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Interaction of Excited Aromatic Hydrocarbons with Aromatic Amines

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It has been established that many aromatic hydrocarbons in *N, N*-dimethyl aromatic amine solvents show their fluorescence spectra at much longer wavelengths than in such inactive solvents as *n*-hexane and toluene. Because the absorption spectra of the hydrocarbons in the amines do not show any essential change, it is confirmed that specific interaction between a hydrocarbon and an amine occurs only in the excited electronic state (the fluorescent state). It has been clearly demonstrated, from the relation between the frequencies of the long-wavelength fluorescence and the electron affinities of the excited aromatic hydrocarbons, the ionization potentials of the amines, *etc.*, that this interaction can be ascribed to the charge transfer from the amine to the excited hydrocarbon, and that the long-wavelength fluorescence is a kind of charge-transfer fluorescence. At the temperature of liquid nitrogen, the interaction becomes much weaker because the rearrangement motions of molecules during the lifetime of the excited state, which are necessary for the charge-transfer complex formation, are more or less hindered in a rigid solvent at low temperatures. It has been confirmed that the interaction is still weaker in the phosphorescent state. This phenomenon has been explained by reference to the electronic processes in the complex.

We have been studying the details and dynamical aspects of molecular interactions by measuring the spectra, the yields, and the decay times of the luminescence. Luminescence measurements are quite suitable for this sort of study.

Because the electronic structure of molecules in the fluorescent state is considerably different from that in the ground state, the strength and, in some cases, the nature of the molecular interaction change when the molecule is excited by light absorption. Usually, this change can occur during the lifetime of the electronically-excited state and considerably affects the luminescence spectra, yields, and decay times.

In general, the electron affinity of a molecule is larger and its ionization potential is smaller in the electronically excited state than in the ground state. Accordingly, it may be possible for electron donor-acceptor interaction to arise in the excited electronic state even if there is no such interaction in the ground state. We have found that this is the case for many aromatic hydrocarbons in the excited electronic state, hydrocarbons which form charge-transfer(CT)-type complexes with various aromatic amines.

We have undertaken detailed kinetic studies of the complex formation-decomposition reaction and the CT interaction processes, and also some quantum theoretical studies of the electronic structures of the complexes. The results of these studies will be published separately. Although the general concept of the CT interaction seems to have been established, we hope that our systematic studies may add something to the elucidation of the CT interaction mechanism.

In this report, we shall describe some results of our investigations into the luminescence of the aromatic hydrocarbons in the aromatic amine solvents, thus giving the general features of the phenomenon.

Experimental

Apparatus. The fluorescence and phosphorescence spectra and phosphorescence decay times were measured with an Aminco-Bowman spectrophotofluorometer, which has been calibrated by using a standard tungsten lamp in order to obtain the luminescence quantum spectrum. The fluorescence decay times were measured by an apparatus similar to the one described elsewhere.[1] The absorption spectra were measured by a Cary 15 spectrophotometer.

Materials. The aromatic hydrocarbons we have examined were phenanthrene, triphenylene, chrysene, pyrene, 9, 10-dimethylanthracene, 9-methylanthracene, anthracene, and perylene. The amines were aniline, *N*-methylaniline, *N, N*-dimethylaniline (DMA), *N, N*-dimethylbenzylamine (DMBA), isomeric *N, N*-dimethyltoluidines (DMT's), napthylamines (NA's), *N, N*-dimethyl-α-napthylamine (α-DMNA), and triethylamine (TEA). Pyrene and perylene were chromatographed and zone-refined. Anthracene, 9-methylanthracene, and 9, 10-dimethylanthracene were purified by extensive zonemelting. Chrysene, triphenylene, and phenanthrene were chromatographed and sublimated in a vacuum. Aniline was purified by the same method as before.[2] *N*-Methylaniline, DMBA,

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[1] N. Mataga, M. Tomura and H. Nishimura, *Mol. Phys.*, **9**, 367 (1965).

[2] N. Mataga and S. Tsuno, This Bulletin, **30**, 711 (1957).

isomeric DMT's, and α-DMNA were distilled in a vacuum several times. DMA was refluxed with acetic anhydride, neutralized by alkali, extracted by ether, and distilled in a vacuum several times. TEA was refluxed with acetic anhydride, dried over activated alumina, and distilled in an atmosphere of dry nitrogen under reduced pressure; n-hexane was dried over metallic sodium and distilled fractionally, and the distillate was passed through a column of activated silica gel. Spectrograde benzene, toluene, and acetonitrile were used without further purification.

All solutions for the measurements were carefully deaerated by repeated freezing, pumping, and thawing.

Experimental Results and Discussion

Several examples of the fluorescence spectra of the aromatic hydrocarbons in amine solvents are shown in Figs. 1—9. In all the cases we have examined, the exciting light was absorbed not by the amines, but the aromatic hydrocarbon molecules.

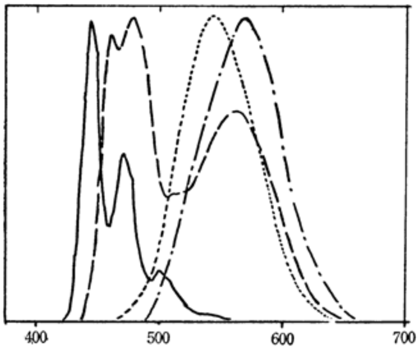

Fig. 1. Fluorescence spectra of perylene (at 300°K).

—— : 10^{-5} mol/l in toluene
— — : 10^{-4} mol/l in α-DMNA
…… : 10^{-4} mol/l in DMA
—·— : 10^{-4} mol/l in p-DMT

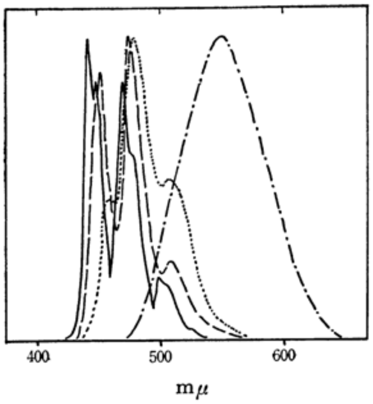

Fig. 2. Fluorescence spectra of perylene.

—— : 10^{-5} mol/l in toluene } at 77°K
— — : 10^{-4} mol/l in α-DMNA } at 77°K
…… : 10^{-4} mol/l in DMA } at 77°K
—·— : 10^{-4} mol/l in m-DMT at 300°K

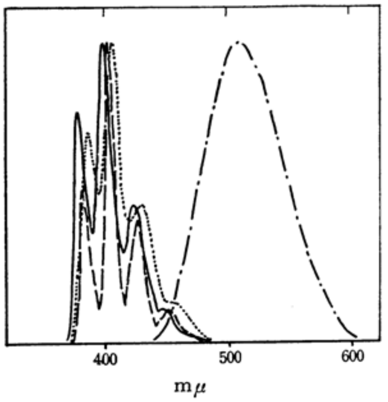

Fig. 3. Fluorescence spectra of anthracene (10^{-4} mol/l).

—— : In toluene at 300°K
—·— : In DMA at 300°K
— — : In toluene at 77°K
…… : In DMA at 77°K

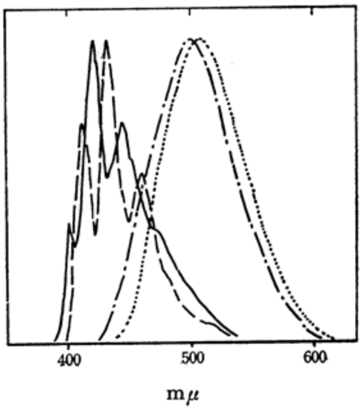

Fig. 4. Fluorescence spectra of 9-methyl- and 9,10-dimethylanthracene in DMA (10^{-4} mol/l).

9-Methylanthracene; —— : at 77°K
…… : at 300°K
9,10-Dimethylanthracene; — — : at 77°K
—·— : at 300°K

One can see from these figures that many aromatic hydrocarbons in N,N-dimethyl aromatic amines at room temperature fluoresce at much longer wavelengths than in such inactive solvents as n-hexane and toluene. In contrast to this, the absorption spectra of the hydrocarbons in these amines do not show any essential difference from those in the inactive solvents, except for the slight shift due to the general (non-specific) solvent effects. These facts indicate that specific interaction between a hydrocarbon and an amine occurs only in the excited electronic state. In the case of

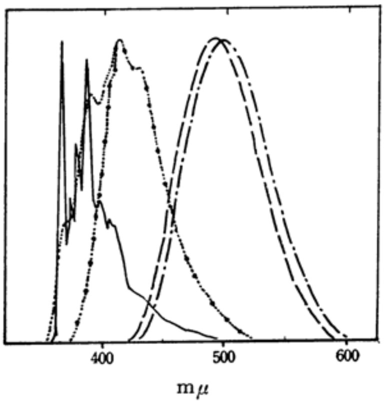

Fig. 5. Fluorescence spectra of pyrene (10^{-4} mol/l).

——— : In toluene at 77°K
…… : In DMA at 77°K
•…• : In *p*-DMA at 77°K
— — : In DMA at 300°K
-·-·- : *p*-DMT at 300°K

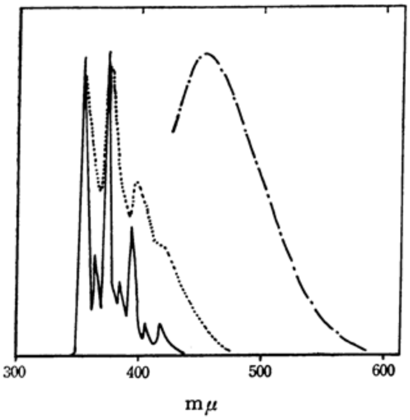

Fig. 6. Fluorescence spectra of chrysene (10^{-4} mol/l).

——— : In *n*-hexane at 77°K
…… : In DMA at 77°K
— - : In DMA at 300°K

perylene, the nature of this interaction has already been studied by several authors[3,4] and has been ascribed to the CT interaction of the excited aromatic hydrocarbon with the aromatic amines.

It seems probable that we can observe similar phenomena in the case of the other aromatic hydrocarbons, and indeed we have actually observed long wavelength fluorescence bands, as Figs. 3—8 show. One of the main purposes of the present work was to establish the mechanism of this fluorescence transition; as will be described below, we have confirmed that this emission is the CT fluorescence of the excited aromatic hydrocarbon-amine complex.

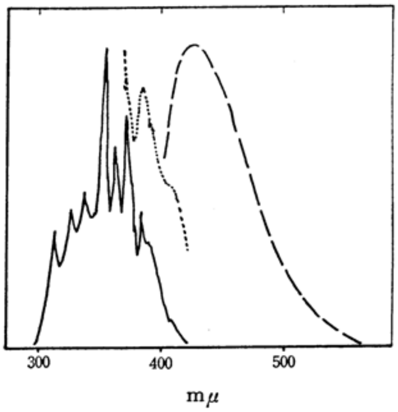

Fig. 7. Fluorescence spectra of triphenylene.

——— : 10^{-4} mol/l in *n*-hexane at 77°K
…… : 10^{-3} mol/l in DMA at 77°K
— — : 10^{-3} mol/l in DMA at 300°K

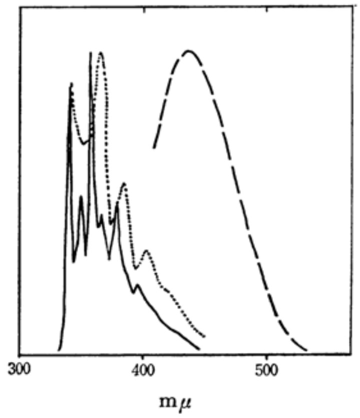

Fig. 8. Fluorescence spectra of phenanthrene.

——— : 10^{-4} mol/l in *n*-hexane at 77°K
…… : 10^{-3} mol/l in DMA at 77°K
— — : 10^{-3} mol/l in DMA at 300°K

We have made extensive measurements of the fluorescence spectra of various hydrocarbons in DMA. As is indicated in Table 1 and Figs. 1—8, the wavelength of the anomalous fluorescence depends on the electron affinity of the aromatic hydrocarbon molecule. That is, the larger the electron affinity of the aromatic hydrocarbon, the greater the wavelength of the fluorescence. The values of the electron affinity used here have been estimated by the equation (in units of eV)[5]:

$$A = 3.03 - 0.701\,\nu(^1\mathrm{L_a}) \tag{1}$$

where ν is the energy of the $^1\mathrm{L_a}$ band in units of eV. The energy of the electron-transfer configuration, $E(\mathrm{A^-}\text{—}\mathrm{D^+})$, when the halves of the

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3) H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys, Chem.*, **67**, 791 (1963).

4) N. Mataga, K. Ezumi and K. Takahashi, *Z. Phys. Chem. N. F.*, **44**, 250 (1965).

5) G. Briegleb, *Angew. Chem. International Ed.*, **3**, 617 (1964).

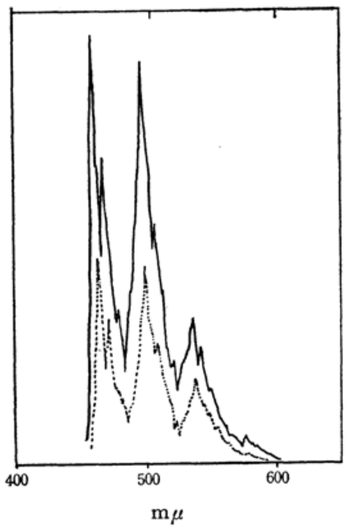

Fig. 9a. Phosphorescence spectra of phenanthrene at 77°K (10^{-3} mol/l).

—— : In n-hexane ⋯⋯ : In DMA

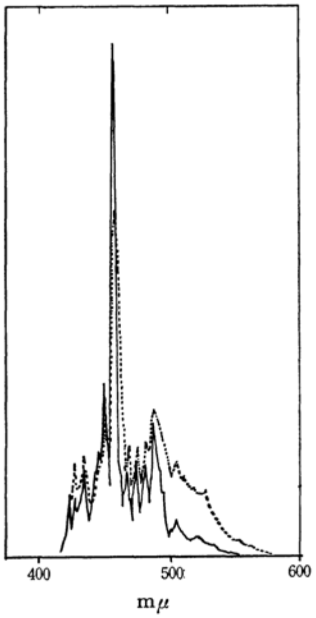

Fig. 9b. Phosphorescence spectra of triphenylene at 77°K (10^{-3} mol/l).

—— : In n-hexane
⋯⋯ : In DMA

A-D pair are interacting with each other at a finite distance, may be given by:

$$E(\mathrm{A}^- \text{-} \mathrm{D}^+) = I - A - C \tag{2}$$

where I is the ionization potential of the donor and C is the coulomb energy between the halves of the A^--D^+ pair. Because the coulomb energy is probably almost constant for all instances of the same type of donor-acceptor pairs, $E(\mathrm{A}^-\text{-}\mathrm{D}^+)$ may be approximately proportional to the A value for the same donor. As one can see from Fig. 10, the energy of the CT fluorescence is almost proportional to the A value of the hydrocarbon. The $E(\mathrm{A}^-\text{-}\mathrm{D}^+)$ values in Fig. 10 have been calculated assuming $C \sim 3$ eV. However, one can observe systematic deviations of the observed energies of the CT fluorescence from the calculated $E(\mathrm{A}^-\text{-}\mathrm{D}^+)$ values. This seems to indicate that the energies of the observed fluorescence transitions depend also on the energies of the excited states locallized in the partners of the D-A pair. Nevertheless, it seems quite plausible that the most important interaction between the partners in the complex may be the charge-transfer from the amine to the excited aromatic hydrocarbon. Therefore, the wave function of the excited complex may be written as:

TABLE 1.

(a) Wave numbers of the heteropolar excimer fluorescence.

	DMA	m-DMT	p-DMT	α-DMNA
Perylene	18300	18300	17500	17600
Anthracene	19500	—	—	—
9-Methyl-anthracene	19700	—	—	—
9, 10-Dimethyl-anthracene	20000	—	—	—
Pyrene	20300	—	20000	—
Chrysene	22000	—	—	—
Phenanthrene	23000	—	—	—
Triphenylene	23300	—	—	—

(b) Phosphorescence decay times of triphenylene (1) and phenanthrene (2) at 77°K (in units of sec).

Solvent	(1)	(2)
n-Hexane	13.4	3.8
DMA	13.8	3.8

$$\Psi \approx a\Phi(\mathrm{A}^*\cdot\mathrm{D}) + b\Phi(\mathrm{A}^-\text{-}\mathrm{D}^+) \tag{3}$$

where A* represents the fluorescent state of the hydrocarbon. However, the more general form of the wave function may be:

$$\Psi \approx \sum_i a_i \Phi(\mathrm{A}^*_i\cdot\mathrm{D}) + \sum_i b_i \Phi(\mathrm{A}\cdot\mathrm{D}^*_i) + c\Phi(\mathrm{A}^-\text{-}\mathrm{D}^+) + d\Phi(\mathrm{A}^+\text{-}\mathrm{D}^-), \tag{4}$$

where A^*_i's and D^*_i's represent various excited states of A and D respectively. Written in this way, it may be possible to regard Eq. (4) as representing the wave function of a "heteroplar excimer" in contrast to such a "homopolar excimer" as the pyrene excimer. In Eq. (4), $a_i \neq b_i$ and $c \neq d$, in contrast to the homopolar case,6) where $a_i =$

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6) For example, J. N. Murrell and J. Tanaka, *Mol. Phys.*, **7**, 363 (1964).

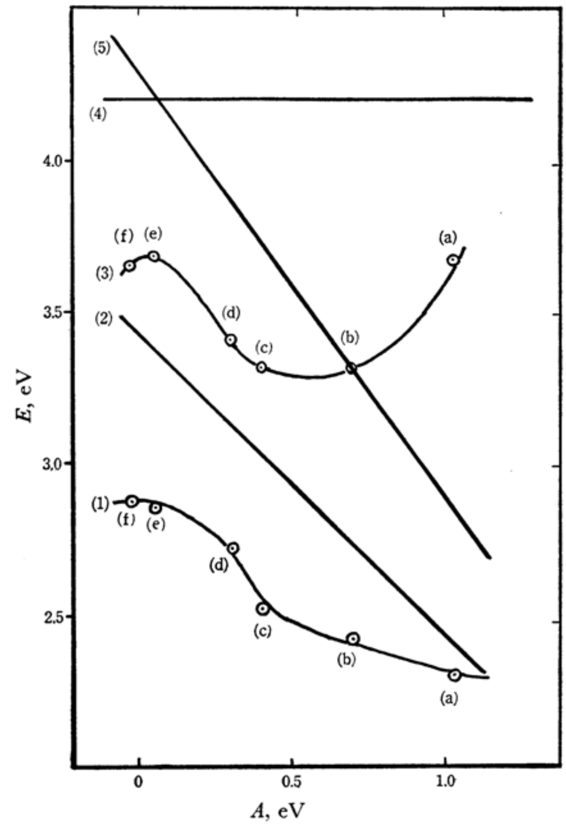

Fig. 10. Relation between the energy of the heteropolar excimer fluorescence and those of the electron transfer configuration as well as the locally excited configurations. The abscissa represents the electron affinity of the aromatic hydrocarbon.

(1) The observed energy of the heteropolar excimer fluorescence in DMA.
(2) The energy of the electron transfer configuration.
(3) The excitation energy to the ^1L_b state of the hydrocarbon.
(4) The excitation energy to the lowest excited singlet state of DMA.
(5) The excitation energy to the ^1L_a state of the hydrocarbon.
(a) Perylene (b) Anthracene (c) Pyrene
(d) Chrysene (e) Phenanthrene
(f) Triphenylene

b_i and $c=d$ represent, respectively, the exciton-type interaction and the charge-resonance interaction. In the case of the homopolar excimer, it has been proposed that the exciton-type interaction due to the excitation to the ^1L_a state and the charge-resonance interaction are the most important interactions. It is interesting that one can see the influence of the contribution from the ^1L_b state of the hydrocarbons on the observed energies of the CT fluorescence (*cf.* Fig. 10).

The CT fluorescence spectra of both perylene and pyrene in *p*-DMT lie at much longer wavelength than in DMA, whereas the CT fluorescence in *m*-DMT lie at almost the same wavelength as in DMA. This fact seems to be in accordance with the above arguments. According to the molecular orbital consideration, the presence of the *p*-methyl group decreases the ionization potential of the amine molecule, whereas such an effect is very small in the case of *m*-DMT.

We can observe the substituent effect also in the anthracene, 9-methylanthracene, and 9, 10-dimethylanthracene series. The wavelength of the CT fluorescence in DMA decreases in this order. This result may be ascribed to the fact that the methyl substitution decreases the electron affinity of the aromatic hydrocarbons.

The CT fluorescence spectrum of perylene in α-DMNA lies at a much longer wavelength than that in DMA. However, in α-DMNA, not only the CT fluorescence, but also the fluorescence of the perylene molecule, can be observed, although the latter fluorescence is somewhat broadened compared with that in an inactive solvent such as toluene. There is some experimental evidence that the steric repression of the resonance effect of the substituent is very strong in α-DMNA.[7] Therefore, the electron density on nitrogen may be larger in α-DMNA than in DMA. Moreover, because of the smaller extent of conjugation, the ionization potential of the dimethylamino group of α-DMNA may be smaller than that of DMA, thus perhaps resulting in the longer-wavelength CT fluorescence in the former. However, the steric hindrance in the CT interaction may be larger in the case of α-DMNA, thus perhaps causing the appearance of the perylene molecule fluorescence even in the pure α-DMNA solution.

The fluorescence spectra of these hydrocarbons in the amines at 77°K are quite different from those at room temperature and are rather close to the spectra in such inactive solvents as *n*-hexane and toluene. Although the spectra in amines at 77°K are a little diffuse compared with those in the inactive solvents, the red shifts of the band maxima in amines, compared with those in the inactive solvents, are generally rather small. Their wave numbers have an order of magnitude of several hundreds in the case of perylene, anthracene, phenanthrene, chrysene, and triphenylene. In contrast to this, the fluorescence spectra of pyrene in DMA and DMT's at 77°K are very diffuse and lie at *ca.* 2200 cm^{-1} wave numbers smaller by *ca.* 2200 cm^{-1} than in *n*-hexane or toluene. These facts indicate that the rearrangement motions of molecules during the lifetime of the excited state, which are necessary for the CT complex formation, are more or less hindered in rigid amine solvents at 77°K. The behavior

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[7] J. W. Smith, *J. Chem. Soc.*, **1961**, 81.

of pyrene, which is very different from that of the other aromatic hydrocarbons, may be ascribed to the very long lifetime of the fluorescent state. According to our measurements, the fluorescence decay times of pyrene in *n*-hexane at 77°K and at room temperature are *ca.* 500 ns and *ca.* 400 ns respectively. In contrast to these values, the decay times in DMA at 77°K and at room temperature are *ca.* 130 ns and *ca.* 40 ns respectively. These results may be interpreted as indicating a considerable amount of fluorescence quenching due to the rearrangement motions of molecules during the lifetime of the excited state and to the CT interactions with DMA molecules at 77°K.

In general, the extent of the spectral change due to the interactions described above may be determined from the strength of the intermolecular force between the excited hydrocarbon and the amine, as well as from the lifetime of the excited state. The fluorescence decay times⁸⁾ of phenanthrene and chrysene in EPA at 77°K are *ca.* 70 ns and 50 ns respectively, which are much longer than those of anthracene (∼6 ns) and perylene (7—8 ns). Nevertheless, the spectral changes of the former are almost the same as those of the latters, a phenomenon which may be ascribed to the relatively smaller electron affinities of the former molecules and accordingly their weaker CT interactions with amines compared with the latter molecules. In the case of pyrene, the electron affinity is not so small and the flourescence decay time is extraordinarily long.

Now, it is possible that there are several different states of interactions between hydrocarbon and amine molecules depending on the temperature of the system. A preliminary examination of the system of perylene in *m*-DMT indicates that there are several different states of interactions between 77°K and room temperature: *i. e.,* the system shows several different fluorescence spectra at different temperature ranges. More detailed studies are now going on in our laboratory.

In addition to the measurements of the fluorescence spectra at low temperatures, we have studied phosphorescence spectra in the case of phenanthrene and triphenylene. The wavelengths of phosphorescence spectra in DMA were practically the same as those in *n*-hexane. Furthermore, the phosphorescence decay times in DMA were the same as those in *n*-hexane, whithin the limits of experimental error. These results indicate that the interaction between the amine and the hydrocarbon in the phosphorescence state is much weaker than the interaction in the fluorescence state. Very similar results have previously been observed in the case of more stable CT complexes, which can exist in the ground state as well as in the excited singlet state.⁹⁾ Even in these stable complexes, the phosphorescence spectra are rather close to those of the aromatic hydrocarbons (which are acting as electron donors in these cases), although one can observe considerable changes in the phosphorescence decay times.⁹⁾ It seems possible that, in the present case as well as in the case of the stable complexes, the interaction between the donor and the acceptor becomes very weak during the radiationless transition from the fluorescent state, and that the hydrocarbon molecules which are completely or incompletely freed from the CT interaction are realized in the phosphorescent state.

In the case of the TEA, aniline, *N*-methylaniline, and DMBA used as electron-donating solvents, we cannot observe the fluorescence spectra of the CT complex, but we can observe the quenching actions of the amines. Quite a similar circumstance can be observed in the case of α- and β-NA's. Although the interpretation of these results is not easy, it is possible to observe the fluorescence of the CT complex even in these cases if the complex can be formed in a rigid matrix at low temperatures. Actually, we have observed the fluorescence of pyrene complexed with aniline, *N*-methylaniline, and DMBA in the cyclohexane matrix at a low temperature.¹⁰⁾ However, in the case of these complexes, the fluorescence yield is much smaller than in the complexes of pyrene with DMA and DMT's. That is, even at low temperatures in the rigid matrix, the radiationless process is much more remarkable in the former complexes than in the latter complexes. More detailed studies, including those of the other amines, are now going on in our laboratory.

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8) J. D. Laposa, E. C. Lim and R. E. Kellog, *J. Chem. Phys.,* **42**, 3025 (1965).

9) J. Czekalla, G. Briegleb, W. Herre and h. J. Vahlensieck, *Ber. Bunsenges. Phys. Chem.,* **63**, 715 (1959). *Ber. Bunsenges. Phys. Chem.,* **63**, 715 (1959).

10) N. Mataga, T. Okada and H. Oohari, This Bulletin, **39**, 2563 (1966).