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Intramolecular Charge Transfer in the Polar Fluorescent State of 1- and 2-Acylanthracenes

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The absorption and emission spectra of 1- and 2-aroyl- and acetylanthracenes were measured in various solvents. The emission spectra moved to longer wavelengths and their forms changed from the structured ones to the structureless ones with increasing solvent polarity, while the absorption spectra showed no appreciable changes under the same conditions. These emissive features became more distinguished with increasing electron-withdrawing ability of the aroyl group. The dipole moments of the fluorescent state as estimated from the Lippert-Mataga formula were 7—16 D for these compounds. The assignments of the low-lying excited states are described in terms of the electronic transitions of the parent anthracene, ^1L_a and ^1L_b, which undergo perturbation by the substitution.

In a recent study on the photoaroylation of anthracene (**1**) with benzoyl chloride, and its *p*- or *m*-substituted compounds, the ketone products formed were found to be positionally selective, the product distribution being different from that of the thermal Friedel-Crafts benzoylation.[1] This positional selectivity has attracted our continuing attention. Since the product distribution obtained is inconsistent with that theoretically expected from the reactivity calculated, which is acceptable for a non-interacting aromatic molecule, we tentatively postulate a specific intermolecular interaction between the reactants to ensure the positional selectivity. In fact, a strong interaction was evidenced by the efficient quenching of the fluorescence of **1** by these aroyl chlorides. Furthermore, the Hammett treatment of the quenching rate constant was indicative of an exciplex formation.

To further elucidate the electronic interaction of **1** with the aroyl system, we planned to study the spectral and emissive behaviors of aroylanthracenes, in which the constituents are intimately combined. The information about the intramolecular interaction may be helpful to account for the mechanisms of the intermolecular interaction concerned.

The introduction of a substituent group into an aromatic ring, in general, leads to a spectral deformation due to degradation of the molecular symmetry and due to effective electronic conjugation with the group.[2] It is well known that the absorption spectra of the anthracene derivatives, except for the meso substitution, are quite different from that of the parent (**1**).[3–5] The factors influencing the spectra are also discussed.

Experimental

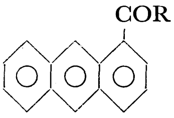
Aroylanthracenes (**2c** and **3b**—**f**) were prepared in similar ways to those described in a preceding paper.[1b] The preparation of acetylanthracenes (**2a** and **3a**) was carried out after Luttinghaus and Kacer.[6] The emission spectra were measured in an air atmosphere, using a Hitachi MPA-2A spectrophotofluorometer. The sample absorbance in a 1-cm square quartz cell was made to be 0.1 at the exciting wavelength (390 nm), so that the reabsorption was negligible and that the relative emission intensities were comparable with each other.

Solvents used were spectro- or G.R. grade reagents (the numbers in parentheses refer to those presented in the figures): hexane (1), cyclohexane (2), carbon tetrachloride (4), dioxane (5), dibutyl ether (6), dipropyl ether (7), chloroform (8), butyl acetate (10), ethyl acetate (11), dichloromethane (13), 1,2-dichloroethane (14), pyridine (15), *t*-butyl alcohol (16), and 2-propanol (17) were used as commercially available; benzene (3), diethyl ether (9), tetrahydrofuran (12), acetone (18), *N*,*N*-dimethylformamide (19), ethanol (20), acetonitrile (21), and methanol (22) were dried by standard procedures and purified by fractional distillation.

The measurements of the fluorescence polarization spectra were made in a glycerol solution in order to minimize the rotational relaxation. The monitoring wavelength was 520 nm.

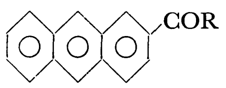
Results and Discussion

Absorption Spectra. The absorption spectra of 1-(**2c**) and 2-benzoylanthracene (**3c**) in hexane are shown in Fig. 1. The intense absorption bands in the short wavelength region (<300 nm) may consist of the transition bands which originate from the constituent aromatic moieties. In this region, the anthryl and the phenyl rings give intense progressions, which are assigned to the ^1B_b and the ^1L_a band, respectively.[2] The assignment of the short wavelength bands was not undertaken in this study.



2

a, $R=CH_3$
c, $R=Ph$



3

a, $R=CH_3$
b, $R=p\text{-}C_6H_4OCH_3$
c, $R=Ph$
d, $R=m\text{-}C_6H_4Cl$
e, $R=m\text{-}C_6H_4CN$
f, $R=p\text{-}C_6H_4CN$

In the longer wavelength region, above 300 nm, the absorption spectra are quite different from that of the parent anthracene (**1**), in which a progression of the ^1L_a transition alone is prominent. As is shown in Fig. 1, the compounds (**2c** and **3c**) give two electronic transition bands, which are closely overlapping each other in the former spectrum and clearly separate in the latter spectrum. These bands are conveniently named as I and II, according to the sequence of their peak energy

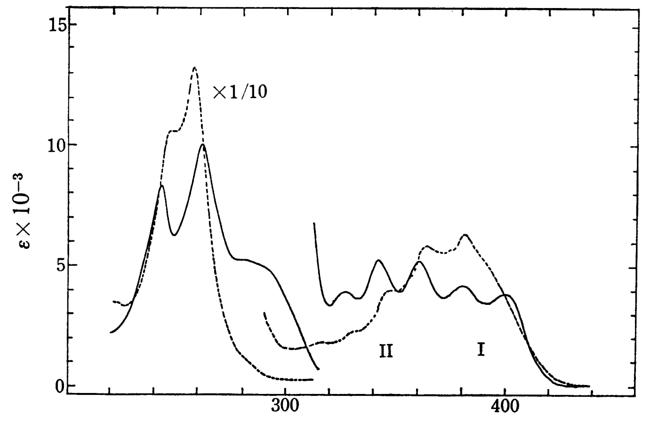


Fig. 1. Absorption spectra of 1-benzoylanthracene (----) and 2-benzoylanthracene (——) in hexane.

(see Fig. 1). The absorption spectra of acetylanthracenes (**2a** and **3a**) are the same as those of the corresponding benzoylanthracenes. Such spectral deformation is rather common to the anthracene to which a powerful substituent group attaches.[2,4,5] Thus, the general form of the absorption spectrum is fundamentally dependent on the aromatic C-position at which the substitution occurs.

It is of special interest to clarify the roots of the I and II transition bands. Although a few papers have discussed the problem, the arguments among articles are confused because the fundamental dissimilarity to the parent spectrum prevents one from deducing conclusive assignments of the transition bands with certainty.[2,4,5] So far, the most plausible assignment arises from the resonance theory,[3,4] which claims that a substituent group largely affects the aromatic transition band lying in the same direction as that of the extending conjugation. Since an 1-substituent group lies nearly along the short axis of an aromatic molecule, it primarily influences the transverse-polarized ^1L_a band. Likewise, since a 2-substituent group lies nearly along the long axis, the longitudinally polarized ^1L_b band is mainly subjected to its influence. These substituent effects are well accepted for naphthalene derivatives: the 1-substitution gives rise to large bathochromic and hyperchromic shifts of the ^1L_a band, and the 2-substitution causes the similar shifts of the ^1L_b band.[2]

Suzuki and Baba have discussed the assignment of the electronic transition bands of anthrol and anthrylamine in terms of such substitution perturbation.[4] On the assumption that the degradation of the molecular symmetry due to substitution would lead to the emergence of the ^1L_b transition, which is forbidden in the parent spectrum, they ascribed the lowest (I) and the second (II) bands of the 1-derivatives to the perturbed ^1L_a and ^1L_b bands, respectively, and those of the 2-derivatives to the perturbed ^1L_b and ^1L_a bands, respectively. These assignments are also favored in the cases of the acylanthracenes studied here, because their absorption spectra have close resemblances to those of the corresponding anthrols or anthrylamines.

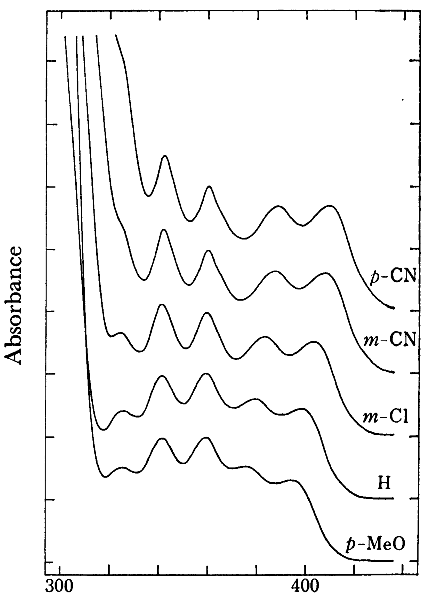


Fig. 2. Absorption spectra of 2-(substituted benzoyl)-anthracene in hexane.

Judging from the MO treatments of the parent spectrum, which suggest that the transition energy of the forbidden band (^1L_b) is slightly higher than that of the predominant band (^1L_a),[7] it appears striking that the former band extensively emerges on the lower frequency side of the latter band, when the substituent group is introduced at the 2-position of **1**. To examine this for the cases of the compounds concerned, we measured the absorption spectra of the series of 2-aroylanthracenes, which have a *p*- or *m*-substituent group on the benzoyl ring. As is shown in Fig. 2, the I band is apparently dependent on the substituent group, whereas the II band is little affected, its peak positions lying at the same wavelengths (325, 342, and 360 nm) for these compounds. The peak positions of their longest wavelength bands and their peak height ratio are listed in Table 1. The results indicate that the bathochromic and presumably hyperchromic effects on the I band become larger with increasing electron-withdrawing ability of the substituent group. The peak energy of the I band is well correlated with the Hammett substituent constant, σ. The ρ value obtained is 2.3, a value close to that derived from the inductive effect on the electron-abstracting process of the benzoyl system.[8]

These spectral features are quite consistent with the transition-band assignments in view of the resonance theory. It appears likely that the substituent perturba-

Table 1. Peak position and peak height ratio of absorption bands of 2-aroylanthracenes

Compound	λ_{II} (nm)	λ_I (nm)	$\varepsilon_I/\varepsilon_{II}$
3b	360	394	0.65
3c	360	399	0.72
3d	360	404	0.77
3e	361	408	0.77
3f	362	410	0.83

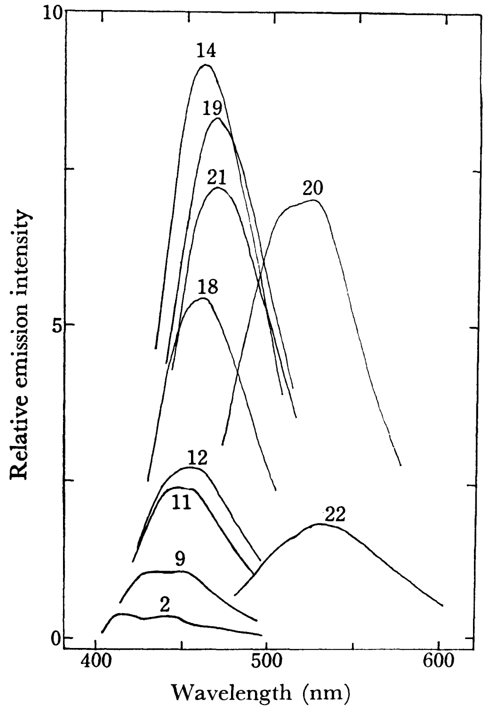


Fig. 3. Emission spectra of 2-benzoylanthracene in various solvents.

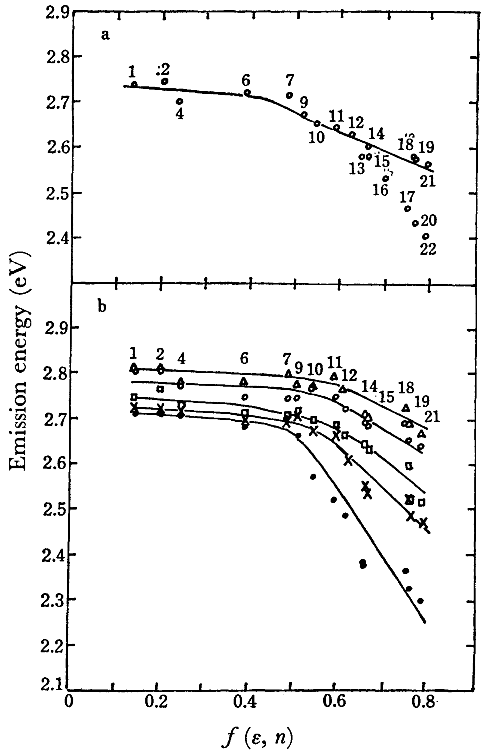


Fig. 4. Solvent effects on the emission peak maxima of 1-benzoylanthracene (a) and 2-(substituted benzoyl)-anthracene (b): *p*-MeO (△), H (○), *m*-Cl (□), *m*-CN (×), *p*-CN (●).

tion extends the spectral deformation, which was first generated from the degradation of the aromatic symmetry.

Solvent Effects on the Emission Spectra. The increase of the solvent polarity degradates the vibrational structure of the I band, with a slight broadening of the band, while the II band undergoes only a slight red-shift without changing its fundamental form. In contrast with these small changes of the absorption spectra, the emission spectra are greatly dependent on the solvent properties, as is shown in Fig. 3. The emission spectra in non-polar solvents are equal to the mirror image of the I band. When the solvent is changed from non-polar to polar, they are converted into structureless bands with large Stokes' shifts. Neverthless, their excitation spectra in all cases are in good agreement with the absorption spectra.

Lippert and Mataga have independently developed the theoretical treatments for solvent-induced changes of the excited electronic structure.[9] In the theory, the emission energy is to a good approximation correlated with the quasimacroscopic parameter for solvent polarity, $f(\varepsilon, n)=2(\varepsilon-1)/(2\varepsilon+1)-(n^2-1)/(2n^2+1)$, in which ε and n are the dielectric constant and refractive index of the continuum medium, respectively. As is shown in Fig. 4, the peak energy in most solvents used is in good correlation with the parameter, $f(\varepsilon, n)$, although the deviation from the plots is observed for some solvents, which specifically interact with the solute. The protic solvents in particular induce anomolous red-shifts, presumably due to formation of the hydrogen bond. The excess of stabilization energy for the hydrogen bond is of the order of 1500 cm^{-1}, as estimated from the difference between the frequencies of the peak maxima in acetonitrile and in methanol, which are of the same polarity. Further discussions for the cases of the protic solvents will not be made.

The emission energy plots obtained for all compounds examined give curvatures which have at least two slopes, as is shown in Fig. 4. The slope in the non-polar region is nearly horizontal and that in the polar region is definitely negative. The inflection appears at the intermediate-polarity solvent, ethyl ether. This solvent dependence indicates that the fluorescent state of **2** and **3** becomes highly polar with increasing the solvation, while the ground state is little affected. In Table 2 are liested the values of the dipole moment in the fluorescent state, as calculated from the Lippert-Mataga formula on the assumption that the radius of the solvent cavity is 5 Å, approximately what would be expected from the molecular model. The values of the dipole moment are 7 D for **2**, 9 D for **3a**, and 10 D for **3c**.

As is shown in Fig. 4b, the peak shift in the polar region is very sensitive to the substituent group of the benzoyl phenyl ring. The greater the electron-withdrawing ability of the substituent group, the more the peak moves to the longer wavelengths and the greater the value of the dipole moment calculated (Table 2).

TABLE 2. DIPOLE MOMENTS IN POLAR FLUORESCENT STATES

Compound	Dipole moment (debye)	Compound	Dipole moment (debye)
2a	7	**3c**	10
2c	7	**3d**	12
3a	9	**3e**	13
3b	9.5	**3f**	16

From these results, it appears probable that the charge transfer occurs from the anthryl ring to the acetyl or benzoyl moiety in the excited equilibrium state.

In this connection, it was observed that *N*,*N*-dimethylaniline, which is an electron donor, strongly quencehd the fluorescence of the compounds (**2** and **3**) to give an exciplex emission in non-polar solvents. On the other hand, an electron acceptor such as dicyanobenzene had no such quenching ability. These facts support the assertion that the anthryl ring is greatly electron-deficient in the excited state owing to the charge transfer to the substituent group.

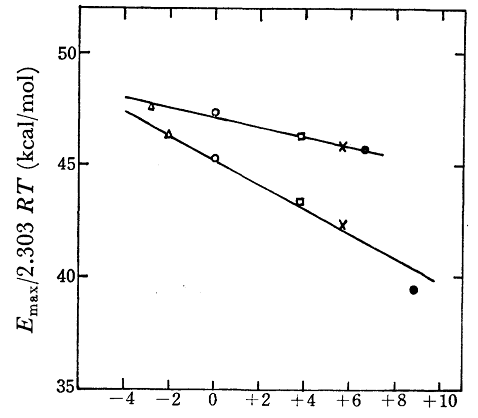


Fig. 5. Hammett correlation of the emission peak maxima of 2-(substituted benzoyl)anthracene in hexane (upper plots) and in acetonitrile (lower plots).

The Hammett plots for the emission energy of **3b**—**f** are shown in Fig. 5. The emission energy in hexane shows a linear Hammett correlation, with ρ equal to that obtained from the similar plots of the absorption energy. While the inductive contribution is importtant for the electronic transition processes in the non-polar solvents, the emission energy in acetonitrile requires an exalted substituent constant, σ^-, to give a linear Hammett correlation, which suggests the validity of the resonance contribution for the stabilization of the polar fluorescent state. The ρ value obtained for the acetonitrile solution is 5.5, a value so high as to be consistent with the charge transfer required in a large electron-demand process.

The solvent dependence of the emission intensity is complicated, as is shown in Fig. 6. Generally speaking, the emission intensity increases with increasing the solvent polarity, and then decreases in a highly polar region. Very weak emission in non-polar solvents may correspond to the case of 9-benzoylanthracene, which is non-fluorescent because of rapid radiationless decay through a thermally activated intersystem crosssing to the upper triplet state in a slightly higher energy level than that of the lowest excited singlet state.[10] It appears likely that the energy gaps between the relevant electronic levels of the compounds (**2** and **3**) are so large that the radiative transition rate is comparable to the radiationless decay rate. If this energy gap is more enlarged when the fluorescent state moves to the lower frequency region with increasing the solvation, the radiative probability would increase at the expense of the intersystem-crossing probability. The decrease of the emission intensity in highly polar solvents is remarkable for the compounds (**3**), which have a powerful substituent group such as a cyanobenzoyl group. This suggests that a complete charge separation would be accomplished for these highly solvated compounds, resulting in the decrease of the radiative transition probability.

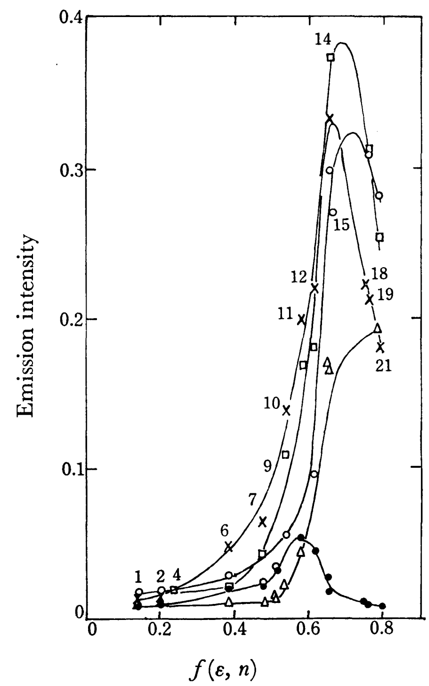


Fig. 6. Solvent effects on the emission intensity of 2-(substituted benzoyl)anthracene: *p*-MeO (△), H (○), *m*-Cl (□), *m*-CN (×), *p*-CN (●).

The excitation-polarization spectra of **2a** and **3a** in glycerol are shown in Fig. 7. When the I band is excited, the degree of the polarization obtained is *ca.* 0.3 suggesting that this band corresponds to the emitting band. If the rotational relaxation is severly inhibited, the polarization degree would become close to the maximum value, 0.5.[11] The excitation of the II band leads to the decrease of the polarization, which supports

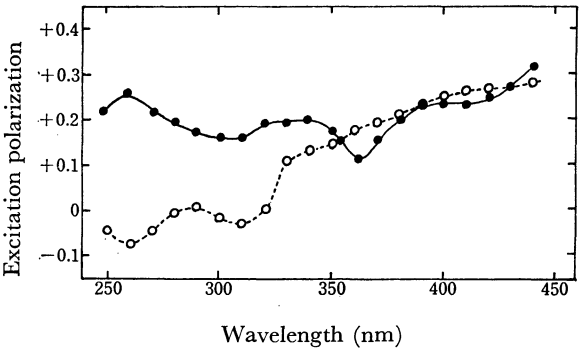


Fig. 7. Excitation polarization spectra of 1-acetylanthracene (----) and 2-acetylanthracene (——) in glycerol. Monitoring wavelength, λ 520 nm.

the idea that the transition moments of the I and II bands are oriented at large angles to each other. While the polarization behaviors of these long wavelengths bands are similar for all compounds examined, the situation of the short wavelengths bands is quite different for the polarization spectra of **2** and of **3**: the former shows a negative polarization (*ca.* −0.1), but the latte shows a large positive polarization (*ca.* 0.25). The dissimilarity in the polarization spectra may reflect the difference in the mutual orientation of the exciting and emitting transition moments of these compounds. The exciting band of acetylanthracene (**2a** and **3a**) in this short wavelength region is ascribed to the anthryl ^1B_b band, although the contribution of the phenyl ^1L_a transition to excitation is unclear in the cases of benzoylanthracene (**2c** and **3c**). Since the ^1B_b band lies along the long axis,⁷⁾ the results for the polarization provide a possible orientation of the I band of **2** and **3**, which is approximately in line with the consequences of the transition-band assignments based on the absorption spectra.

The emissive features of aroylanthracenes are informative to account for the mechanisms of the intermolecular interaction between **1** and the aroyl chlorides:¹⁾ 1) the charge transfer in the polar fluorescent state is related to an intermolecular exciplex formation; and 2), the inversion of the excited states in 2-benzoylanthracene is indicative of the validity of the ^1L_b state in determining the positional selectivity in the photoaroylation.

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