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On the Emission of Excited Complexes Formed between Condensed Aromatic Hydrocarbons and Aliphatic Amines*[1]

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Anomalous emission observed at long wavelengths in the systems of condensed aromatic hydrocarbons and aliphatic tertiary amines has been studied. The anthracene-tri-*n*-butylamine system has been dealt with in detail. On the basis of the absorption spectrum, the temperature dependence of the long-wavelength emission and the relation between the quenching of the hydrocarbon fluorescence and the intensity of the long-wavelength emission, it has been concluded that this emission originates from the excited complex formed between an excited hydrocarbon and an amine. The interaction involved in excited-complex formation is of a charge-transfer type. This was confirmed by the correlation of the wavelengths of the excited-complex emission with the ionization potentials of amines and the electron affinities of aromatic hydrocarbons and by the large dipole moment of the excited complex.

In general, the behavior of a molecule in the electronically excited state differs considerably from that in the ground state. Its ionization potential is smaller and its electron affinity is larger in the excited state, so that the molecular interaction may be expected to bring about new interesting phenomena. Many aromatic hydrocarbons dissolved in such solvents as *N,N*-dialkyl aromatic amines have been demonstrated to fluoresce at much longer wavelengths than in inert solvents.[1-4] As the absorption spectra of the hydrocarbons in the amines do not suffer any essential change, it is evident that no specific interaction exists between a ground-state hydrocarbon and an amine. From this observation it has been concluded that the new fluorescence can be ascribed to the excited complex formed exclusively from an excited-state hydrocarbon and an amine. Based on the relation of the energies of the new fluorescence with the electron affinities of the hydrocarbons and the ionization potentials of the amines, it has also been confirmed

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1) H. Leonhardt and A. Weller, *Z. physik. Chem.*, *N. F.*, **29**, 277 (1961); *Ber. Bunsenges. physik. Chem.*, **67**, 791 (1963).

2) N. Mataga, K. Ezumi and K. Takahashi, *Z. physik. Chem.*, *N. F.*, **44**, 250 (1965); N. Mataga, T. Okada and K. Ezumi, *Mol. Phys.*, **10**, 201 (1966); N. Mataga, K. Ezumi and T. Okada, *ibid.*, **10**, 203 (1966); N. Mataga and K. Ezumi, This Bulletin, **40**, 1355 (1967).

3) H. Knibbe, D. Rehm and A. Weller, *Z. physik. Chem.*, *N. F.*, **56**, 95 (1967).

4) H. Beens, H. Knibbe and A. Weller, *J. Chem. Phys.*, **47**, 1183 (1967).

that the charge-transfer(CT) interaction between an excited hydrocarbon and an amine is responsible for the formation of an excited complex. The fact that the appearance of the new fluorescence is accompanied by the quenching of the hydrocarbon fluorescence seems to suggest that the fluorescence quenching should be intimately connected with the excited-complex formation.

Since similar excited complexes have been discovered in many other systems,[5-9] it can reasonably be proposed that the excited CT complex formed diffusionally as an intermediate species plays an important role in the mechanism of fluorescence quenching.

The present author has found that anomalous emission can be observed in the systems of the condensed aromatic hydrocarbons and some of the aliphatic amines in various solvents. The absorption spectra indicated such small interactions between the ground-state hydrocarbons and the amines that the emission should be considered to originate from some kind of molecular complex existing only in the excited state.

In the case of aromatic amines the interaction involved should be classified as a π-π interaction, whereas that for aliphatic amines may be regarded as an n-π interaction. No fluorescence study of this has yet been reported. Thus, it is worth while to undertake an investigation with a view to clarifying the character of the interaction and its correlation with fluorescence quenching.

The present paper reports the results of some experiments on the systems of the condensed aromatic hydrocarbons and the aliphatic amines. The system of anthracene and tri-*n*-butylamine was studied in some detail.

Experimental

All the amines used were dried over pellets of potassium hydroxide and/or distilled. Triethylamine, tri-*n*-butylamine and diethylamine were further distilled fractionally in an atmosphere of nitrogen under reduced pressure. Naphthalene and phenanthrene were recrystallized from ethanol, zone-refined and sublimed in a vacuum. Acenaphthene and triphenylene were recrystallized from ethanol. 1,2-Benzanthracene was recrystallized from benzene. 9,10-Diphenylanthracene was recrystallized from xylene and sublimed in a vacuum. Anthracene was purified by recrystallization from xylene, zone-refining and sublimation in a vacuum. Pyrene was recrystallized from xylene, chromatographed, zone-refined and sublimed in a vacuum. Perylene was chromatographed and recrystallized. *n*-Hexane used was a Super special grade reagent of Wako Junyaku Co. G. R. grade cyclohexane and acetone, also from Wako Junyaku Co., were used without further purification. Benzene, chloroform and dichloromethane used were Dotite Spectrosol reagents of Dojin Yakukagaku Co. Spectro-grade carbon tetrachloride from Tokyo Kasei Co. was used. Chlorobenzene was a G. R. grade reagent from Koso Kagaku Co. and was fractionally distilled after being dried with phosphorus pentoxide. Fluorobenzene of British Drug Houses Ltd. was used without purification. G. R. grade ethyl ether was a product of Showa Ether Co. and was fractionally distilled after being dried with sodium. G. R. grade di-*n*-butyl ether from Tokyo Kasei Co. was dried with sodium and distilled. Ethyl acetate, cyclohexanone and benzonitrile of Wako Junyaku Co., G. R. grade, were treated with phosphorus pentoxide and distilled twice. Dibutyl phthalate of Wako Junyaku Co. was distilled twice under reduced pressure. Anisole was distilled in a nitrogen atmosphere. Tetralin and decalin were distilled. 1,2-Dichloroethane and dioxane of Wako Junyaku Co., *p*-xylene, isopropylbenzene and *t*-butylbenzene of Tokyo Kasei Co., G. R. or E. P. grade, were used. Spectro-grade *N*,*N*-dimethylformamide of Tokyo Kasei Co. was used without further purification. Methanol was a G. R. grade reagent of Wako Junyaku Co. Toluene was distilled from a G. R. grade reagent of Wako Junyaku Co.

The fluorescence and absorption spectra were measured with a Hitachi EPS-2U recording spectrophotometer.

The exciting light source was a Toshiba SHL-100UV high-pressure mercury lamp, combined with a UV filter or a Bausch & Lomb grating monochromator to select the wavelength of excitation.

The wave numbers of the emission-band maxima were determined from the emission spectra corrected for the spectral sensitivity of the instrument.

Measurements were made on the aerated samples at room temperature. For the anthracene - tri-*n*-butylamine toluene system, however, the sample solutions were repeatedly degassed by the usual freeze-pump-thaw method.

For measuring the temperature dependence of the emission spectra, a Pyrex tube containing the sample solution was immersed in a quartz Dewar with liquid nitrogen or a mixture of dry ice and acetone for low temperatures, or with warm water above room temperature. The usual concentrations of the aromatic hydrocarbons and the amines were 10^{-4}—10^{-3} M and 0.1—1 M, respectively. It was confirmed that the amines used exhibited no emission, though they slightly absorbed the exciting light at higher concentrations.

Results and Discussion

The absorption spectra of the solutions used for the observation of emission showed no essential change, except for the slight differences due to the ordinary solvent effects, in absorbance and wavelength, as is shown in Fig. 1. This indicates that an amine makes no specific interaction with a ground-state condensed aromatic hydrocarbon; no

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[5] J. Czekalla and K. O. Meyer, *Z. physik. Chem.*, *N. F.*, **27**, 185 (1961).

[6] T. Miwa and M. Koizumi, This Bulletin, **39**, 2588 (1966); K. Kaneta and M. Koizumi, *ibid.*, **40**, 2254 (1967).

[7] E. A. Chandross and J. Ferguson, *J. Chem. Phys.*, **47**, 2557 (1967).

[8] A. Nakajima and H. Akamatu, This Bulletin, **41**, 1961 (1968).

[9] H. Beens and A. Weller, *Chem. Phys. Letters*, **2**, 140 (1968).

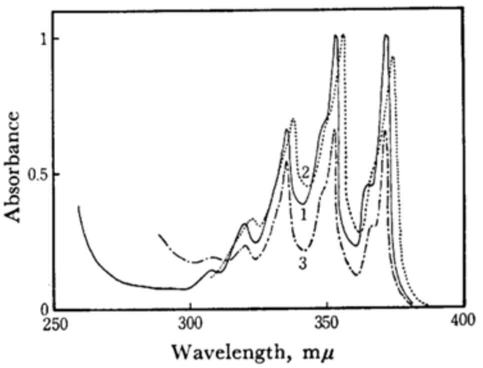

Fig. 1. Absorption spectra of anthracene.
(1) in *n*-hexane, $[A]=1.2\times10^{-4}$ M
(2) in tri-*n*-butylamine (reference: TBA), $[A]=1.2\times10^{-4}$ M
(3) in *n*-hexane, $[A]=8.4\times10^{-5}$ M, $[TBA]=8.4\times10^{-2}$ M

trace is found of such a stable complex as can be detected in the absorption spectrum.*3

Wavelengths of Anomalous Emission Observed in Solutions Containing Aromatic Hydrocarbons and Aliphatic Amines. The emission spectra were measured on the systems of the condensed aromatic hydrocarbons and various aliphatic amines. While the normal fluorescence of an aromatic hydrocarbon was quenched considerably, a new anomalous emission was observed for some kinds of amines at longer wavelength regions. This long-wavelength emission should be regarded as a kind of fluorescence because it decayed instantaneously after the exciting light was shut off. Table 1 gives the results for the *n*-hexane solutions of anthracene and the amines. The same behavior was also found with 1,2-benzanthracene.

The observed emissions may be ascribed to some excited species formed diffusionally from the excited-state aromatic hydrocarbons and the amines.

As can be seen from Table 1, the appearance of a long-wavelength emission seems to depend largely upon the property of the amine employed; only the tertiary amines may be considered to satisfy the requirements for its appearance. Primary amines uniformly quenched anthracene fluorescence with the increase of their concentration without any other emission, while secondary amines showed a new emission at about 530 mμ, obviously due to the photochemical reaction products. However, the absorption and fluorescence spectra for the solutions involving the tertiary amines remained reproducible after irradiation by the exciting light. Although the explanation does not seem to be easy, the hydrogen atom attached to the nitrogen atom of an amine may have some connection with its quenching action; the hydrogen atom of a secondary amine should be considered as very reactive. It may be favorable for the appearance of the long-wavelength emission that tertiary amines have no reactive hydrogen atom and their ionization potentials are relatively low. As the importance of tertiary amines seemed to have been confirmed, a similar experiment was performed for the *n*-hexane solutions containing naphthalene and the tertiary amines, the result of which is given in Table 2.

TABLE 1. LONG-WAVELENGTH EMISSION OBSERVED IN THE ANTHRACENE - AMINE -*n*- HEXANE SYSTEMS
(excitation wavelength: 365 mμ)

Amine		Wavelength
Primary	*n*-Butylamine *t*-Butylamine Dodecylamine	not observed
Secondary	Diethylamine Di-*n*-butylamine	photoproduct emission (*ca.* 530 mμ)
Tertiary	Triethylamine	489±2 mμ
	Tri-*n*-butylamine	483±2 mμ

It may be said that the increasing order of the wavelengths of the long-wavelength emission, despite their rather small differences, corresponds to the decreasing order of the ionization potentials of the amines, as is shown in Table 2.

TABLE 2. NAPHTHALENE - *t*-AMINE - *n*-HEXANE SYSTEMS
(excitation wavelength: 310 mμ)

Tertiary amine	Wavelength of long-wavelength emission (mμ)
Triethylamine	405±3
Tripropylamine	405±3
Tri-*n*-butylamine	411±2
N,N-Dimethylcyclohexylamine	416±3

The long-wavelength emission was measured for the systems of tri-*n*-butylamine (TBA) and the aromatic hydrocarbons in toluene. Table 3 lists their wavelengths. For the pyrene-TBA system, pyrene excimer fluorescence overlapped the long-wavelength emission, and discrimination between them was difficult. In the cases of 9,10-diphenylanthracene and perylene, a slight quenching of the fluorescence occurred with no long-wavelength emission, and even in pure TBA only the broadening of the fluorescence spectrum of the hydrocarbon was observed. This may be interpreted neither in terms of their short fluorescence lifetimes, which are comparable with that of anthracene, nor in terms of the formation of the non-emissive solvated ions in view of the solvent polarity.[1,10] It can be inferred

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*3 No CT band could be observed at a longer wavelength. The increase in absorbance in the short-wavelength region for the curve (3) in Fig. 1 is due to the absorption of tri-*n*-butylamine.

10) H. Knibbe, K. Rollig, F. Schafer and A. Weller, *J. Chem. Phys.*, **47**, 1184 (1967).

from Table 3 that the wavelengths of the long-wavelength emission are related to the electron-affinities of the aromatic hydrocarbons.[*4] Dependence of the wavelengths of the long-wavelength emissions on the ionization potentials of the amines and the electron affinities of the aromatic hydrocarbons suggests that the CT interaction is important.[1–4,6,7]

TABLE 3. TRI-*n*-BUTYLAMINE - AROMATIC HYDROCARBON - TOLUENE SYSTEMS

Aromatic hydrocarbon	Emission wavelength (mμ)	Excitation wavelength (mμ)
Naphthalene	437±5	310
Acenaphthene	416±5	
Triphenylene	442±5	
Phenanthrene	445±5	
1,2-Benzanthracene	512±2	365
Anthracene	524±2	
Pyrene	520?	
9,10-Diphenylanthracene	not observed	
Perylene	not observed	

Dependence of the Intensities of Anthracene Fluorescence and the long-wavelength Emission on TBA concentration. Variations in the relative intensities of anthracene fluorescence and the long-wavelength emission were measured for different TBA concentrations. The anthracene concentration was maintained at 4.22×10^{-4} M and the solvent was *n*-hexane. The result is shown in Fig. 2.

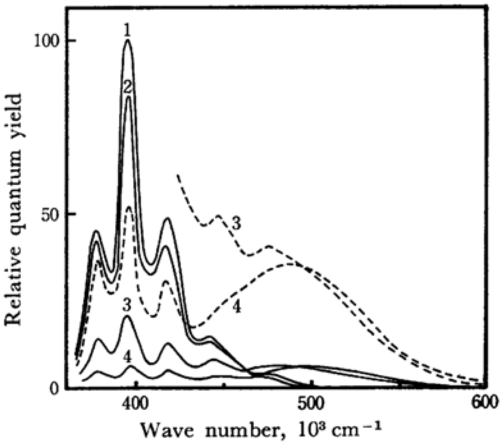

Fig. 2. Emission spectra for the anthracene-TBA - *n*-hexane system.
[TBA] M: 1) 0, 2) 2.04×10^{-2}, 3) 4.01×10^{-1}, 4) 1.34. [A]: 4.22×10^{-4} M.
(The broken lines: ×6)
(corrected for the spectral sensitivity)

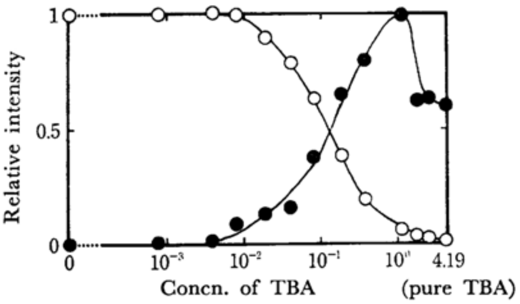

Fig. 3. Quenching curve for anthracene fluorescence and the intensity change of the long-wawelength emission with the respect to TBA concentration.
[A]=4.22×10^{-4} M, solvent: *n*-hexane.
○: anthracene fluorescence
●: long-wavelength emission

The quenching curve for anthracene fluorescence and the intensity change of the long-wavelength emission are shown in Fig. 3. The quenching constant of TBA for anthracene fluorescence was estimated as 7.9 M^{-1}; this value is smaller than that assumed for a diffusion-controlled process,[*5] suggesting the small reaction probability or the establishment of equilibrium in the excited state. That the increasing intensity of the long-wavelength emission is accompanied by the decreasing intensity of anthracene fluorescence implies the formation of an excited complex from excited anthracene and TBA. In the region of higher TBA concentrations, the long-wavelength emission diminished to a considerable extent, indicating the existence of the quenching effect of TBA on the excited complex or the formation of a triple complex[9] with no emissivity.

Effect of Temperature on the Intensities of the Long-wavelength Emission and Anthracene Fluorescence. In order to obtain information on the fluorescence quenching and the origin of the long-wavelength emission, anthracene fluorescence and the long-wavelength emission were measured on a degassed solution for the anthracene-TBA-toluene system at various temperatures from −196 to 95°C. Their temperature dependence is illustrated in Fig. 4.

At liquid nitrogen temperature, anthracene fluorescence is very intense and its spectrum is somewhat sharper than that at room temperature. At low temperatures where molecular diffusion is prevented, only anthracene fluorescence is observed. With

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[*4] The electron affinities of many aromatic hydrocarbons are given in: G. Briegleb, *Angew. Chem.*, **76**, 326 (1964).

[*5] The quenching constant for a diffusion-controlled quenching process is given by the following equation:

$$K_q = \frac{8\boldsymbol{RT}\tau}{3000\,\eta} \sim 80$$

where η is the viscosity of *n*-hexane (3.2×10^{-3} poise) and τ, the fluorescence lifetime of anthracene (5×10^{-9} sec).

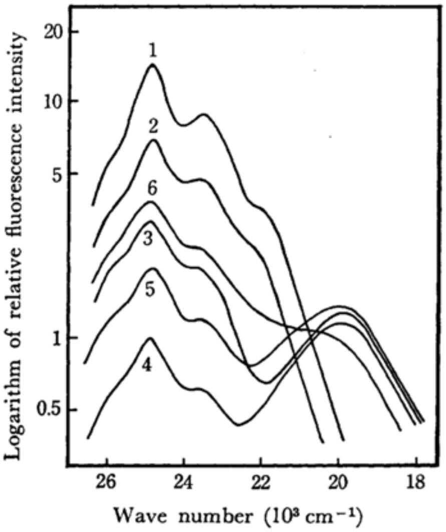

Fig. 4. Temperature dependence of anthracene flouorescence and the long-wavelength emission for the anthracene-TBA-toluene system.
[A]$=5.1\times10^{-4}$ M, [TBA]$=0.84$ M
Temperature °C: (1) −196, (2) −33, (3) 11, (4) 29, (5) 61, (6) 95
(uncorrected for the instrumental factors)

TABLE 4. SOLVENT EFFECT ON THE LONG-WAVELENGTH EMISSION FOR THE ANTHRACENE-TBA STSTEM

No.	Solvent	f	Wave number (10^3 cm^{-1})	Intensity*
1	*n*-Hexane	0.0934	20.5	++
2	Cyclohexane	0.0999	20.7	++
3	*p*-Xylene	0.1162	20.0	+++
4	Benzene	0.1168	19.8	+++
	Carbon tetrachloride	0.1178	—	0
5	Decalin	0.1183	20.6	++
6	Dioxane	0.1221	18.5	+++
7	Toluene	0.1267	19.8	+++
8	*t*-Butylbenzene	0.1270	20.1	+++
9	Isopropylbenzene	0.1272	19.9	+++
10	Tetralin	0.1501	19.8	+++
11	Di-*n*-butyl ether	0.1923	20.1	++
12	Anisole	0.2290	19.0	+++
13	Chloroform	0.2517	19.0	+++
14	Ethyl ether	0.2541	19.6	+++
15	Chlorobenzene	0.2607	19.5	+++
16	Fluorobenzene	0.2653	19.2	++
17	Dibutyl phthalate	0.2797	18.4	+
18	Ethyl acetate	0.2928	18.2	++
19	Dichloromethane	0.3199	18.0	+++
20	1,2-Dichloroethane	0.3254	18.0	++
21	Benzonitrile	0.3532	18.1	+
22	Cyclohexanone	0.3540	18.0	+
23	Acetone	0.3749	17.8	+
	N,N-Dimethylformamide	0.3777	—	0
	Methanol	0.3887	—	0

* +++: strong, ++: medium, +: weak, 0: none.

increasing temperature the long-wavelength emission appears at about 520 mμ at the expense of anthracene fluorescence and gradually grows up to a maximum intensity at about 60°C. Above this temperature the intensity of the long-wavelength emission falls off, while that of anthracene fluorescence rises to some extent, suggesting the dissociation of the excited complex backward into excited anthracene and TBA. It is not fully understood at present that both anthracene fluorescence and the long-wavelength emission increase with the rise of temperature at temperatures somewhat above room temperature. A diffusional excited-complex formation may account for their general temperature behaviors.

Solvent Effect on the Long-wavelength Emission. The effects of the solvents of different polarities on the long-wavelength emission for the anthracene-TBA system were examined and were found to be very remarkable.[4-6,11] The result is summarized in Table 4.

With the increase of solvent polarity, the emission-band maximum shifts to the longer wavelength and the intensity increases and finally decreases toward zero. This behavior may be understood on the basis of the fact that the excited CT complex can exist more stably in moderately polar solvents than in non-polar solvents, whereas its dissociation into the solvated radical ions occurs in highly polar solvents, such as methanol and *N,N*-dimethylformamide.[1,2,6,10,11] probably carbon tetrachloride reacts with excited anthracene.[12]

If the solvent shift of the emission band can be attributed to the dipole moment m of the excited CT complex, the wave number $\bar{\nu}$ of the emission band maximum is approximately expressed as follows:[4,5]

$$\bar{\nu}=-\frac{2m^2}{hca^3}\left(\frac{\varepsilon-1}{2\varepsilon-1}-\frac{n^2-1}{4n^2+2}\right)$$
$$+\text{ small terms }+\text{ constant}$$

where ε and n denote the dielectric constant and the refractive index of the solvent, respectively; a is the assumed cavity radius for the complex.

Figure 5 shows the plots of $\bar{\nu}$ against

$$f=(\varepsilon-1)/(2\varepsilon+1)-(n^2-1)/(4n^2+2).$$

The straight line in the figure was obtained by the least-squares method from 20 points exclusive of those for benzene, toluene and dioxane, which are

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[11] N. Mataga, T. Okada and N. Yamamoto, This Bulletin, **39**, 2562 (1966).

[12] E. J. Bowen, *Discussions Faraday Soc.*, **14**, 146 (1953).

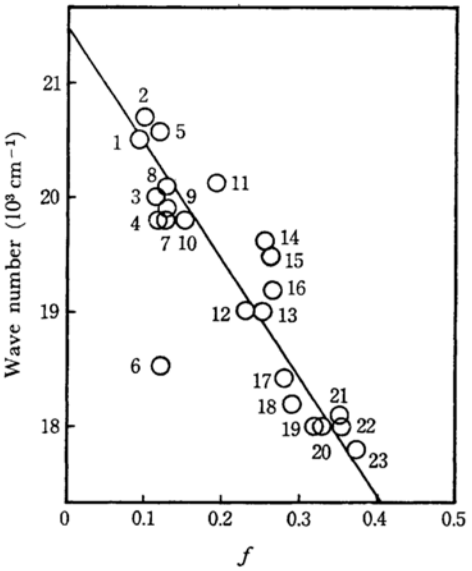

Fig. 5. Evaluation of the dipole moment of the excited complex of anthracene-TBA.
The numerals refer to the respective numbers for the solvents in Table 4.

known to be specific in the solvent effects. From the slope of this line, the value of m was evaluated as 12.8 D, assuming that $a \sim 5.5$ Å.[*6] This is a very reasonable value for an excited CT complex in view of those reported by various authors.[4,5,11]

Conclusion

The anomalous emission observed at the long wavelengths in the systems of the condensed aromatic hydrocarbons and the tertiary amines seems to show every behavior of an emission due to an excited CT complex, the nature of which has already been studied by several authors.[1-7,9-11] In fact, the following conclusions can be derived:

1) According to the abosorption spectra of the solutions, the temperature dependence of the long-wavelength emission and the relation between the quenching of the hydrocarbon fluorescence and the intensity of the long-wavelength emission, the species responsible for the long-wavelength emission is considered as an excited-state complex formed dynamically from an excited-aromatic hydrocarbon and a tertiary amine.

2) The correlation of the wavelengths of the long-wavelength emission with the electron affinities of the aromatic hydrocarbons and the ionization potentials of the amines, as well as the large dipole moment estimated for the excited complex indicates the importance of the CT interaction.

The present work may have cleared to some extent the relation between the quenching phenomenon and the excited-CT-complex formation.

It is very plausible that the CT interaction occurs between the lone pair of electrons on the nitrogen atom and the π-electrons of the aromatic ring. Such an n–π interaction is of great interest because the localization of the n-electrons may restrict the region of interaction in the CT complex to part of the π-system and the n-orbital and the CT complex formed may assume such a configuration as minimizes the localization energy of the π-system. Thus, the model involved seems somewhat simpler and a theoretical consideration on this problem will be fruitful

The temperature dependence and variations with TBA concentration of the intensities of anthracene fluorescence and the long-wavelength emission may be analyzed by a kinetic approach.

The author wishes to thank Professor Hideo Akamatu for his continuous support and encouragement during the course of this work.

Note added in proof: After this work had been completed, a similar report appeared: M. G. Kuzmin and L. N. Guseva, *Chem. Phys. Letters*, **3**, 71 (1969).

[*6] This value was estimated from the molal volumes of anthracene and TBA.