossible in the cases of P_1 and P_2. Presumably, it is a structure of sandwich type where the donor and the acceptor are in the stacked form and distance between two moieties is rather short.

The present spectra of P_3 are similar to those of intermolecular Py-*N*,*N*-diethylaniline (DEA) system in nonpolar solvents.[5] The following interpretations might be possible with respect to this broad band.

(a) The overlap between MO's of both ions causes the back CT transition from the anion to the cation.

The sum of the latter transitions and the local excitation of the Py anion leads to the broadening of the band at 20000 cm^{-1}. Since the transition moment between the CT and locally excited configurations is zero as a first approximation, the intensity of the back CT transition comparable to that of ion bands should be due to rather strong mixing of both configurations in the fluorescent state, which is inconsistent with the experimental[7,8] and theoretical[21] results indicating large dipole moment of the exciplex. An alternative interpretation may be the mixing in the higher excited state, to which the transition occurs.

(b) The electrostatic interaction between both ions may be rather strong in the case of P_3, which seems to produce the spectral broadening. This interpretation has been suggested in studies on the electronic spectra of ion-pairs produced in rigid matrix.[22]

Although correct interpretation is beyond our present knowledge, the spectral change due to the differences in distance and orientation between two moieties is demonstrated.

Intermolecular Exciplex Systems in Alcoholic Solutions. The fluorescence quantum yield of exciplex is higher and its lifetime longer in alcohols than in aprotic solvents with similar dielectric constant. This can be ascribed to high viscosity and long dielectric relaxation time of alcohols. The electron transfer from DMA to the excited Py is not followed by the solvation to free ions, which can be attributed to network structure of solvent due to hydrogen bonding. The resulting exciplex in alcohols has the same structure and property as those in nonpolar aprotic solvents. This is not in line with the results on the transient absorption spectra. The spectra of Py–DMA intermolecular system in 2-propanol and 1-pentanol are in agreement with the superposition of bands of the Py anion and the DMA cation and are similar to the spectra of P_1 and P_2 in 2-propanol, but they differ a great deal from the spectra of intermolecular Py–DEA in nonpolar solvents and of P_3 in 2-propanol.

A possible explanation is to assume the role of geminate ion-pair, introduced by Goodall *et al.*[23] It is postulated that the exciplexes in these alcohols are produced through the recombination of a geminate ion-pair or they are in equilibrium with the geminate ion-pair.[3,23,24] If the geminate ion-pair is the main chemical species which exists during the observed exciplex fluorescence lifetime, the spectra measured should be reproduced by the superposition of bands of the Py anion and the DMA cation. The excess energy corresponding to an energy gap between the encounter complex and the geminate ion-pair permits diffusional motion, which leads to a longer distance than that of the stretched P_3. However, the produced pair cannot be completely separated from each other since they are captured in the network of hydrogen bond, leading to the exciplex formation due to recombination.

In order to elucidate these problems magnetic field modulations of the Py triplet and Py anion concentrations formed through quenching of singlet excited Py molecules by amines in polar solvents have been recently investigated.[24,25] In the case of Py–DEA–methanol system, magnetic field modulation has been actually observed. The effect has been interpreted to be due to a magnetic field dependent triplet production in the geminate radical ion-pair induced by hyperfine interaction of the unpaired electrons. Thus, in this case, the existence of the geminate ion-pair is confirmed and the geminate pair as well as the dissociated radical ions can be the main product of the fluorescence quenching reaction.[25] However, in the case of Py–DEA–2-propanol system no magnetic field dependence of the triplet as well as the ion radical concentrations was observed. Thus, exciplex is a predominating species instead of a geminate ion-pair. Since the same conclusion is expected in both Py–DEA and Py–DMA systems, the main transient is exciplex, which gives the above transient absorption spectra of Py–DMA–2-propanol system.

The structure of the P_3 exciplex in 2-propanol differs from that of the Py–DMA intermolecular exciplex in the same solvent. The latter might have a more loose structure owing to the more extensive solvation as compared with the former of the sandwich type structure. The present result indicates that the structure of the exciplex is affected considerably by the properties of solvent.

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