Electron Donor–Acceptor Interactions in the Fluorescent State of Tetracyanobenzene–Aromatic Hydrocarbon Complexes

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Abstract: Electron donor–acceptor interactions in *s*-tetracyanobenzene and tetrachlorophthalic anhydride–aromatic hydrocarbon complexes in their lowest excited singlet state (lowest charge-transfer state) have been investigated by fluorescence measurements. The effects of temperature and solvent polarity on the wave numbers of fluorescence spectra, relative fluorescence quantum yields, and fluorescence decay times of the complexes clearly showed a considerable difference of the energies as well as the structures between the excited Franck–Condon state and equilibrium state which originated from the large difference between the electronic structures in the ground and excited state of the complex. The so-called "mirror-symmetry" relation between the absorption and fluorescence spectra did not hold for these complexes at higher temperature, although the fluorescence excitation spectra agreed exactly with the absorption spectra, respectively. Furthermore, the existence of a rather large solvent effect on the structure of the fluorescent state of the complex has been shown to be likely.

The nature of the charge-transfer (CT) interaction in the electron donor–acceptor (EDA) complexes is a subject under the most lively investigation at present. Although there are quite numerous investigations on the EDA complexes by the absorption spectral measurements, the studies by fluorescence spectral measurements are rather scarce except at low temperatures because the fluorescence yield of the EDA complex in solution at room temperature is extremely small.[1] Therefore, it is very hard, in general, to obtain direct information concerning the excited equilibrium state of the complexes which seems to reflect directly the electronic structure of the lowest excited singlet state of the complex. However, somewhat detailed studies in this direction are possible in the case of *s*-tetracyanobenzene (TCNB)–aromatic hydrocarbon EDA complexes since they are rather strongly fluorescent in solution at room temperature when the solvent dielectric constant, ϵ, is not large ($\epsilon \lesssim 10$).

On the other hand, it is well known that there is another group of EDA complexes which are stable in the excited state while unstable (dissociative) in the ground state. These complexes are called the excimers or exciplexes.[2] When the partners in the complex are not the same molecule, the complex may be called the heteroexcimer (h.e.).[3] The electron donor–acceptor interaction can become quite strong in the excited electronic state in general even if it is negligibly small in the ground state. Thus, the h.e. may be a special case of EDA complex. Namely, the h.e. might be regarded as a limiting case of weak EDA complexes.

Because the TCNB–aromatic hydrocarbon EDA complexes are rather weak ones, some comparisons of these EDA complexes with the h.e. will be possible to elucidate the nature of the CT interactions.

In the present paper, fluorescence and absorption studies have been made with EDA complexes of various aromatic hydrocarbons with TCNB in various solvents and at various temperatures. The observed fluorescence and absorption spectra are believed to correspond to "charge-transfer states" of the complexes stated. Special attention has been paid to the large difference between the structures of Franck–Condon and equilibrium states as revealed by the spectral measurements. The results have been discussed on the basis of the electronic structures of the weak EDA complex. Furthermore, the spectral behavior of these complexes have been compared with those of the heteroexcimer.

Experimental Section

The fluorescence and phosphorescence spectra were measured with an Aminco-Bowman spectrophotofluorometer which was calibrated to obtain the correct luminescence quantum spectrum. All luminescence spectra of the EDA complexes measured were excited at the wavelength of the first CT absorption band. The luminescence excitation spectra were measured also by the Aminco-Bowman spectrophotofluorometer which was calibrated by the method of quantum counter.[4] The fluorescence decay times were measured by an apparatus similar to the one described previously using appropriate filters or a monochromator to excite at the wavelength of the CT absorption band and to take out only the CT fluorescence light.[5] The measurement of the temperature effect on the fluorescence was conducted by using a metal dewar with quartz windows. The temperature of a solution in a quartz cuvette placed in the dewar was controlled by a constant flow of cold nitrogen gas. The flow of the gas was controlled by heating liquid nitrogen, and the temperature of the solution was measured by a thermocouple. The detectors for luminescence were photomultipliers of Type RCA 1P28, R213, or EMI 9558. The absorption spectra were measured by a Cary 15 spectrophotometer.

TCNB was prepared by the method of Lawton and McRichie[6] and was purified by repeated recrystallization from ethanol and sublimation under vacuum. The melting point of the purified TCNB agreed well with the literature value. Cyclohexane was passed through a column of activated silica gel twice, dried over metallic sodium, and distilled. Other solvents were purified by the methods described in the literature.[7] Aromatic hydrocarbons

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(1) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe," Springer-Verlag, Berlin, 1962; R. S. Mulliken and W. B. Person, *Ann. Rev. Phys. Chem.*, **13**, 107 (1962).

(2) Th. Förster, *Pure Appl. Chem.*, **7**, 73 (9163); J. B. Birks, *Nature*, **214**, 1187 (1967).

(3) H. Leonhardt and A. Weller, *Ber. Bunsenges. Physik. Chem.*, **67**, 791 (1963); N. Mataga, T. Okada, and K. Ezumi, *Mol. Phys.*, **10**, 201, 203 (1966); N. Mataga, T. Okada, and N. Yamamoto, *Bull. Chem. Soc. Japan*, **39**, 2562 (1966); N. Mataga and K. Ezumi, *ibid.*, **40**, 1355 (1967); H. Beens, H. Knibbe, and A. Weller, *J. Chem. Phys.*, **47**, 1183 (1967); H. Knibbe, K. Röllig, F. P. Schäffer, and A. Weller, *ibid.*, **47**, 1184 (1967); H. Knibbe, D. Rehn, and A. Weller, *Z. Physik. Chem.* (Frankfurt), **56** 95, 99 (1967); N. Mataga, T. Okada, and N. Yamamoto, *Chem. Phys. Letters*, **1**, 119 (1967); W. R. Ware and H. P. Richter, *J. Chem. Phys.*, **48**, 1595 (1968).

(4) W. H. Melhuish, *J. Opt. Soc. Am.*, **52**, 1256 (1962).

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

(6) E. A. Lawton and D. D. McRichie, *J. Org. Chem.*, **24**, 26 (1959).

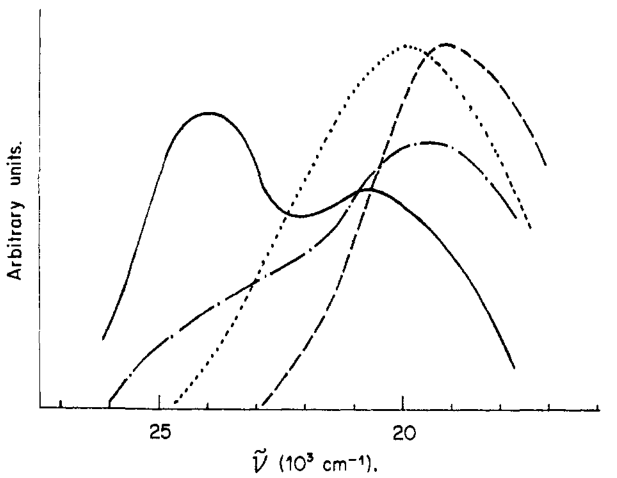

Figure 1. Luminescence quantum spectra of the TCNB–toluene system at several temperatures. [TCNB] = 2.0 × 10^{-4} *M* at room temperature: ———, 77°K; —·—, 150°K; — — — —, 183°K; - - - - -, 298°K. The band at 20.5 × 10³ cm⁻¹ in the spectrum at 77°K is due to the CT phosphorescence.

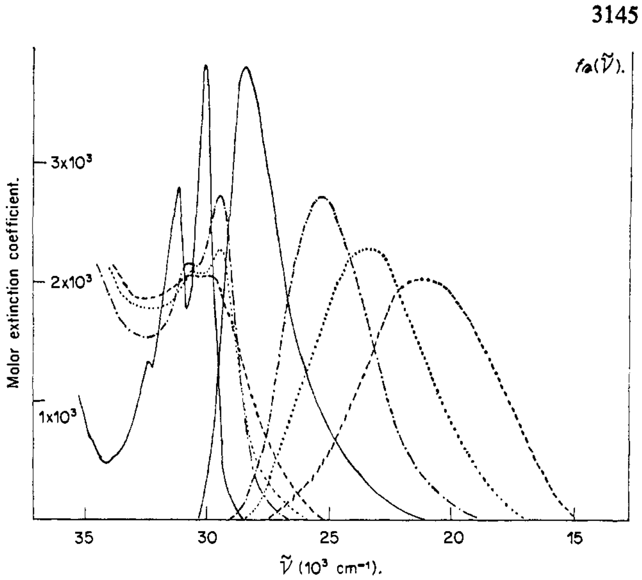

Figure 2. The absorption and fluorescence spectra of TCPA in various hydrocarbon solvents: ———, *n*-hexane; —·—, benzene; - - - - - -, toluene; — — —, *p*-xylene.

and their methyl derivatives were chromatographed on activated alumina and silica gel, recrystallized, and sublimed under vacuum. In addition to these purification procedures, naphthalene, pyrene, and anthracene were further purified by extensive zone melting. The impurities involved in solvents and solutes were checked by carefully measuring absorption and luminescence spectra.

In the case of the measurements of fluorescence decay times and quantum yields, the solutions in the cuvette were carefully deaerated by an ordinary procedure with an evacuating system equipped with a rotary and oil diffusion pump.

Results

As an example, the luminescence spectra of TCNB–toluene system at several temperatures are indicated in Figure 1. At room temperature, the absorption band maximum of the complex is $\tilde{\nu}_a$ = 31,700 cm⁻¹. Therefore, the Stokes shift of the fluorescence spectrum is anomalously large. At slightly lower than room temperature, the Stokes shift of the fluorescence band becomes still greater, while at 77°K it is not anomalously large but shows a quite reasonable value. Although there appear two peaks in the luminescence spectrum at 77°K, we have confirmed that the band with peak at 20.5 × 10³ cm⁻¹ can be ascribed to the CT phosphorescence of the TCNB–toluene complex by means of the phosphorescence measurement at 77°K. The observed CT phosphorescence spectrum and the phosphorescence decay time agreed with those measured by Iwata, *et al.*[8] Similar results with respect to the CT fluorescence can be observed also for the solutions of TCNB in benzene, *p*-xylene, and mesitylene, respectively, as well as for those of tetrachlorophthalic anhydride (TCPA) in benzene, toluene, and *p*-xylene, respectively. The absorption and fluorescence spectra of TCPA in *n*-hexane as well as TCPA–benzene, toluene, and *p*-xylene systems, respectively, are indicated in Figure 2. The absorption spectrum of the TCPA–benzene system is only a little broader than that of TCPA in *n*-hexane, the vibrational structure is still retained in the former spectrum, and no remarkable red shift of the spectrum can be observed compared to that in *n*-hexane solution. Nevertheless, the fluorescence spectrum of the TCPA–benzene system appears at much smaller wave numbers compared to that of TCPA in *n*-hexane. In any way, the interaction between the halves of these complexes in the ground state is quite weak. For example, the heat of formation of the TCNB–benzene complex in tetrachloroethane was determined by Iwata, Tanaka, and Nagakura to be 0.4 kcal/mol.[9]

Although the interaction between the donor and acceptor in the ground state is quite weak in these complexes, there seems to occur a large change of the donor–acceptor interaction during the lifetime of the fluorescent state of the complex which brings out the anomalously large Stokes shift.

One can observe this circumstance more clearly from Tables I–III. In Table I, the wave numbers of the absorption and fluorescence ($\tilde{\nu}_f$) band maxima as well as the fluorescence lifetimes (τ_F) at 295 and 77°K, respectively, are shown together with the radiative fluorescence lifetimes (τ_0) calculated from the intensity of the absorption band at room temperature. Although we have not determined the τ_0 value at 77°K by the measurement of the absorption intensity, it may not be much different from the value at room temperature. (Probably, the value at 77°K will be a little smaller than that of room temperature because of the increase of the refractive index of the medium at low temperature.)

Table I. Fluorescence and Absorption Band Maxima and Fluorescence Lifetimes of TCNB–Benzene and TCNB–Toluene Systems

	295°K			79°K		
	$\tilde{\nu}_a$ (10³ cm⁻¹)	$\tilde{\nu}_f$ (10³ cm⁻¹)	τ_F[a]	$\tilde{\nu}_f$ (10³ cm⁻¹)	τ_F[a]	τ_0[a]
TCNB–benzene	32.5	20.3	150	25.0	42	50
TCNB–toluene	31.7	20.0	148	23.8	56	60

[a] In nanoseconds.

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(7) A. Weissberger, Ed., "Technique of Organic Chemistry," Vol. VII, Interscience Publishers, New York, N. Y., 1955.

(8) S. Iwata, J. Tanaka, and S. Nagakura, *J. Chem. Phys.*, 47, 2203 (1967).

(9) S. Iwata, J. Tanaka, and S. Nagakura, *J. Am. Chem. Soc.*, **88**, 894 (1966).

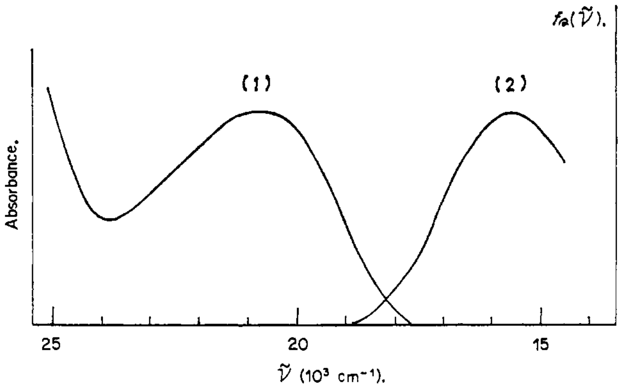

Figure 3. Absorption and fluorescence spectra of TCNB–pyrene complex in benzene: (1) absorption, (2) fluorescence.

The most important fact in Table I seems to be that the observed fluorescence lifetimes of these complexes at room temperature are much longer than the radiative lifetimes. Contrary to this, the observed values at 77°K are a little smaller than the radiative lifetimes. These facts clearly indicate considerable change of the structure of the complex during the fluorescence lifetime at room temperature where the molecular rearrangement motions including the surrounding solvent molecules can occur easily, while such rearrangement motions occur with difficulty at 77°K during the fluorescence lifetime.

Table II shows the temperature effects on the wave numbers, the relative quantum yield, and the lifetime of fluorescence from the TCNB–toluene system in a little more detail. It has been confirmed that the results given in Table II are not affected by changing the concentration of TCNB from 10^{-5} to 10^{-3} *M*. One can see the following results from Table II. Namely, the fluorescence band maximum continuously shifts to red and the fluorescence yield as well as the lifetime decrease as the temperature is lowered from 293 to 212°K. From 212 to 165°K, the band still continues the red shift while the yield begins to increase, although experimental values of the yield are not given (see footnote *b* to Table II). Furthermore, at lower temperature than 154°K, the fluorescence band shows a considerable blue shift until it appears at 23.8×10^3 cm^{-1} at 77°K. The extent of the decrease of τ_{F} values as the temperature is lowered at relatively high-temperature regions is rather small, whereas the corresponding decrease of the φ_{F} value is much stronger. Therefore, it is evident that the radiative transition probability decreases as the temperature is lowered. However, at still lower temperature regions, the radiative transition probability will increase and the radiationless transition probability will decrease, leading to the large increase of the fluorescence yield.

Table II. Temperature Effects on the Fluorescence of TCNB–Toluene System

Temp, °K	$\tilde{\nu}_{\mathrm{f}}$ (10^3 cm^{-1})	φ_{F}[a]	τ_{F} (nsec)
293	20.0	1.0	148
272	19.8	0.8	140
232	19.3	0.4	130
212	19.2	0.3	130
183	19.0	. . .[b]	. . .[b]
165	18.9	. . .[b]	. . .[b]
156	19.0	. . .[b]	. . .[b]
154	19.1	. . .[b]	. . .[b]
150	19.4	5[c]	. . .[b]

[a] Relative fluorescence quantum yield taking the value at 293°K as a standard. [b] Because of the strong scattering of light due to the crystallization of toluene at low temperatures, accurate measurements were not possible. [c] A roughly estimated value.

The results similar to the case of temperature effects can be observed also in the case of the change of toluene concentration in the three-component system, TCNB–toluene–cyclohexane, as it is shown in Table III. At smaller concentration of toluene, no accurate measurements of τ_{F} and φ_{F} were possible because of the very small fluorescence yields. One can see from Table III that the $\tilde{\nu}_{\mathrm{f}}$ value as well as the k_{F} value decrease with the increase of the concentration of toluene. This fact indicates the change in the fluorescent state, which may be caused by the interaction of the complex with the surrounding toluene molecules during the lifetime of the fluorescent state because the wave number of the absorption band of the complex remains almost unchanged at various concentrations of toluene. Thus, the above-described results for the complexes, which show only a quite weak intermolecular CT interaction in the ground state, seem to indicate a quite large change of the CT interaction in the fluorescent state; *i.e.*, the interaction becomes much stronger in the fluorescent state compared with the ground state.

Table III. Fluorescence of TCNB–Toluene–Cyclohexene System at 22°

[Toluene] (*M*)	$\tilde{\nu}_{\mathrm{f}}$ (10^3 cm^{-1})	τ_{F} (nsec)	φ_{F}[a]	k_{F}[b]
9.4	20.0	134	1.0	1.0
7.52	20.1	146	1.2	1.1
5.64	20.2	160	1.5	1.2
3.76	20.7	179	1.9	1.4
1.88	21.3	123	1.5	1.6
1.50	21.5	104	1.3	1.8
1.32	21.6	100	1.4	1.9
0.94	22.0	76	1.2	2.1
0.75	22.1	. . .	. . .	. . .
0.56	22.1	. . .	. . .	. . .
0.38	22.2	. . .	. . .	. . .

[a] Relative fluorescence quantum yield taking the yield of pure toluene solution as a standard. [b] Relative value of radiative lifetime taking the value for pure toluene solution as a standard ($k_{\mathrm{F}} \propto \varphi_{\mathrm{F}}/\tau_{\mathrm{F}}$).

Now, it might be possible that, although TCNB forms a 1:1 complex with benzene or toluene in the ground state, it can make a 1:*n* ($n > 2$) complex during the lifetime of the fluorescent state with these hydrocarbon molecules, which may lead to the anomalously large Stokes shifts. Actually, Walker, Bednar, and Lumry[10] found such association (1:2) of the excited indole and indole derivatives with some polar solvent molecules. Although our system is quite different from theirs, similar association in the excited state might be possible. However, the concentration dependence of the wave-number shifts and of the fluorescence yields is not so strong as in the case of the indoles. Furthermore, in view of the quite large change of the $\tilde{\nu}_{\mathrm{f}}$ values of TCNB complexes due to the quite small

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(10) M. S. Walker, T. W. Bednar, and R. Lumry, *J. Chem. Phys.*, **47**, 1020 (1967).

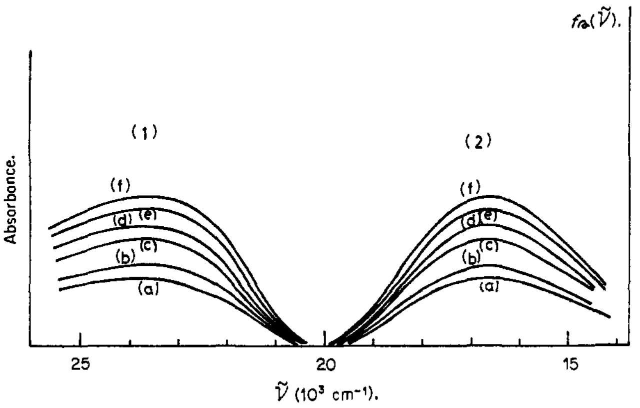

Figure 4. The dependence of the absorption and fluorescence spectra of the TCNB-HMB complex on the concentration of HMB in benzene solution at room temperature: (1) absorption, (2) fluorescence. [HMB] (M): (a) 1.70×10^{-1}, (b) 2.15×10^{-1}, (c) 2.80×10^{-1}, (d) 3.23×10^{-1}, (e) 4.03×10^{-1}, (f) 4.68×10^{-1}. [TCNB] = 2.40×10^{-4} M.

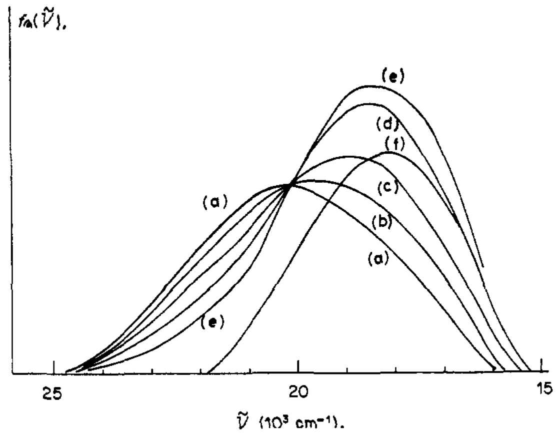

Figure 5. Fluorescence spectra of the TCNB-naphthalene complex in benzene at room temperature at various concentrations of naphthalene. [TCNB] = 2.22×10^{-4} M. Concentrations of naphthalene (M): (a) 0, (b) 2.38×10^{-4}, (c) 5.96×10^{-4}, (d) 1.19×10^{-3}, (e) 3.41×10^{-3}, (f) 2.28×10^{-1}.

change of the solvent polarity as it will be described later, $1{:}n$ ($n \geq 2$) complex formation in the fluorescent state may be ruled out in our systems.

Let us now turn our attention to more strong complexes of TCNB. In Figure 3, the absorption and fluorescence spectra of the TCNB-pyrene complex in benzene is indicated. One can see that the Stokes shift for this complex, being 5.1×10^3 cm^{-1}, is much smaller than those ($\approx 12 \times 10^3$ cm^{-1}) in the TCNB-benzene and TCNB-toluene systems. In Table IV, the wave numbers of the absorption and fluorescence band maxima of some TCNB complexes are given. The ($\tilde{\nu}_a - \tilde{\nu}_f$) values for these complexes are 5×10^3 $\sim 8 \times 10^3$ cm^{-1}.

Table IV. $\tilde{\nu}_a$ and $\tilde{\nu}_f$ Values for Some TCNB Complexes in Benzene Solution (at Room Temperature, ~20°)

Donor	$\tilde{\nu}_a$ (10^3 cm^{-1})	$\tilde{\nu}_f$ (10^3 cm^{-1})	($\tilde{\nu}_a - \tilde{\nu}_f$) ($10^3$ cm^{-1})	I (eV)^a
Durene	25.6	17.9	7.7	8.05^b
HMB	23.6	16.8	6.8	7.85^b
Biphenyl	26.4	18.9	7.5	8.27^c
Naphthalene	25.1	18.1	7.0	8.12^d
Phenanthrene	24.9	17.9	7.0	8.02^d
Triphenylene	25.1	18.1	7.0	8.13^d
Chrysene	22.3	17.2	5.1	7.72^d
Pyrene	20.7	15.6	5.1	7.58^d
Anthracene	20.1	15.0	5.1	7.24^d

^{a} First ionization potential of the aromatic hydrocarbons. ^{b} F. I. Vilesov, *Soviet Phys.-Usp.*, **6**, 888 (1964). ^{c} K. Watanabe, Nakayama, and J. Mottle, *J. Quant. Spectry. Radiative Transfer*, **2**, 369 (1962). ^{d} F. A. Matsen, *J. Chem. Phys.*, **24**, 602 (1956).

Now, the possibility of $1{:}n$ complex formation in the excited state can be examined in a more quantitative way for these slightly stronger complexes. For example, the dependence of the absorption and fluorescence spectra of the TCNB-HMB complex in benzene at room temperature on the concentration of HMB is shown in Figure 4, where the wave number of the band maximum of fluorescence, as well as that of the absorption, was unchanged when the HMB concentration was varied. Moreover, the fluorescence yield was constant throughout the range of the HMB concentrations indicated in the figure. Since we have confirmed that only the 1:1 complex is formed in the ground state from the dependence of the absorbance on the HMB concentrations, it is now clear that only the 1:1 complex is formed also in the fluorescent state.

Figure 5 shows the case of a stronger complex, TCNB-naphthalene, in benzene solution at room temperature, where (a) is the fluorescence band of the TCNB-benzene system, and the absorption band due to the TCNB-benzene complex was excited in the case of (a)-(e), while the absorption band due to the TCNB-naphthalene complex was excited in the case of (f). The curves representing the fluorescence band cross with each other at a point. This result clearly shows that there is a 1:1 equilibrium or reaction of complex formation between the TCNB-benzene system and the TCNB-naphthalene complex. Furthermore, it has been confirmed that, when the fluorescence band due to the TCNB-benzene complex is subtracted from each band (b)-(e), the wave numbers of the band maxima agree completely with that of (f), *i.e.*, 18.3×10^3 cm^{-1}. Thus, it is evident now that only the 1:1 complex is formed also in this case.

Figure 6 shows the plots of various energies relevant with TCNB complexes against the ionization potential of aromatic hydrocarbons. Curves 1 and 2 represent respectively the fluorescence and the absorption band maxima of TCNB complexes. Curve 3 represents the energy of the electron-transfer configuration which may be given by $E(\mathrm{A}^- - \mathrm{D}^+) = I - A - C$, where I is the ionization potential of the donor, A is the electron affinity of the acceptor, and C is the Coulomb energy between the halves of the A^-–D^+ pair. A was taken as 0.4 eV,[11] which is not of essential importance here because we are mainly interested only in the relative shape of the curves. C was assumed to be 4.3 eV[11] for all A^-–D^+ pairs, because the Coulomb energy may presumably be almost constant for all instances of similar types of donor-acceptor pairs. In Figure 6A, (4) and (5) represent respectively the excitation energies of the $^1\mathrm{L}_a$ and $^1\mathrm{L}_b$ band of the aromatic hydrocarbons; (6) and (7) represent the energies of the lowest excited singlet states of TCNB above the ground state. Quite analogously, in the case of Figure 6B, (5) and

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(11) G. Briegleb, *Angew. Chem. Intern. Ed. Engl.*, 3, 617 (1964).

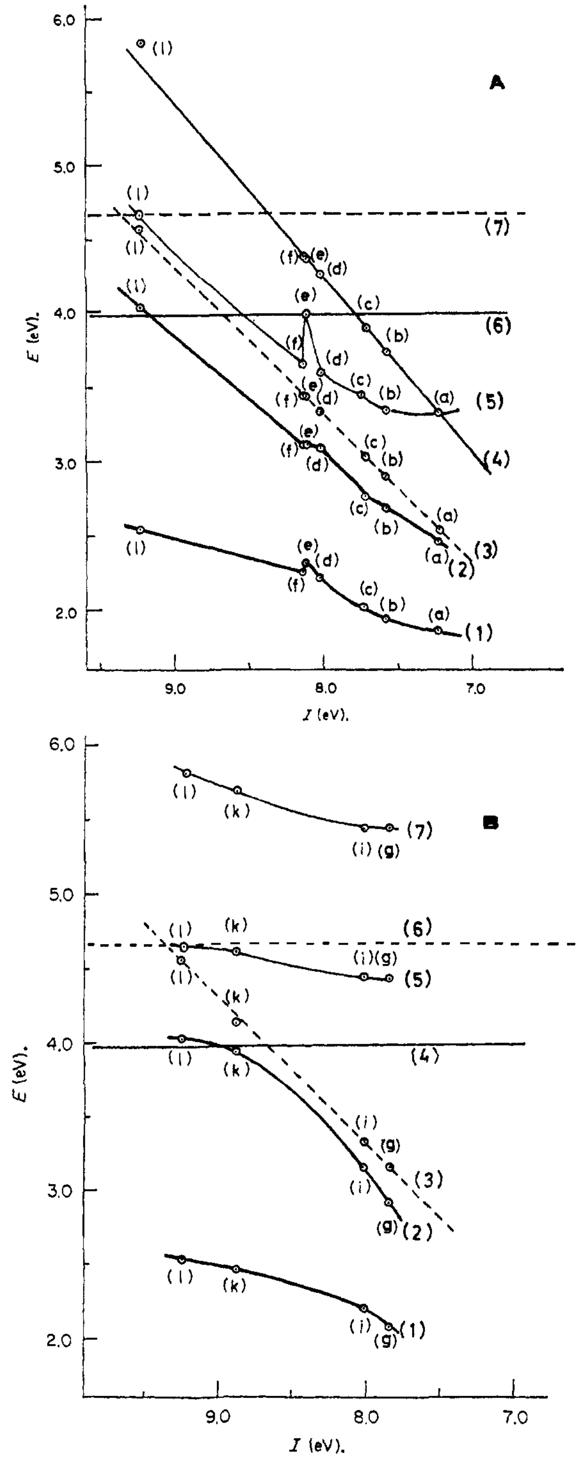

Figure 6. Various energies relevant with TCNB complexes plotted against ionization potentials of aromatic hydrocarbons.

(7) represent respectively the excitation energies of the ^1L_b and ^1L_a bands of the aromatic hydrocarbons; (4) and (6) are the same excitation energies of TCNB as in the case of Figure 6A. We have separated Figure 6 into A and B because the circumstances for the nonsubstituted aromatic hydrocarbon donors (A) are somewhat different from that for the series of benzene and methyl-substituted benzene donors (B) and also because the diagram becomes too complicated when they are put altogether in one figure. The hydrocarbons in Figure 6 are as follows: (a) anthracene, (b) pyrene, (c) chrysene, (d) phenanthrene, (e) naphthalene, (f) triphenylene, (g) HMB, (i) durene, (k) toluene, (l) benzene. In the case of benzene and toluene, the observed energies of the fluorescence and absorption band maxima are those for the two-component systems TCNB–benzene and TCNB–toluene. In other cases, the energies of the band maxima are those for the three-component systems, TCNB–aromatic hydrocarbon in benzene.

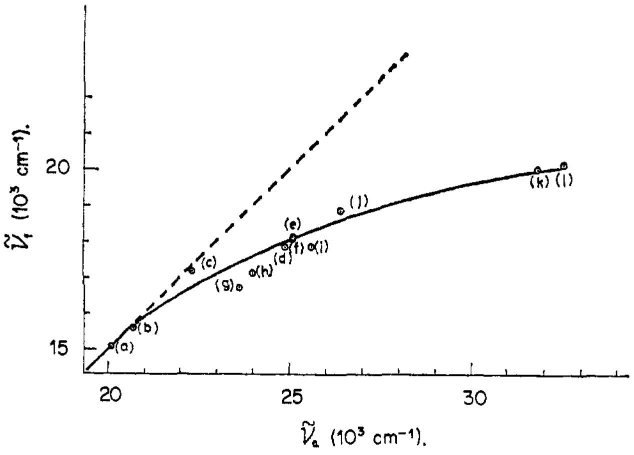

Figure 7. $\tilde{\nu}_a$ *vs.* $\tilde{\nu}_f$ relation for the TCNB complexes.

Roughly speaking, curves 1 and 2 are proportional to I in both Figure 6A and B, and the inclination of curve 2 is rather close to that of curve 3. However, there are considerable deviations in shape of curve 1 from the linear relation of curve 3. The deviations are larger for the weaker complexes than for the stronger ones. Similar result was also reported by Rosenberg and Eimutis[12] for the complexes between the pyromellitic dianhydride and methyl-substituted benzenes. This result for the large difference between the energies of the fluorescence and absorption bands of TCNB complexes can be observed more clearly in Figure 7 where $\tilde{\nu}_a$ is plotted against $\tilde{\nu}_f$ and the broken line has an inclination of 45°. Thus, the dependence of $\tilde{\nu}_f$ on I is quite different from that of $\tilde{\nu}_a$, and the so-called "mirror symmetry" relation does not hold for these systems. In Figure 7, (h) and (j) represent respectively the benzene solution of TCNB–2,3-dimethylnaphthalene and TCNB–biphenyl systems. These systems were omitted from Figure 6 because the circumstance was somewhat different for the substituted naphthalene compared to the nonsubstituted hydrocarbon series in the case of (h), and the positions of the 0–0 transitions in the ^1L_a and ^1L_b bands of biphenyl were uncertain. Of course, it has been confirmed for all of these systems that the fluorescence excitation spectrum completely agrees with the absorption band of the complex. It is somewhat interesting that one can see the influence of the contributions from the excited state of TCNB as well as the ^1L_b state of the aromatic hydrocarbons on the observed transition energies of the complexes, especially on the $\tilde{\nu}_f$ values.

Now, in order to get a more detailed information about the electronic structures of the fluorescent state of the complex, we have studied the effect of solvent polarity on the CT spectra of the TCNB–HMB com-

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(12) H. M. Rosenberg and E. C. Eimutis, *J. Phys. Chem.*, 70, 3494 (1966).

plex. The results are collected in Table V. It may be possible to estimate the dipole moment of the complex in the fluorescent state by using the result given in Table V. Such an analysis indicates that the dipole moment in the fluorescent state is more than 10 D. However, $\bar{\nu}_a-\bar{\nu}_f$ values plotted against appropriate functions of n and ϵ as is usually made[13] show quite large deviations from the linear relation, which might be due to the strong interaction between the excited complex and the surrounding solvent molecules specific to each solvent. Therefore, it does not seem to be very meaningful to make such a plot and to estimate the excited-state dipole moment, but the fact that the electronic structure of the complex seems to be affected rather easily by the interactions with the polar solvent molecules may be rather important.

Table V. Solvent Effect on the Band Maxima of the TCNB–HMB Complex (at Room Temperature, ~20°)

Solvent	n	ϵ	$\bar{\nu}_a$ (10^3 cm^{-1})	$\bar{\nu}_f$ (10^3 cm^{-1})
Cyclohexane	1.4263	2.06	23.6	18.0
Benzene	1.5014	2.28	23.6	16.7
Toluene	1.4992	2.34	23.7	16.8
Dioxane	1.4251	3.0	24.2	16.4
Ethyl ether	1.3526	4.4	24.5	16.7
Chlorobenzene	1.5216	5.53	23.4	16.1
n-Butyl chloride	1.4014	7.0	24.0	16.6
o-Dichlorobenzene	1.549	10.2	23.2	16.0
1,2-Dichloroethane	1.4476	10.36	23.5	16.4

Not only the wave number of the band maximum but also the fluorescence quantum yield of the TCNB–HMB complex depends rather strongly on the nature of the solvent. A rough estimation of the relative fluorescence yield in several solvents shows that it decreases strongly with the increase of the solvent polarity. For example, φ_F(benzene) $\approx$ $(^1/_5{-}^1/_{10})\varphi_F$(cyclohexane), φ_F(ethyl ether) = $(^1/_5{-}^1/_{10})\varphi_F$(benzene), and φ_F(1,2-dichloroethane) $\approx$ $(^1/_5{-}^1/_{10})\varphi_F$(ethyl ether). In the more polar solvents such as benzonitrile, acetonitrile, and ethanol, it was not possible to detect the fluorescence from the complex.

Table VI. Relative Fluorescence Quantum Yields of Some TCNB Complexes

Donor	φ_F[a]	I (eV)[b]	Donor	φ_F[a]	I (eV)[b]
Benzene[c]	2.6 × 10	9.24[f]	Triphenylene[e]	5.1 × 10	8.13
Toluene[d]	2.2 × 10	8.81[f]	Phenanthrene[e]	1.2 × 10	8.02
Durene[e]	1.4 × 10	8.05	Chrysene[e]	8.1	7.72
HMB[e]	2.8	7.85	Pyrene[e]	1.3	7.58
			Anthracene[e]	1.0	7.24

[a] The φ_F value of anthracene complex was taken as a standard. [b] First ionization potential of the aromatic hydrocarbon. [c] TCNB–benzene two-component system. [d] TCNB–toluene two-component system. [e] Benzene solution. [f] F. I. Vilesov, *Soviet Phys.-Usp.*, **6**, 888 (1964). The ionization potentials other than those for benzene and toluene are the same as those given in Table IV.

The relation between the fluorescence yield and the electronic structure is a quite complicated problem. Nevertheless, we can observe a systematic relation between the fluorescence yield and the ionization potential of the aromatic hydrocarbons in the series of TCNB complexes as is indicated in Table VI.

We can see from Table VI that the fluorescence yield of the TCNB complex becomes smaller as the ionization potential of the electron donor is decreased in the series of the donors benzene and methyl-substituted benzenes as well as in the series of the condensed ring aromatic hydrocarbon donors.

Discussion and Concluding Remarks

The wave functions for an EDA complex in the excited state and the ground state may be written in general as follows

$$\Psi_e \approx \sum_i a_i\Phi_i(\mathrm{A}^*\cdot\mathrm{B}) + \sum_j a_j\Phi_j(\mathrm{A}\cdot\mathrm{B}^*) + \sum_k a_k\Phi_k(\mathrm{A}^-\text{–}\mathrm{B}^+) + \sum_l a_l\Phi_l(\mathrm{A}^+\text{–}\mathrm{B}^-) + a_m\Phi_m(\mathrm{A}\cdot\mathrm{B}) \quad (1)$$

$$\Psi_g \approx \sum_i b_i\Phi_i(\mathrm{A}^*\cdot\mathrm{B}) + \sum_j b_j\Phi_j(\mathrm{A}\cdot\mathrm{B}^*) + \sum_k b_k\Phi_k(\mathrm{A}^-\text{–}\mathrm{B}^+) + \sum_l b_l\Phi_l(\mathrm{A}^+\text{–}\mathrm{B}^-) + b_m\Phi_m(\mathrm{A}\cdot\mathrm{B})$$

where Ψ_e and Ψ_g represent the excited and the ground-state wave functions, respectively. It should be noted here that the wave functions (Φ's) as well as their coefficients (a's and b's) are functions of nuclear configurations including the surrounding solvent molecules, respectively.

For a weak complex, certainly $|b_m| \gg \Sigma_i|b_i|$, $\Sigma_j|b_j|$, $\Sigma_k|b_k|$, $\Sigma_l|b_l|$, while $\Sigma_i|a_i|$ or $\Sigma_j|a_j| \gg |a_m|$ and $\Sigma_k|a_k|$ or $\Sigma_l|a_l| \gg |a_m|$. Iwata, Tanaka, and Nagakura[9] made a semiempirical calculation on the electronic states of some TCNB–aromatic hydrocarbon complexes and showed that both of the contributions from Φ_i and Φ_k, where A represents TCNB, were large in Ψ_e while the contribution of Φ_m was predominant in Ψ_g.

Relation between the Properties of Weak Complexes of TCNB or TCPA with Aromatic Hydrocarbons and Those of the Heteroexcimer. Now, the weak complex of TCNB or TCPA with an aromatic hydrocarbon seems to have many properties in common with the h.e.[3] formed by an aromatic hydrocarbon and an aromatic amine. In order to compare their properties with each other, we have summarized briefly the behavior of the h.e.

(i) Aromatic hydrocarbons such as pyrene, chrysene, phenanthrene, and triphenylene in such aromatic amines as DMA and isomeric N,N-dimethyltoluidines show broad structureless h.e. fluorescence bands with maxima in the range of 20 × 10^3–23 × 10^3 cm^{-1} at room temperature, while their fluorescence spectra at 77°K are quite close to those in the inactive solvents such as *n*-hexane and toluene, respectively. This fact shows that the rearrangement motions of molecules during the lifetime of the excited state are necessary for the formation of the h.e. state.

(ii) In the case of three-component system, the frequency of the h.e. fluorescence depends strongly

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[13] E. Lippert, *Z. Naturforsch.*, **10a**, 541 (1955); *Ber. Bunsenges. Physik. Chem.*, **61**, 962 (1957); N. Mataga, Y. Kaifu, and M. Koizumi, *Bull. Chem. Soc. Japan*, **28**, 690 (1955); **29**, 465 (1956); E. G. McRae, *J. Phys. Chem.*, **61**, 562 (1957); L. Bilot and A. Kawski, *Z. Naturforsch.*, **17a**, 692 (1962).

on the polarity of the solvent. The larger the static dielectric constant of the solvent, the smaller is the frequency of the fluorescence. Moreover, the quantum yield and the decay time of the h.e. fluorescence decrease as the solvent dielectric constant is increased, where the extent of the decrease of the quantum yield is much larger than that of the decay time, in general. This result for the solvent effect on the quantum yield and the decay time seems to arise because of the decrease of the radiative transition probability and the increase of the radiationless transition probability of the h.e. with the increase of the solvent polarity. In weakly polar solvents such as toluene, monochlorobenzene, and dichloroethane, the extent of the decrease of the radiative transition probability is larger than that of the increase of the radiationless transition probability. The decrease of the radiative transition probability in a polar solvent may be interpreted by using wave functions similar to (1). Because of strong solute–solvent interactions, the weight of Φ_k or Φ_l in Ψ_e may become larger, and those of Φ_i and Φ_j may become smaller in a polar solvent than in a less polar solvent. Then, the radiative transition probability becomes smaller in a polar solvent since the matrix element $\langle\Phi_m|\Sigma r|\Phi_k\rangle$ or $\langle\Phi_m|\Sigma r|\Phi_l\rangle$ in the transition moment is rather small compared with the matrix elements arising from the locally excited configuration, *i.e.*, $\langle\Phi_m|\Sigma r|\Phi_i\rangle$ and $\langle\Phi_m|\Sigma r|\Phi_j\rangle$. Furthermore, the A–B distance in the h.e. might increase in the polar solvent because of strong solvation, which makes the matrix element $\langle\Phi_m|\Sigma r|\Phi_k\rangle$ or $\langle\Phi_m|\Sigma r|\Phi_l\rangle$ smaller because these matrix elements are very sensitive to the A–B distance, being approximately proportional to the overlap integral between the electron-donating and accepting orbitals.

(iii) When the same aromatic amines are used for various aromatic hydrocarbons, the frequency of the h.e. fluorescence is approximately proportional to the electron affinity of the hydrocarbon.

(iv) The frequency of the fluorescence of a h.e. in a three-component system is affected not only by the solvent polarity but also by the temperature of the system. When the temperature is lowered, the fluorescence shows a red shift, and the extent of this red shift is larger in a polar solvent than in a less polar solvent.

Now, let us return to our present problem of weak EDA complexes. From the comparison of the above-described properties of the h.e. with the experimental results for the weak complexes such as TCNB–benzene and TCNB–toluene systems, one may see easily that they are quite similar to each other, except that there are small intermolecular binding energies in the ground state in the case of TCNB or TCPA complexes contrary to the case of the h.e. where no such binding between the donor and acceptor exists but the intermolecular potential surface is rather strongly dissociative in the ground state.

The results in Tables I–III for the TCNB–benzene and the TCNB–toluene systems are quite similar to those for the h.e. described in (i), (ii), and (iv). The large change of the electronic structure of these TCNB complexes during the lifetime of the excited state as revealed by the fluorescence measurements may be ascribed to the strong interaction between the complex and the surrounding solvent molecules.

The interpretation for the decrease of the radiative transition probability with the increase of toluene concentration as given in Table III may be quite similar to that given in (ii) for the h.e. The temperature effects given in Tables I and II may be explained as follows. The anomalously large value of the observed fluorescence lifetime at room temperature may be ascribed to the large decrease of the radiative transition probability owing to the strong solute–solvent interaction as described above. The decrease of the radiative transition probability with the lowering of the temperature at the relatively high-temperature region may be due to the decrease of the thermal disturbance to the solvation at lower temperatures. At still lower temperatures, the rearrangement motions of the surrounding solvent molecules may become rather difficult, which will make the radiative lifetime smaller. Thus, at 77°K, where the rearrangement motions of the solvent molecules during the fluorescence lifetime are impossible, the observed fluorescence lifetime becomes very close to the radiative lifetime estimated from the absorption intensity of the CT band. The change of the $\tilde{\nu}_f$ value depending on the temperature and the solvent polarity may be explained also on the basis of the solute–solvent interactions. The blue shift observed at lower temperatures than 154°K as shown in Tables I and II may certainly be ascribed to the same circumstance as described above for the decrease of the radiative lifetime at low temperatures. The red shift caused by the increase of the concentration of toluene as shown in Table III may be ascribed to the increase of the solvation at higher concentration of toluene. However, there are two factors which can bring out these changes of $\tilde{\nu}_f$ value. One is the stabilization of the excited equilibrium state by solvation, and the other is the destabilization of the Franck–Condon ground state (which has nonpolar structure) caused by the strong solvation in the very polar excited equilibrium state. In the case of h.e.'s formed by several aromatic hydrocarbons with DMA, the ground-state Franck–Condon destabilization energy and the heat of formation have been measured.[14] According to this study, the principal cause of the red shift of the h.e. fluorescence can be ascribed to the increase of the Franck–Condon destabilization energy in the ground state produced by the increase of the solvent polarity and by the lowering of the temperature in the liquid solvent.

Because we have not determined experimentally the Franck–Condon destabilization energy or the binding energy in the fluorescent state for our present complexes, we cannot say here which one of the two factors is predominant for the shifts of the fluorescence band. However, in view of the very similar behaviors of the weak TCNB complexes to those of the h.e. as described above, it seems to be quite probable that the same factor is predominantly working for the shifts of the fluorescence bands.

In any way, it is now clear that TCNB–benzene and TCNB–toluene systems have many properties in common with the h.e. formed by the aromatic hydrocarbon and the aromatic amine. One may expect this result in principle since the electron affinity of a molecule is

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(14) T. Okada, H. Matsui, H. Oohari, H. Matsumoto, and N. Mataga, *J. Chem. Phys.*, in press; N. Mataga, T. Okada, and coworkers, submitted for publication.

larger and its ionization potential is smaller in the electronically excited state than in the ground state, which makes it possible for strong electron donor–acceptor interaction to arise in the excited electronic state even if there is no such interaction or only a very weak interaction in the ground state. Thus, one can say that the h.e. is only a special case of the ordinary EDA complexes.

We should point out here a connection between the charge-transfer and electron-transfer mechanism of the fluorescence quenching and the results of the present work. Although the essentially stronger decrease of the fluorescence quantum yield of the h.e. compared to the decay time with the increase of the solvent polarity has been ascribed in (ii) to the decrease of the radiative transition probability as the solvent polarity is increased, an alternative interpretation, which is due to Weller,[3] seems to be possible for this phenomenon. Namely, Weller and coworkers assumed the competition of the following two processes

$$\mathrm{A^* + B \xrightarrow{(a)} (A^{-\delta}\text{---}B^{+})}$$

$$\mathrm{A^* + B \xrightarrow{(b)} (A_S{}^{-}\text{---}B_S{}^{+})}$$

where $(\mathrm{A^{-\delta}\text{---}B^{+\delta}})$ is the fluorescent h.e. and $(\mathrm{A_S{}^{-}\text{---}B_S{}^{+}})$ represents solvated ion pair which is nonfluorescent. It is assumed that process b depends on the solvent polarity, (*i.e.*, the rate of this process increases with the increase of the solvent polarity), while process a is independent of the solvent polarity. It is quite evident that Weller's interpretation cannot be applicable to the present results in Tables II and III, because we are exciting directly the ground-state EDA complex in the present work. Accordingly, as far as the results of the present work are concerned, our interpretation[3] described in (ii) may be preferred to Weller's one.

Fluorescence Behavior of Stronger TCNB Complexes. In the case of slightly stronger TCNB–aromatic hydrocarbon complexes, one can see from Table IV and Figure 6 the same circumstance as observed for the ordinary EDA complexes in general. Namely, the wave number of the CT band is roughly proportional to the ionization potential of the aromatic hydrocarbon. However, $\tilde{\nu}_a$ and $\tilde{\nu}_f$ show different dependences on the ionization potential, respectively, as one can see from Table IV, Figures 6 and 7. Roughly speaking, the smaller the ionization potential of the aromatic hydrocarbon, the smaller is the Stokes shift $(\tilde{\nu}_a - \tilde{\nu}_f)$; *i.e.*, the Stokes shift is smaller for the stronger complex. This fact shows that, for these a little stronger complexes, the extent of the molecular rearrangements during the lifetime of the fluorescent state is smaller than in the case of the TCNB–benzene or the TCNB–toluene system. One may expect this result because the difference between the weights of the electron-transfer configuration Φ_k or Φ_l in Ψ_g and Ψ_e of eq 1 may be larger in the case of this weaker complex than in the stronger complexes, which may result in a more extensive rearrangement within the complex as well as including the surrounding solvent molecules in the case of the former than in the case of the latter. However, as we have already described, the electronic states of the present complexes may not be expressed by the simple wave functions which are superposition of the no-bond configuration and the dative configuration, but the locally excited configuration plays an important role, especially for the excited state. One may see from Figure 6 that the rearrangement to the excited equilibrium state makes stronger the mixing with the locally excited configurations ($^1\mathrm{L_b}$ state of the hydrocarbon and the lowest excited single state of TCNB) and the mixing seems to be stronger for the complexes involving the hydrocarbon with larger ionization potential, because of the small energy difference between the electron-transfer configuration and the locally excited configuration for these complexes.

The solvent effect on the $\tilde{\nu}_a$ and $\tilde{\nu}_f$ values of TCNB–HMB complex indicated in Table V is somewhat similar to the result given by Czekalla and Mayer for TCPA–HMB system.[15] The solvent effect on the fluorescence yield of TCNB–HMB complex seems to show the increase of the radiationless transition probability in the more polar solvent, and it is quite plausible that the excited complex shifts to a solvated ion pair or dissociates into the solvated cation and anion radicals in the strongly polar solvent, which results in the complete quenching of fluorescence. However, in view of results for k_F given in Table III as well as those in the case of the pyrene–DMA h.e. in slightly polar solvents,[3] it is probable that the decrease of the radiative transition probability due to the change of electronic structure (change to a more polar one) caused by the interaction with the polar solvent molecules also affects the fluorescence yield considerably.

On the other hand, in a series of the aromatic hydrocarbon donors, the smaller the ionization potential of the aromatic hydrocarbon, the smaller is the fluorescence yield of the TCNB complex with the aromatic hydrocarbon. There are many factors affecting the fluorescence yields, *i.e.*, the radiative transition probability (k_f), the probability of the internal conversion to the ground state (k_{IC}), and the probabilities of the intersystem crossings ($\mathrm{k_C}$) to the triplet states.

The above-described result indicates that the fluorescence yield of the TCNB complex can be related to the change of the electronic structure of the complex. According to the calculation by Iwata, Tanaka, and Nagakura,[9] the weight of Φ_i in Ψ_e increases with the increase of the ionization potential of the electron donor. Actually, the observed intensity of the first CT absorption band of the TCNB complex decreases with the decrease of the $(I - A)$ value. Furthermore, the rearrangement motion during the lifetime of the excited state will more or less increase the weight of Φ_k in Ψ_e, which will make k_f a little smaller. Iwata, *et al.*, showed also the possibility that the electron donor–acceptor interaction increases the singlet–triplet mixing. However, the relation between the ionization potential of donor and the degree of the singlet–triplet mixing was not very clear. Nevertheless, in view of the observed fact that the phosphorescence decay time of the TCNB complex with methyl-substituted benzene decreases with the decrease of the ionization potential of donor,[8] it may be possible that the probability of the intersystem crossing increases with the decrease of the ionization potential of donor. It is possible also that k_{IC} increases with the decrease of the ionization po-

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(15) J. Czekalla and K. O. Mayer, *Z. Physik. Chem.* (Frankfurt), **27**, 185 (1961).

tential of donor because of the decrease of the energy gap between the fluorescent state and the ground state. This circumstance may be expected from the general theory of the radiationless transitions.[16]

From the above discussions, one may expect the decrease of k_f and increase of k_{IC} as well as k_C and, accordingly, the decrease of the fluorescence yield with the decrease of the ionization potential of donor, in agreement with the observed results.

Before ending the discussions, we should make the following remark. The change of the structure of the complex during the lifetime of the excited state, as it is assumed in the above discussions, may be observed more directly by the measurements of the absorption spectra of the excited complexes in various environmental states. This is a problem common to both the ordinary EDA complex and h.e. Such measurements may be possible if one uses the nanosecond laser photolysis method. Investigations along this line are now going on in this laboratory.

Acknowledgment. The authors are indebted to Professor S. Nagakura of the University of Tokyo for his helpful discussions.

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(16) S. H. Lin, *J. Chem. Phys.*, **44**, 3759 (1966); W. Siebrand, *ibid.*, **46**, 440 (1967).

Long-Range Electrostatic Effects in 4-Substituted Bicyclooctanecarboxylic Acids by CNDO/2

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Received September 30, 1968

Abstract: Relative total energies, as calculated by the CNDO/2 method, successfully account for the order of dissociation constants of a number of 4-substituted bicyclooctanecarboxylic acids, provided a molecule of hydrogen-bonded water is included in the calculations on the 4-hydroxy derivative. Further solvent structuring for a number of members of the series improves the over-all correlation. The results are interpreted in terms of the electrostatic energy between the ionizable proton and the remainder of the molecule. It is further shown that the so-called "field effect" of the substituent is sufficient to account for differences in the *calculated* acidities of these compounds. This is done by comparing the CNDO/2 results to a calculation on a classical electrostatic model. The effective dielectric constant used in the latter calculation is based on representing the molecule as a dielectric material through which the charge or dipole substituent acts on the acid proton. CNDO/2 results are in good agreement with the result from electrostatic theory that such a dielectric material always increases the effect of the substituent over what it would have been in a vacuum, and that the increase is proportionally greater for a dipole than for a charged substituent.

The CNDO/2 method as originally developed by Pople, Santry, and Segal,[1] explicitly includes electrostatic interactions between all valence electrons and nuclei and contains parameters which give charge distributions in line with more exact limited basis set calculations on small molecules. The CNDO/2 method has also led to an interesting generalization concerning the distribution of charges in organic molecules, namely that atoms or groups of atoms can induce an alternation of charge density in σ systems similar but reduced in magnitude to that found in π systems.[2]

The calculation of long-range substituent effects in σ systems should be a good test of the validity of the CNDO/2 approach. Such long-range substituent effects are usually electrostatic in origin,[3-5] and should therefore be amenable to treatment by CNDO/2. Even the alteration of the long-range substituent effects due to any induced alternation of charge densities in an intervening σ system should be accountable for by CNDO/2 and might be important. As a test series, the 4-substituted bicyclooctanecarboxylic acids were chosen because of the geometric rigidity of these compounds and the availability of experimental data.

However, quantum mechanical machine calculations of expectation values pertaining to chemical systems such as these do not themselves yield a complete understanding of the chemical processes involved. While such an approach has an important predictive quality, another useful goal in quantum chemistry is to explain or interpret results in terms of familiar concepts. A question examined here is whether the field-effect concept, defined here in terms of an appropriate model, is consistent with the CNDO/2 level of approximation.

The approach chosen is to calculate total CNDO/2 energies as an approximation to total free energies of the solvated acids and bases and then to compare the energy changes in the acid–base reactions. The results are analyzed in terms of charge densities and potential energies and are then related to a field effect model of substituent effects in which the substituent acts on the acid proton through an effective dielectric constant.

Kirkwood and Westheimer[3] were the first to calculate such an effective dielectric constant by structuring the medium into two parts: a sphere or ellipsoid repre-

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(1) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966); **43**, S136 (1965); J. A. Pople, D. P. Santry, and G. A. Segal, *ibid.*, **43**, S129 (1965).

(2) J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

(3) J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, **6**, 506 (1938); F. H. Westheimer and J. G. Kirkwood, *ibid.*, **6**, 513 (1938).

(4) N. Bjerrum, *Z. Physik. Chem.*, **106**, 219 (1923).

(5) S. Ehrenson, *Progr. Phys. Org. Chem.*, **2**, 195 (1964).