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Photochemistry of the Electron Donor-Acceptor System. I. Exciplex Fluorescence and the Fluorescence of the Charge-Transfer Complex in the Aromatic Hydrocarbon–Fumaronitrile System

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The fluorescence of a series of aromatic hydrocarbons was quenched by the addition of fumaronitrile, which is consistent with the charge-transfer or electron-transfer mechanism. The fluorescence quenching was accompanied by the appearance of a new, broad structureless emission band attributed to the fluorescence from the exciplex in non-polar or slightly polar solvents. In highly polar solvents only quenching of the fluorescence occurred. The energies of the band maxima of the exciplex fluorescences and the magnitude of the ionization potentials of a series of fluorescers showed a good correlation with each other. Solvent and temperature dependence of the exciplex fluorescence was examined and discussed. The present aromatic hydrocarbon–fumaronitrile system also formed a charge-transfer complex in their ground states at relatively high concentrations of each component. The selective excitation of the ground state charge-transfer complex gave rise to the fluorescence emission in a fluid solution at room temperature at the same wavelength region as observed for the exciplex fluorescence. It was susgested that the electronic structure of the fluorescent state of the exciplex and the excited charge-transfer complex is the same.

Since the works by Leonhardt and Weller it has been established that the charge-transfer or electron-transfer process is an important mechanism for the quenching of fluorescence.[1] Detailed studies have since been made, particularly on the mechanism of the electron-transfer process in the excited state in relation to the fluorescence quenching.[2-4] Fluorescence quenching is often accompanied by the appearance of a new fluorescence emission attributed to the exciplex in non-poalr or weakly polar solvents, while in strongly polar solvents only quenching of the fluorescence takes place. The fluorescence emission from the exciplex has so far been observed mostly in the polynuclear aromatic hydrocarbons–aromatic amines systems, where the fluorescer acts as an electron acceptor and the quencher as an electron donor.[1,5,6] The opposite case in which the fluorescer acts as an electron donor and the quencher as an electron acceptor has also been observed in a few systems, *e.g.*, *N*,*N*-dimethyl-β-naphthylamine–methyl benzoate or dimethyl isophthalate systems[7] or *N*-vinylcarbazole–fumaronitrile or diethyl fumarate systems.[8] An examination of the effects of solvent and temperature on the exciplex fluorescence was expected to provide information on the electronic structure of exciplex. Studies from this viewpoint were made by Mataga *et al.*[5] and Beens *et al.*[6] in the polynuclear aromatic hydrocarbon–*N*,*N*-dialkylaniline system, and a dipolar nature of the exciplex with a large dipole moment of more than 10 D was indicated. However, only a few clear-cut experimental data are available.

We have found that the fluorescence of a series of aromatic hydrocarbons is quenched by the addition of fumaronitrile, the fluorescent exciplex being formed between the fluorescer which acts as an electron donor and the quencher which acts as an electron acceptor in non-polar or weakly polar solvents. The effects of solvent and temperature on the exciplex fluorescence were examined. It was found that the present aromatic hydrocarbon–fumaronitrile system shows a charge-transfer interaction in their ground states at a relatively high concentration of each component and that the excited charge-transfer complex formed by the selective excitation of the ground state charge-transfer complex emits the fluorescence in a fluid solution at room temperature. Observation of both the intermolecular exciplex fluorescence and the fluorescence of the charge-transfer complex in the same system enabled us to make a direct comparison of the electronic structures of the exciplex and the excited charge-transfer complex.

Experimental

Materials. Fumaronitrile (*trans*-1,2-dicyanoethylene) of pure grade was recrystallized three times from pure benzene, fractionally sublimed twice *in vacuo*, stored and vacuum-sublimed once more immediately before use. Extra pure grade naphthalene, phenanthrene, acenaphthene, fluorene and anthracene were recrystallized from methanol, chromatographed on an activated alumina column with benzene as an eluent, recrystallized from methanol several times, and then fractionally sublimed twice *in vacuo*. Pyrene of pure grade was recrystallized twice from ethanol and benzene, chromatographed on alumina and then silica gel columns, recrystallized from ethanol several times and then fractionally sublimed twice *in vacuo*. Benzene was purified and dried in the usual way, and then refluxed with metallic sodium for a long time, and distilled from it immediately before use. Chloroform and dichloromethane were shaken with concd. sulfuric acid, water, and 5% sodium hydroxide solution, and washed with water repeatedly, dried over calcium chloride, refluxed with calcium hydride and distilled from it immediately before use. Tetrahydrofuran and α-methyltetrahydrofuran were refluxed with solid potassium hydroxide for a long time, distilled from it, and again distilled from lithium aluminum hydride immediately before use. Acetonitrile was refluxed with phosphorus pentoxide for a long time and distilled twice from it, and then refluxed with anhydrous potassium carbonate and distilled twice from it immediately before use.

Apparatus and Measurements. The ultraviolet and visible absorption spectra were measured with a Hitachi 124 spectrophotometer. The fluorescence emission and excitation spectra were measured with a Hitachi MPF-3 spectrophotofluorometer equipped with a constant-temperature cell holder. Emission measurements were made at 77 and 196 K using a Pyrex tube of about 3.5 mm diameter in a quartz Dewar containing liquid nitrogen and dry ice-methanol, respectively, as a refrigerant. The system used for the measurement was not degassed.

Results and Discussion

The fluorescence of a series of aromatic hydrocarbons, *e.g.*, naphthalene, phenanthrene, fluorene, acenaphthene pyrene, and anthracene, was found to be quenched by the addition of fumaronitrile, new broad structureless fluorescence emissions being observed in non-polar or slightly polar solvents with maxima in the range 21100—17400 cm^{-1}. The intensity of the new emissions increased with quencher concentration with an isoemissive point in each system. The excitation spectra for the new fluorescence were the same as those for the fluorescence of the aromatic hydrocarbons, being in good agreement with the absorption spectra of the corresponding aromatic hydrocarbons. New emissions were, therefore, attributed to the fluorescence from the exciplexes formed between the excited singlet aromatic hydrocarbons which act as electron donors and the ground state fumaronitrile which acts as an electron

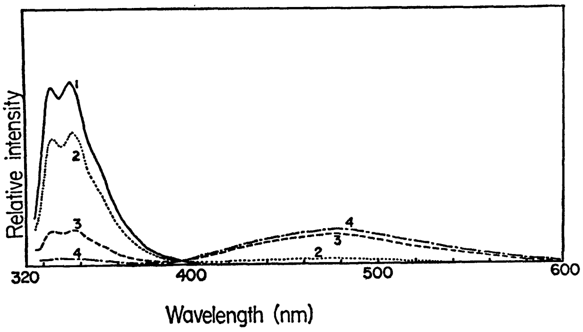


Fig. 1. Corrected fluorescence spectra of the naphthalene-fumaronitrile system in benzene at room temperature.
Excitation wavelength, 312 nm. [naphthalene] = 3×10^{-3} M. [fumaronitrile]: 1)——0; 2)······ 1×10^{-3} M; 3)---- 1×10^{-2} M; 4)—·— 5×10^{-2} M.

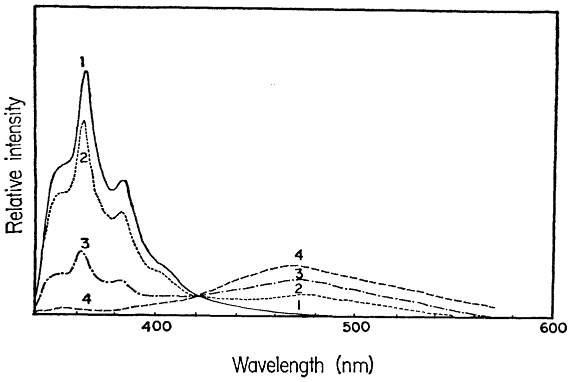


Fig. 2. Corrected fluorescence spectra of the phenanthrene-fumaronitrile system in benzene at room temperature.
Excitation wavelength, 331 nm. [phenanthrene] = 3×10^{-3} M.. [fumaronitrile]: 1)—— 0; 2)······ 1×10^{-3} M; 3)—·— 1×10^{-2} M; 4)---- 1×10^{-1} M.

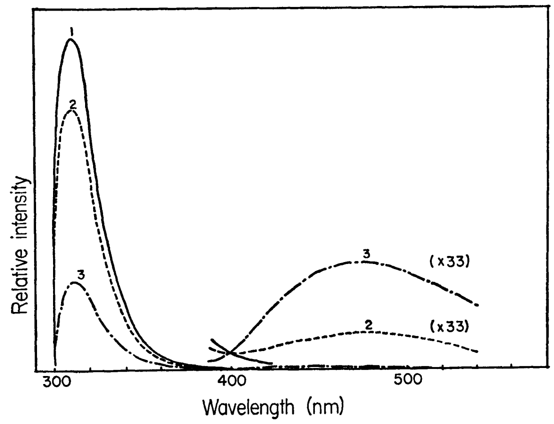


Fig. 3. Corrected fluorescence spectra of the fluorene-fumaronitrile system in benzene at room temperature.
Excitation wavelength, 301 nm. [fluorene] = 1×10^{-4} M. [fumaronitrile]: 1)—— 0; 2)---- 1×10^{-3} M; 3)—·— 1×10^{-2} M.

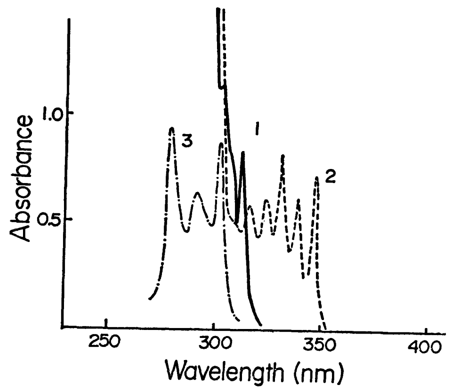


Fig. 4. The absorption spectra of naphthalene, phenanthrene, and fluorene.
Solvent, tetrahydrofuran, 1)—— naphthalene (3×10^{-3} M); 2)---- phenanthrene (3×10^{-3} M); 3)—·— fluorene (1×10^{-4} M).

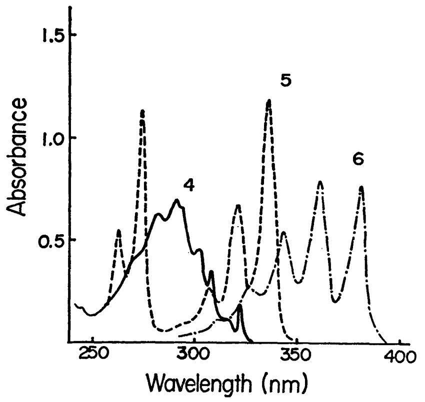


Fig. 5. The absorption spectra of acenaphthene, pyrene, and anthracene.
Solvent, tetrahydrofuran, 4)—— acenaphthene (1×10^{-4} M); 5)---- pyrene (1×10^{-5} M); 6)—·— anthracene (1×10^{-4} M).

TABLE 1. WAVE NUMBERS (cm^{-1}) OF THE BAND MAXIMA OF THE EXCIPLEX FLUORESCENCE EMISSION IN THE AROMATIC HYDROCARBON–FUMARONITRILE SYSTEM MEASURED IN SOLVENTS OF DIFFERENT POLARITY AT ROOM TEMPERATURE[a)]

Aromatic hydrocarbon	I_p(eV)[b)]	Solvent (dielectric constant)				
		Benzene (2.27)	$CHCl_3$ (4.70)	THF (7.39)	CH_2Cl_2 (8.90)	CH_3CN (37.5)
Naphthalene	8.10	21,100 (22,200)	20,200 (21,500)	20,000 (21,300)	18,900 (20,800)	—[c)]
Phenanthrene	8.09	21,100 (22,200)	19,800 (20,800)	19,600 (20,800)	18,700 (20,400)	—[c)]
Fluorene	7.99	20,800 (22,200)	19,800 (20,800)	19,400 (20,600)	18,700 (20,200)	—[c)]
Acenaphthene	7.66	19,000 (20,600)	18,500 (19,200)	18,300 (19,000)	—[c)]	—[c)]
Pyrene	7.55	18,700 (19,800)	17,900 (18,500)	17,700 (18,300)	—[c)]	—[c)]
Anthracene	7.40	18,000 (19,200)	17,400 (18,200)	—[c)]	—[c)]	—[c)]

a) Corrected values within ±200 cm^{-1} errors; non-corrected values in parentheses. b) Ionization potential determined from the charge-transfer absorption band.[14a)] c) No exciplex fluorescence emission detected.

acceptor. The corrected fluorescence emission spectra of a few aromatic hydrocarbon–fumaronitrile systems measured in benzene are shown in Figs. 1—3. The emissivity of the exciplex formed in the anthracene–fumaronitrile system was much weaker than that in other systems. The absorption spectra of a series of aromatic hydrocarbons (concentration was the same as that for the measurement of fluorescence emission) are shown in Figs. 4 and 5.

Appearance of the exciplex fluorescence depends on the magnitude of the ionization potential of the aromatic hydrocarbon as well as solvent polarity. Thus, as the polarity of the solvent increased from benzene (dielectric constant 2.27 at 25 °C) to dichloromethane (dielectric constant 8.9 at 25 °C), the exciplex fluorescence was no longer observed with respect to acenaphthene, pyrene and anthracene which possess relatively low ionization potentials (Table 1). In strongly polar solvent like acetonitrile (dielectric constant 37.5 at 20 °C) no exciplex fluorescence was detected, only quenching of the fluorescence of the aromatic hydrocarbon occurring. The wave number of the exciplex fluorescence maximum became smaller with the decrease of the ionization potential of the electron donor. A nearly linear relationship was found between the energies corresponding to the exciplex fluorescence maxima and the magnitude of the ionization potentials of a series of electron donors (Fig. 6).

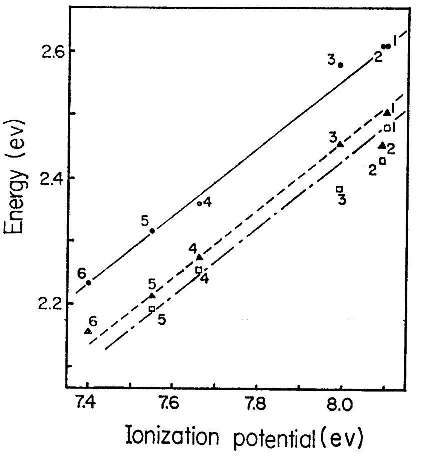


Fig. 6. Correlation between the energy of the exciplex fluorescence maximum in the aromatic hydrocarbon-fumaronitrile system and the ionization potential of the aromatic hydrocarbon in solvents of different polarity.
Solvent: —— benzene; ---- chloroform; —·— tetrahydrofuran.
1 naphthalene; 2 phenanthrene; 3 fluorene; 4 acenaphthene; 5 pyrene; 6 anthracene.

A remarkable effect of solvent polarity was observed on the exciplex fluorescence maximum. With the increase in the polarity of solvent, the exciplex fluorescence maximum shifted toward the red region accompanied by the decrease in the emission intensity, and the energies corresponding to the exciplex fluorescence maxima were roughly correlated with the static dielectric constant of the solvent (Table 1 and Fig. 7). As the temperature was lowered from 298 K to 196 K, the exciplex fluorescence maximum also showed a red shift accompanied by the decrease in the exciplex fluorescence intensity and the increase in the fluorescence intensity of the aromatic hydrocarbon (Table 2). In α-methyltetrahydrofuran matrix at 77 K neither the production of the exciplex fluorescence emission nor the quenching of the fluorescence of the aromatic hydrocarbon occurred.[9,10)]

The Stern-Volmer plots of F_0/F against the concentration of the quencher were linear up to *ca.* 5×10^{-2} M concentration of the quencher, where F_0 and F represent the fluorescence intensity of the aromatic hydrocarbon in the absence and presence of the quencher, respectively. When the concentration of the quencher exceeded *ca.* 5×10^{-2} M, the plots deviated upward from the linear relation in all the systems except anthracene probably due to the occurrence of the photoabsorption

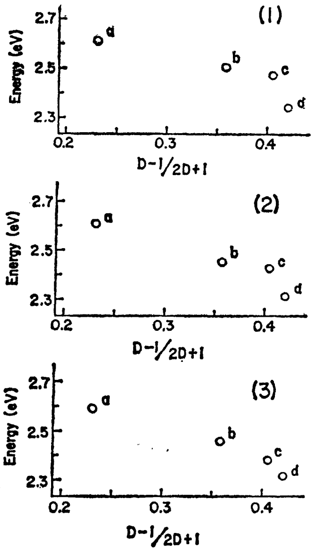


Fig. 7. Correlation between the energy of the exciplex fluorescence maximum in the aromatic hydrocarbon-fumaronitrile system and the dielectric constant of the solvent. (1) naphthalene-fumaronitrile system; (2) phenanthrene-fumaronitrile system; (3) fluorene-fumaronitrile system. a benzene; b chloroform; c tetrahydrofuran; d dichloromethane.

TABLE 2. WAVE NUMBERS (cm^{-1}) OF THE BAND MAXIMA OF THE EXCIPLEX FLUORESCENCE EMISSION IN THE AROMATIC HYDROCARBON-FUMARONITRILE SYSTEM MEASURED IN α-METHYLTETRAHYDROFURAN AT 298, 196, AND 77 K[a)]

Aromatic hydrocarbon	Temperature		
	298 K	196 K	77 K
Naphthalene	20,000	18,500	—[b)]
Phenanthrene	19,600	18,500	—[b)]
Fluorene	19,600	18,200	—[b)]
Acenaphthene	18,300	17,700	—[b)]
Pyrene	18,000	17,200	—[b)]
Anthracene	—[b)]	—[b)]	—[b)]

a) Corrected values within ±200 cm^{-1} errors. b) No exciplex emission detected.

TABLE 3. QUENCHING CONSTANTS AND APPROXIMATE QUENCHING RATE CONSTANTS OF THE FLUORESCENCE OF AROMATIC HYDROCARBONS BY FUMARONITRILE IN BENZENE AT 298 K

Aromatic hydrocarbon	(τ_0)[a)]	Quenching constant (M^{-1})	Quenching rate constant ($M^{-1}s^{-1}$)
Phenanthrene	(60)	185	3.1×10^9
Acenaphthene	(46)	269	5.9×10^9
Pyrene	(~400)	329	8.2×10^8
Anthracene	(4.1)	64	15.5×10^9

a) Fluorescence lifetime (nano second) of the aromatic hydrocarbon.[14b)]

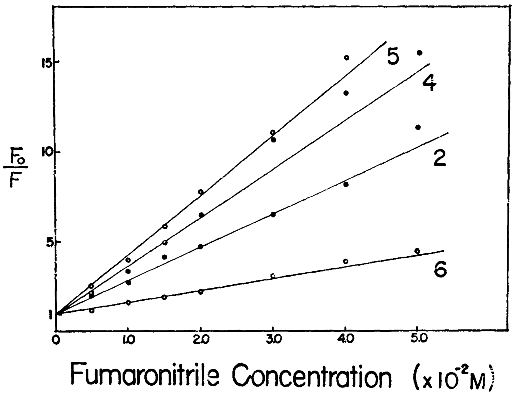


Fig. 8. Stern-Volmer plots of F_0/F against the quencher concentration measured in benzene at 298 K.
2 phenanthrene-fumaronitrile system; 4 acenaphthene-fumaronitrile system; 5 pyrene-fumaronitrile system; 6 anthracene-fumaronitrile system.

by the quencher molecule, since the tail absorption band of fumaronitrile of the concentration above *ca.* 5×10^{-2} M covers the wavelength of the exciting light. This tendency was conspicuous with respect to naphthalene and fluorene since excitation was carried out at a shorter wavelength than with the other aromatic hydrocarbon systems, the deviation occurring at the quencher concentration below 5×10^{-2} M. Some results are shown in Fig. 8. The quenching constants obtained from the slope of the Stern-Volmer plots and the approximate quenching rate constants γk_1 ($\gamma=k_3/(k_2+k_3)$ in Scheme 1) at 298 K in benzene calculated by using the known values of τ_0 (fluorescence lifetime) are summarized in Table 3.

The features of the fluorescence quenching of a series of aromatic hydrocarbons by fumaronitrile are consistent with the charge-transfer or electron-transfer mechanism in the excited state. The present results led to the following conclusions on the exciplex, which are essentially in good agreement with the conception as regards the exciplex formed in the aromatic hydrocarbon–aromatic amine system.[5,6,11)] (a) The exciplex which is stable only in the excited state is produced by the molecular motion of the electron donor and acceptor molecules during the lifetime of the excited state of the fluorescer (here the excited singlet state). Thus, no exciplex formation takes place in the rigid matrix at 77 K in which the molecular motion is restricted. (b) Just as the energies of the exciplex fluorescence maxima are correlated with the magnitude of the electron affinities of the aromatic hydrocarbons for a given aromatic amine,[6b,11)] they are correlated with the magnitude of the ionization potentials of the aromatic hydrocarbons in the present systems where the fluorescers act as electron donors. (c) The electronic structure of the exciplex in the equilibrium state is very polar, and the orientation of the solvent molecules takes place during the lifetime of the exciplex. The red shift of the exciplex fluorescence maximum observed when the temperature is lowered may be explained to be due to the increase in the polarity of the solvent at low temperatures. (d) It is suggested that as the solvent polarity increases the exciplex dissociates into ions to produce solvated ion pairs with no emissivity, and that in strongly polar solvents the electron transfer occurs from the encounter complex.2–4)

The present aromatic hydrocarbons–fumaronitrile systems also showed a weak charge-transfer interaction in their ground states at relatively high concentrations of each component (*ca.* 10^{-1} M or above), as evidenced from the electronic absorption spectra. Although no distinct charge-transfer bands separated from the component absorptions were observed, the absorption spectra of the aromatic hydrocarbons–furmaronitrile systems shifted to the red region as compared with the sum of the absorptions of each component of the same concentration. It was found that selective excitation of the ground state charge-transfer complex gave rise to the fluorescence emission in a non-polar fluid solution at room temperature in the same wavelength region as observed for the exciplex fluorescence. As an example, the absorption and the fluorescence emission spectra of the charge-transfer complex in the acenaphthene–fumaronitrile system measured at 298 K are shown in Fig. 9. The result is consistent with the known characteristic features of the fluorescence of the charge-transfer complex, *viz.*, a large Stokes shift is observed in a room temperature fluorescence in a fluid solution (the maximum wavelength of the charge-transfer absorption band is shorter than 400 nm). That the emission is not the exciplex fluorescence produced by the local excitation of the tail band of the aromatic hydrocarbon, but the so-called charge-transfer fluorescence from the excited charge-transfer complex, was further confirmed by the measurement at 77 K where no exciplex fluorescence was produced. The fluorescence emission was likewise observed at 77 K by the selective excitation of the ground state charge-transfer complex, but at a shorter wavelength than that observed at 298 K (Fig. 10). This is understandable since the fluorescence in a rigid medium takes place from the lowest point reached from the excited Franck-Condon state and the fluorescence in a fluid solution from the excited equilibrium state, which is stabilized due to the reorientation of the solute and the solvent molecules.12d) Measurement of the correct excitation spectrum was difficult due to the effect of the reabsorption of the emission. The fluorescence of the charge-transfer complex was also dependent on the polarity of the solvent: the fluorescence wavelength maximum shifted to the red region accompanied by the decrease in the emission intensity as the polarity of the solvent increased; no fluorescence emission was detected in a strongly polar solvent such as acetonitrile. Observation of a room temperature fluorescence of a charge-transfer complex in a fluid solution has so far been reported only in a few systems.11,12) Hardley any examples bave been reported except the *s*-tetracyanobenzene–α-methylstyrene system13) in which both the exciplex fluorescence and the fluorescence of the charge-transfer complex stable in the ground state are observed in the same system. A direct comparison of the exciplex fluorescence and the charge-transfer fluorescence emissions in the same system enabled us to obtain information on the comparable electronic structure or the geometry of the exciplex and the excited charge-transfer complex. In the *s*-tetracyanobenzene–α-methylstyrene system the fluorescence from the excited charge-transfer complex, very weak in its intensity, appears at a different wavelength from the exciplex fluorescence, and different geometries have been suggested for the exciplex and the excited charge-transfer complex. The present result in which the exciplex fluorescence and the charge-

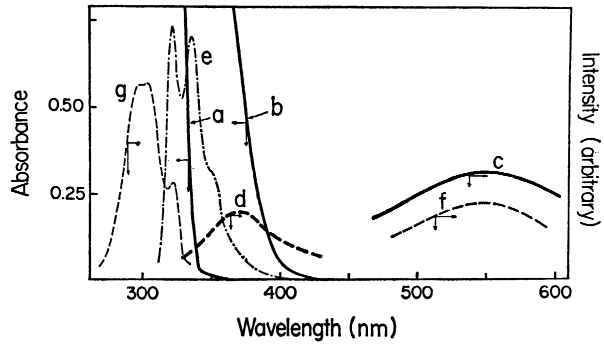


Fig. 9. The absorption and fluorescence emission and excitation spectra of the acenaphthene-fumaronitrile charge-transfer complex measured in α-methyltetrahydrofuran at 298 K. (a) absorption spectrum of acenaphthene(0.1 M); (b) absorption spectrum of the acenaphthene(0.1 M)-fumaronitrile(0.1 M) system; (c) the fluorescence spectrum of the charge-transfer complex produced by the excitation in the charge-transfer band at 370 nm in the above system; (d) excitation spectrum for the charge-transfer fluorescence(c); (e,f) fluorescence spectrum of acenaphthene and exciplex fluorescence spectrum produced by the excitation of acenaphthene (1×10^{-4} M) at 321 nm in the presence of fumaronitrile (2.5×10^{-2} M). (g) excitation spectrum for the fluorescence emissions (e) and (f).

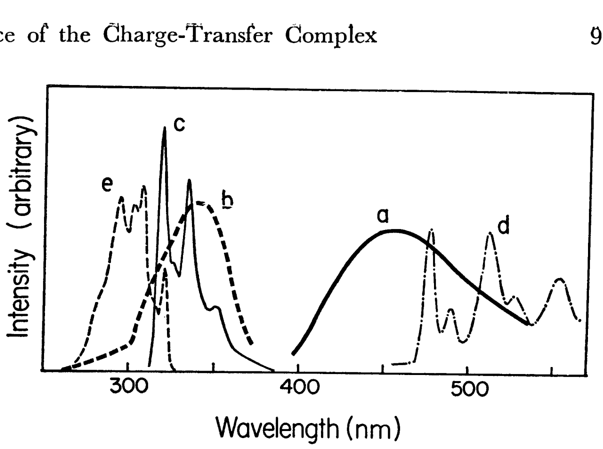
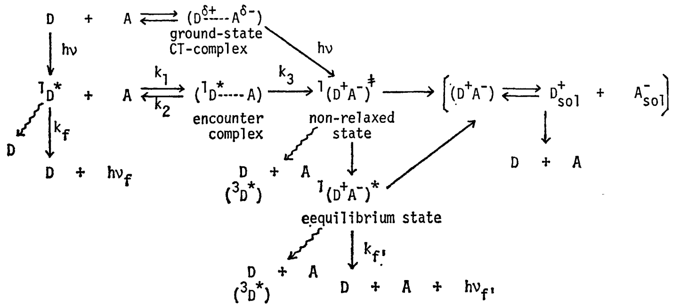


Fig. 10. The charge-transfer fluorescence and excitation spectra of the acenaphthene–fumaronitrile charge-transfer complex measured in α-methyltetrahydrofuran at 77 K. (a) the fluorescence spectrum of the charge-transfer complex produced by the excitation in the charge-transfer band at 370 nm in the acenaphthene-(0.1 M)-fumaronitrile(0.1 M) system; (b) excitation spectrum for the charge-transfer fluorescence (a); (c) fluorescence spectrum of acenaphthene produced by the excitation of acenaphthene (1×10^{-4} M) at 321 nm in the presence of fumaronitrile (2.5×10^{-2} M); (d) phosphorescence spectrum of acenaphthene produced simultaneously with the fluorescence (c); (e) excitation spectrum for the emissions (c) and (d).

transfer fluorescence emissions were observed at the same wavelength region in a few solvents of different polarity suggests that the electronic structure of the fluorescent state of the exciplex and the excited charge-transfer complex is the same. We have also obtained the same result in the *N*-vinylcarbazole–fumaronitrile system.[8] The photochemical primary processes of the aromatic hydrocarbon–fumaronitrile system are shown in Scheme 1.



Scheme 1. The photochemical primary processes in the aromatic hydrocarbon-fumaronitrile system.

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9) The phosphorescence emission of each aromatic hydrocarbon was observed at 77 K.

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