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Electronic Structures of Carbazole and Indole and the Solvent Effects on the Electronic Spectra

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The results of the experimental studies on the solvent effects upon the fluorescence and the absorption spectra of carbazole and indole are described, which makes it possible to estimate the difference of the electronic structures in the fluorescence state from those in the ground state.

The electronic structures of the molecules are studied theoretically on the basis of the experimental results.

Die Beeinflussung der Absorptions- bzw. Fluoreszenzspektren von Carbazol und Indol durch Lösungsmitteleffekte wird untersucht. Aus den Ergebnissen werden Rückschlüsse auf die Elektronenstrukturen der Grund- und Fluoreszenzzustände gezogen. Eine auf den experimentellen Resultaten basierende theoretische Behandlung der Elektronenstrukturen schließt sich an.

Nous avons étudié les effects de solvant sur les spectres d'émission et d'absorption du carbazol et de l'indole. Les résultats permettent des conclusions sur la différence entre les structures électroniques des états excité et fondamental. Des calculs sur ces structures sont faits à l'aide des données expérimentales.

I. Introduction

The nature of the electronic states of the series, pyrrole, indole and carbazole, seems to be not so well understood as those of benzenoid hydrocarbons, aza-aromatics and their derivatives, although there have been some theoretical studies [3, 4]. We have studied various solvent effects on the absorption and fluorescence spectra of carbazole and indole in order to elucidate the nature of the electronic states of this series of molecules [13—15]. It has been confirmed by measuring the absorption and fluorescence spectra of solutions that hydrogen bonding of carbazole in the lowest excited singlet state with triethylamine (TEA) or n-butyl-acetate in cyclohexane becomes appreciable at considerably smaller concentrations ($\lesssim 1/10$) of proton acceptors than in the ground electronic state [13]. This fact indicates that the excited carbazole has much greater tendency to make hydrogen bond with the acceptors and is in accordance with the observed spectral shift caused by the hydrogen bonding (red shift). The ionic dissociation of carbazole in aqueous solution in the sense, $>N\text{-}H \rightarrow N^- + H^+$, occurs easily in the lowest excited singlet state [14]. At pH ~14, we can observe only the fluorescence band due to the carbazole anion, although no change of the absorption spectrum occurs in the pH range, 7 ~14. Thus the ionic dissociation energy in the excited state is far smaller than that in the ground state. These facts seem to be of some interest from the viewpoint of the electronic structure of this series of molecules.

In the present report, we shall describe the results of our measurements on the absorption and fluorescence spectra of indole and carbazole in various organic solvents and also on the ion-pair formation of the excited carbazole with TEA in polar organic solvents. Further, the results of some quantum chemical studies on the electronic structures and spectra of these molecules together with the discussions of the observed results on the basis of the theoretical calculations will be given.

II. Electronic Spectra of Indole and Carbazole in Various Organic Solvents and the Increase of the Dipolemoment in the Fluorescent State

As an example of the solvent effects upon the electronic spectra of these molecules, the fluorescence and absorption spectra of indole in several solvents are shown in Fig. 1. The absorption band in the region, $34000 \sim 40000$ cm^{-1},
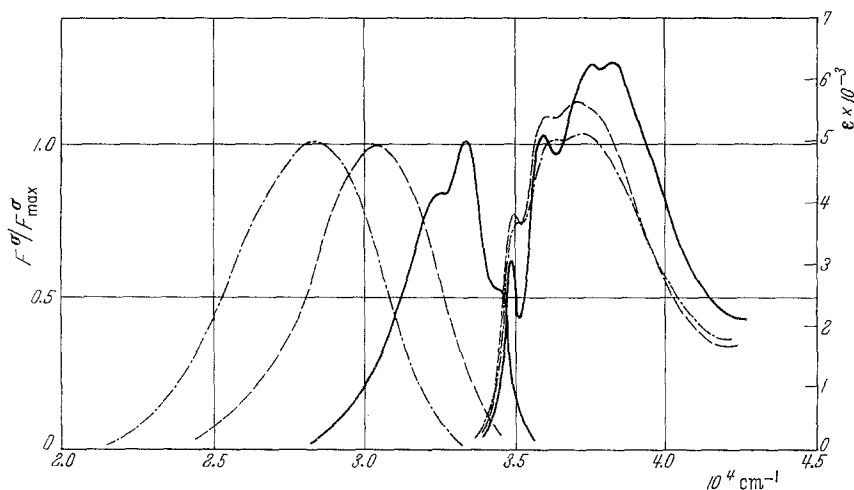

Fig. 1. Absorption and fluorescence spectra of indole in solution. Concentration of indole $\sim 10^{-4}$ mol/l. Solvents: ————— cyclohexane, — — — — acetonitrile, — . — . — water

appears to consist of two electronic bands, one of which at ~ 35000 cm^{-1} may be assigned to ^1L_b band and the other at ~ 37000 cm^{-1} to ^1L_a band by comparing the absorption spectrum of indole with those of the other iso-π-electronic compounds such as naphthalene and quinoline, and also with the absorption spectrum of styrene. The latter compound has a very weak band near 34000 cm^{-1} and a strong band near 41000 cm^{-1}. The former is assigned to ^1L_b and the latter to ^1L_a. It may be possible to regard indole as composed of styrene and $>N$-H group. Then the observed spectra indicate that the ^1L_a band of styrene is affected considerably by the interaction with the $>N$-H group (strong red shift), although the ^1L_b band is affected only slightly by this interaction.

An analogous reasoning to the case of indole may be possible for carbazole. In this case, the molecule may be regarded as composed of biphenyl and the $>N$-H group, and the very weak ^1L_b band of biphenyl which lies close to the strong ^1L_a band is affected to a quite remarkable extent (strong red shift and intensification) by the interaction with the $>N$-H group. However, the ^1L_a band is affected

only slightly by this interaction. Our theoretical studies on the electronic structures and spectra of these molecules are based on the models described above.

As indicated in Fig. 1, the shift of the absorption bands of indole in the polar solvents is rather small. In fact, the wave number of the ^1L_b band seems to be practically the same in cyclohexane, acetonitrile and water. In contrast to this, the red shift of the fluorescence band in the polar solvents is very large. This fact indicates a large increase of the dipole moment in the excited state and a much greater stabilization caused by the solute-solvent interactions in the fluorescent state than in the ground state and the Franck-Condon excited state [1, 5, 6, 9, 10].

The vibrational structure of the absorption band can be ascribed certainly to ^1L_b, and the ^1L_a band does not seem to have such a sharp structure. The fluorescence spectrum of the cyclohexane solution has a vibrational structure which corresponds quite well to the structure of the ^1L_b absorption band. However, the
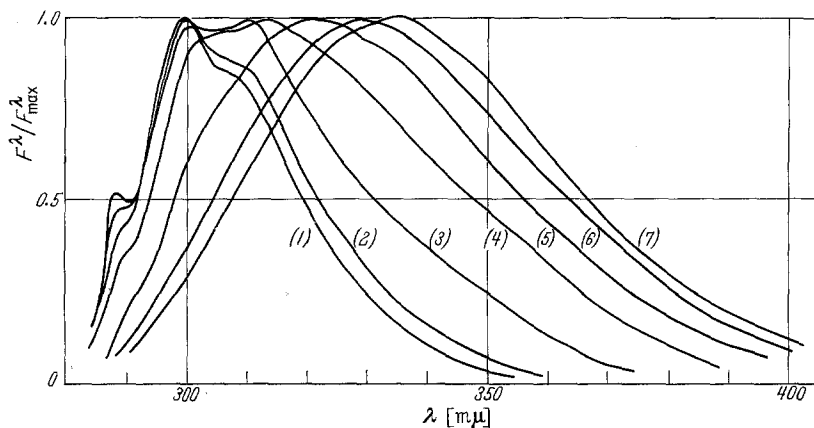

Fig. 2. Fluorescence spectra of indole in n-hexane-ethanol mixtures. Concentration of indole ~ 10^{-4} mol/l. Concentration of ethanol: (1) 0, (2) 0.017 mol/l, (3) 0.085 mol/l, (4) 0.17 mol/l, (5) 0.51 mol/l, (6) 2.55 mol/l, (7) 8.52 mol/l

fluorescence spectrum in the polar solvent does not show such a vibrational structure. Moreover, the fluorescence spectra of indole in n-hexane-ethanol mixtures, as shown in Fig. 2, indicate that the relative intensity of the fluorescence band (^1L_b) decreases and a broad band arises at much longer wavelength region and this broad band further shifts to red as the concentration of ethanol is increased, until the fluorescence band coincides with that of the pure ethanol solution.

In view of the facts described above, it may be plausible that the ^1L_a state in which indole seems to have a large dipole moment in contrast to the ^1L_b state is strongly stabilized by the interaction of the solute with the surrounding polar solvent molecules and may probably become the lowest excited singlet state during the radiationless process from the Franck-Condon to the equilibrium excited state. We have measured the fluorescence decay curve of indole in cyclohexane and acetonitrile by using an ultraviolet light pulse of very short duration for the excitation [19]. Our preliminary results indicate that the decay curve has apparently two components and the proportion of the short life component (which may be ascribed to the ^1L_a fluorescence) is quite dominant in the polar solvent. This fact is in accordance with the above described reasoning.

The reversal of the ^1L_b and the ^1L_a states during the life time of the excited state is not limited to the present case. The most clearcut example of this pheno-menon has been observed by LIPPERT [7] in the case of p-cyano-N,N-dimethylaniline. Analogous phenomenon also seems to occur in the case of 1-naphthylamine [16]. More-over, this phenomenon is not confined to the case of the π-π^* excited states. BREDERECK, FÖRSTER and OESTERLIN [2] have observed and interpreted the reversal of the n-π^* and the π-π^* state of pyrene-3-aldehyde in polar solvents during the life time of the excited state.

The difference between the dipole moments in the fluores-cent state ($\vec{\mu}_f$) and the ground state ($\vec{\mu}_g$), $\Delta \vec{\mu} = (\vec{\mu}_f - \vec{\mu}_g)$, can be estimated by measuring the wave numbers of the band maxima of fluorescence (σ_f^m) and absorption (σ_a^m) spectra in various solvents and by using the following equation [1, 5, 6, 9, 10].

$$h c (\sigma_a^m - \sigma_f^m) \simeq Const. + \\ + F(D, n) \cdot \delta$$

$$F(D, n) = \left[\frac{2(D-1)}{2D+1} - \right.$$

$$\left. - \frac{2(n^3-1)}{2n^2+1} \right], \delta = (\Delta\vec{\mu})^2 / R^3. \quad (1)$$

In (1), D and n are the static dielectric constant and the re-fractive index of the solvent, respectively and R is the cavity radius in Onsager's theory of the reaction field. The observed ($\sigma_a^m - \sigma_f^m$) versus $F(D, n)$ rela-tions for carbazole and indole are shown in Fig. 3 and 4, re-spectively. Although both values of σ_a^m, i. e., those for ^1L_a as well as for ^1L_b, are examined in Fig. 4, the δ values are practically the same in both cases because the shift of the absorption spectrum is much smaller than that of the fluorescence spectrum. From these relations, $\Delta \vec{\mu}$
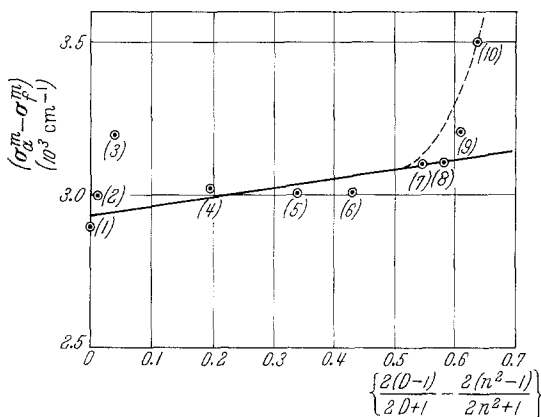

Fig. 3. $(\sigma_a^m - \sigma_f^m)$ vs. $\left[\frac{2(D-1)}{2D+1} - \frac{2(n^2-1)}{2n^2+1} \right]$ relation for car-bazole.

Solvent: (1) cyclohexane and n-hexane; (2) benzene; (3) dioxane; (4) chloroform; (5) n-butylacetate; (6) methylacetate; (7) n-butyl-alcohol; (8) ethylalcohol; (9) acetonitrile; (10) water
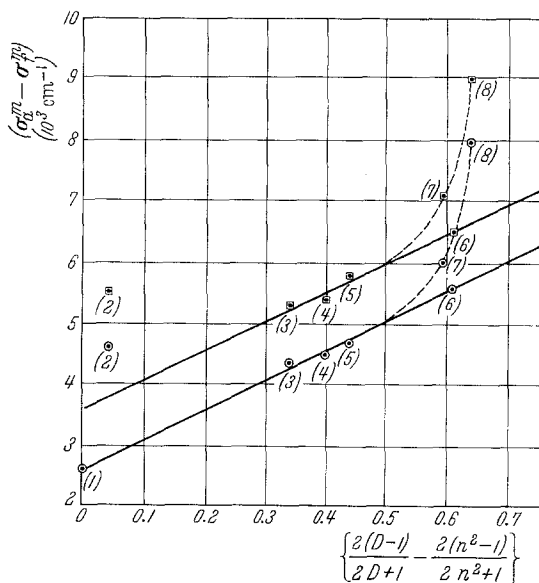

Fig. 4. $(\sigma_a^m - \sigma_f^m)$ vs. $\left[\frac{2(D-1)}{2D+1} - \frac{2(n^2-1)}{2n^2+1} \right]$ relation for indole

$\boxdot$: σ_a^m value is that of ^1L_a, $\odot$: σ_a^m value is that for the second peak of ^1L_b (the first is the lowest frequency peak)

Solvent: (1) cyclohexane and nh-exane; (2) dioxane; (3) n-butyl-acetate; (4) ethylacetate; (5) dichloroethane; (6) acetonitrile; (7) ethanol; (8) water

values can be evaluated as follows assuming $R \sim 4$ Å for carbazole and $R \sim 3$ Å for indole: carbazole: $1 \sim 1.5\ D$, indole: $\sim 5\ D$.

The $\Delta \vec{\mu}$ value for carbazole is rather small compared with that of indole.
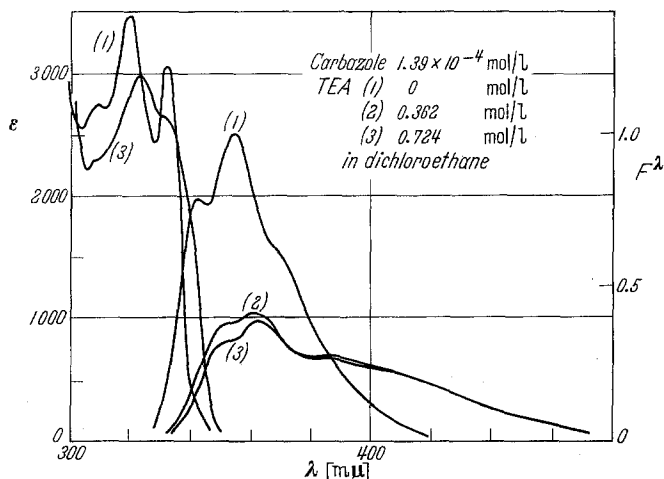

Fig. 5.
Change of the fluorescence and absorption spectra of carbazole in dichloroethane caused by the addition of TEA

However, this fact does not necessarily mean that the decrease of the electron density on nitrogen in the fluoerscent state of carbazole is very small, in view of the red shift of the fluorescence and absorption spectra caused by the hydrogen
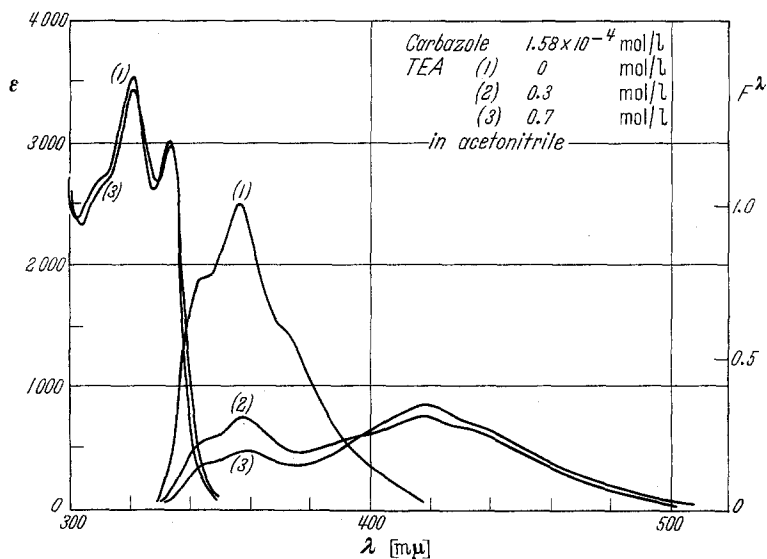

Fig. 6.
Change of the fluorescence and absorption spectra of carbazole in acetonitrile caused by the addition of TEA

bonding and the proton dissociation in the fluorescent state as described in I. Moreover, in some polar solvents such as dichloroethane and acetonitrile, the hydrogen bonded complex of carbazole and TEA seems to shift to an ion-pair in

the excited equilibrium state from which the fluorescence transition occurs, in view of the very large fluorescence spectral shifts as indicated in Fig. 5 and 6. In the case of the acetonitrile solution there might be the possibility that the ion-pair is dissociated during the lifetime of the excited state.

On the other hand, in the case of the acetonitrile solution of the excited 2-naphthylamine, we can observe neither the ion-pair formation with TEA nor the ionic dissociation, although $\Delta \vec{\mu} \simeq 3.5\ D$ for 2-naphthylamine [16].

Thus, it seems to be quite plausible that the decrease of the electron density on nitrogen in the fluorescent state of carbazole is not small. Because of the C_{2v} symmetry, this molecule has nonvanishing dipole moment only along the short molecular axis in contrast to the case of indole and naphthylamines. This fact is probably the main cause for the small $\Delta \vec{\mu}$ value of carbazole.

In contrast to the ^1L_b band, the ^1L_a band of carbazole is affected only slightly by the hydrogen bonding interaction. Moreover, the replacement of the >N-H hydrogen by alkyl group causes a large red shift of ^1L_b band but only a small shift of ^1L_a band. These facts may be closely related to the behaviours of the ^1L_b and the ^1L_a band of biphenyl, respectively, caused by the interaction with the >N-H group, as it has been described already.

III. Theoretical Studies on the Electronic Structures and Discussions

The method developed by LONGUET-HIGGINS and MURRELL [8] can be used for the calculation based on the model described in II.

If the π-MO's of the aromatic hydrocarbon residue are written $\psi_1 \cdots \psi_n$ from the lowest occupied to the highest vacant orbitals and that of the >N-H group θ, then the energy of the charge transfer (CT) configuration ($^1\chi_{sk}$) which arise from the transfer of one electron from θ to a vacant orbital ψ_k, is given by:

$$\langle {}^1\chi_{sk} \mid \mathscr{H} \mid {}^1\chi_{sk} \rangle = \varepsilon_k - \varepsilon_s - \langle \theta(1)\,\psi_k(2) \mid G_{12} \mid \theta(1)\,\psi_k(2) \rangle \qquad (2)$$

where ε_k and ε_s are orbital energies of ψ_k and θ respectively, and ψ_k's are linear combinations of 2pπ AO's $\varphi_1 \cdots \varphi_n$,

$$\psi_k = \sum_\mu c_{k\mu}\, \varphi_\mu. \qquad (3)$$

G_{12} is the two-electron operator, e^2/r_{12}, r_{12} being the inter-electronic distance. ε_s will be given to a good approximation, by the observed ionization potential of ammonia [20]. The difference between the observed and the calculated value of the electron affinity of benzene, $\Delta A = A_{\text{obs.}}^B - A_{\text{calc}}^B$ [12], has been added to the calculated values of ε_k.

With neglect of differential overlap,

$$\langle \theta(1)\,\psi_k(2) \mid G_{12} \mid \theta(1)\,\psi_k(2) \rangle \simeq \sum_\mu c_{k\mu}^2\, \gamma_{s\mu}$$

$$\gamma_{s\mu} = \langle \theta(1)\,\varphi_\mu(2) \mid G_{12} \mid \theta(1)\,\varphi_\mu(2) \rangle. \qquad (4)$$

The matrix elements of the interactions between the CT configurations and various local configurations in the aromatic hydrocarbon residue can be evaluated from the following formulas,

$$\langle {}^1\chi_{sk} \mid \mathscr{H} \mid {}^1\chi_{jl} \rangle = -\delta_{kl} \langle \theta(1) \mid H(1) \mid \psi_j(1) \rangle \qquad (5)$$

where δ_{kl} is Kronecker's delta and H is the core Hamiltonian.

$$\langle {}^1\chi_{sk} \,|\, \mathscr{H} \,|\, \chi_0\rangle = \sqrt{2}\, \langle \theta\,(1) \,|\, H\,(1) \,|\, \psi_k\,(1)\rangle \tag{6}$$

where χ_0 is the ground configuration.

$$\langle {}^1\chi_{sk} \,|\, \mathscr{H} \,|\, {}^1\chi_{sl}\rangle = -\,\langle \theta\,(1)\,\psi_k\,(2) \,|\, G_{12} \,|\, \theta\,(1)\,\psi_l\,(2)\rangle$$

$$= -\sum_\mu c_{k\mu}\,c_{l\mu}\,\langle \theta\,(1)\,\theta_\mu\,(2) \,|\, G_{12} \,|\, \theta\,(1)\,\varphi_\mu\,(2)\rangle. \tag{7}$$

It is assumed that,

$$\langle \theta\,(1) \,|\, H\,(1) \,|\, \psi_j\,(1)\rangle \simeq \sum_r c_{jr}\,\langle \theta\,(1) \,|\, H\,(1) \,|\, \varphi_r\,(1)\rangle = \sum_r c_{jr}\,\beta^c, \tag{8}$$

the substituent being attached to the r-th carbon atom.

Carbazole. — Wave functions and energies for the ground state as well as for the excited states of planar biphenyl calculated by Mataga [17] were used. In this semiempirical ASMO CI calculation [17] with zero differential overlap apprxoimation, Hückel MO's were used and the core resonance integral $\beta_{\mu\nu}$ was taken into account only for the nearest neighbours and neglected for more distant neighbours: $\beta = -2.39$ eV for all the nearest neighbours. The electron repulsion integrals were evaluated by the same method as used before [11]. The state functions and energies calculated in this way are given in Tab. 1.

Table 1. *State functions, energies and oscillator strengths for planar biphenyl (singlets)*

Symmetry	State Function	E(eV)	f
A_{1g}	χ_0	0	—
$B_{3u}\,(L_a)$	$0.9933\,\chi_{67} + 0.0815\,\chi_{58} + 0.0819\,\chi_{49}$	4.800	1.02
$B_{1u}\,(L_b)$	$(\chi_{68} - \chi_{57})/\sqrt{2}$	5.013	0
B_{2g}	$(\chi_{47} - \chi_{69})/\sqrt{2}$	5.269	0
B_{2g}	$(\chi_{47} + \chi_{69})/\sqrt{2}$	6.234	0
$B_{1u}\,(B_b)$	$(\chi_{68} + \chi_{57})/\sqrt{2}$	6.387	1.25
$B_{3u}\,(B_a)$	$0.1183\,\chi_{67} - 0.7588\,\chi_{58} - 0.6405\,\chi_{47}$	6.466	1.41

The angle C_5NC_5, (see Fig. 7) was assumed to be 120° and the core resonance integral in (8) between N and C_5 was taken to be -2.0 eV. This value of the core resonance integral seems to be appropriate in view of the result of our previous study [16]. The $\gamma_{s\mu}$ values in (4) were evaluated in two different ways as follows.
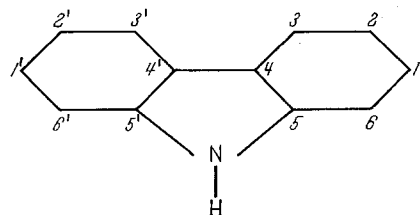
a) The formula [11],

$$\gamma_{s\mu} = e^2/(a_{CN} + R_{s\mu}) \tag{9}$$

was used, where $a_{CN} = 1.042$ A. This a_{CN} value is the harmonic mean of the a value for carbon and that for the mono-positive nitrogen ion in the trigonal hybrid state.

Fig. 7. The numbering of atoms in carbazole

b) For γ_{N4} and γ_{N5}, the formula,

$$\gamma_{s\mu} = a\,R_{s\mu}^2 + b\,R_{s\mu} + c \tag{10}$$

was used, where $a = 0.32$, $b = -3.3978$, $c = 12$ and the last value was determined by using the γ value for the mono-positive nitrogen calculated by Brown and

HEFFERNAN [3] by the VESCF method. For the evaluation of the other $\gamma_{s\mu}$'s, the bipolar expansion formula proposed by PARR [18] was used, i. e.,

$$\gamma_{s\mu} \simeq (a_0 / R_{s\mu}) - 6 (Z_N^2 + Z_C^2) (a_0 / R_{s\mu})^3 / (Z_N^2 \cdot Z_C^2) + 324 (a_0 / R_{s\mu})^5 / (Z_N^2 \cdot Z_C^2) \quad (11)$$

where a_0 is the Bohr radius and $Z_N = 3.9$, $Z_C = 3.25$.

The energy matrices calculated with approximation (a) are (in unit of eV):

For A_1 symmetry:

$$
\begin{array}{ccccc}
\chi_0 & L_b & B_b & \chi_{s7} & \chi_{s9} \\
\end{array}
$$
$$
\begin{pmatrix}
0 & 0 & 0 & -1.6924 & -2.0 \\
 & 5.0129 & 0 & 1.0 & 0 \\
 & & 6.3874 & -1.0 & 0 \\
 & & & 6.0164 & 0.3865 \\
 & & & & 7.0720
\end{pmatrix}
$$

For B_1 symmetry:

$$
\begin{array}{ccc}
L_a & B_a & \chi_{s8} \\
\end{array}
$$
$$
\begin{pmatrix}
4.7991 & 0 & -0.1152 \\
 & 6.4665 & 1.0730 \\
 & & 7.0294
\end{pmatrix}
$$

The electronic state functions, energies and the oscillator strengths for the transitions from the ground state to excited states are given in Tab. 2.

The observed spectra of carbazole in cyclohexane show an absorption band with moderate intensity at 3.9 eV, a strong band at 4.27 eV and the other more or less strong bands at ca. 5 eV and 5.32 eV, respectively.

Table 2. *State functions, energies and oscillator strengths for carbazole (singlets)**

State Function	E(eV)	f
Approximation (a)		
Ψ_0 $0.9453\,\chi_0$ $-0.0388\,L_b$ $+0.0315\,B_b$ $+0.2292\,\chi_{s7}$ $+0.2263\,\chi_{s9}$	-0.8892	—
Ψ_1 $0.1283\,\chi_0$ $+0.7811\,L_b$ $-0.2575\,B_b$ $-0.5279\,\chi_{s7}$ $+0.1684\,\chi_{s9}$	4.3371	0.13
Ψ_2 $0.9961\,L_a$ $-0.0473\,B_a$ $+0.0739\,\chi_{s8}$	4.7906	1.02
Ψ_3 $0.0825\,L_a$ $+0.7911\,B_a$ $-0.6060\,\chi_{s8}$	5.6446	0.58
Ψ_4 $0.0528\,\chi_0$ $-0.5631\,L_b$ $-0.6776\,B_b$ $-0.4227\,\chi_{s7}$ $+0.2056\,\chi_{s9}$	5.7636	$0{,}67$
Ψ_5 $0.0791\,\chi_0$ $+0.2032\,L_b$ $-0.6142\,B_b$ $+0.4176\,\chi_{s7}$ $-0.6330\,\chi_{s9}$	7.0673	0.66
Approximation (b)		
Ψ_0 $0.9340\,\chi_0$ $-0.0424\,L_b$ $+0.0345\,B_b$ $+0.2544\,\chi_{s7}$ $+0.2447\,\chi_{s9}$	-0.9850	—
Ψ_1 $0.1443\,\chi_0$ $+0.5907\,L_b$ $-0.2700\,B_b$ $-0.6835\,\chi_{s7}$ $+0.3002\,\chi_{s9}$	3.8556	0.15
Ψ_2 $0.9729\,L_a$ $-0.1239\,B_a$ $+0.1952\,\chi_{s8}$	4.7760	0.90
Ψ_3 $0.2295\,L_a$ $+0.6219\,B_a$ $-0.7487\,\chi_{s8}$	5.1749	0.40
Ψ_4 $0.0056\,\chi_0$ $+0.7721\,L_b$ $+0.4058\,B_b$ $+0.3656\,\chi_{s7}$ $-0.3246\,\chi_{s9}$	5.4864	0.20
Ψ_5 $0.1723\,\chi_0$ $+0.0657\,L_b$ $-0.7341\,B_b$ $+0.0992\,\chi_{s7}$ $-0.6459\,\chi_{s9}$	6.5225	1.16

* Only the six lower states are shown among the eight calculated states.

Although the agreement between the calculated and the observed excitation energies themselves is not very good, the calculated results interpret satisfactorily the general aspect of the observed spectra. The transitions $\Psi_0 \to \Psi_1$ and $\Psi_0 \to \Psi_2$ correspond quite well to the observed bands at 3.9 eV and 4.27 eV, respectively.

The state function Ψ_1 shows that the very weak ^1L_b band of biphenyl is modified considerably in carbazole because of the mixing with χ_{s7} and also with ^1B_b. However, the contribution from the CT configuration is very small in Ψ_2 compared with that in Ψ_1. On the basis of these results, we can interpret the

effects of the hydrogen bonding and the replacement of the $>N\text{-}H$ hydrogen by alkyl group on the ^1L_b and the ^1L_a band of carbazole as described in II. Namely, both the alkyl replacement and the hydrogen bonding lower the energy of the CT configuration and increase the core resonance integral between the carbon and nitrogen. Accordingly, ^1L_b of biphenyl mixed with CT configuration is lowered considerably, whereas the lowering of ^1L_a may be quite small because of the very small interaction with CT configurations.

The theoretical expression for $\Delta\vec{\mu}$ in terms of the state function, Ψ, is given by:

$$\Delta\vec{\mu} = \langle\Psi_1|M|\Psi_1\rangle - \langle\Psi_0|M|\Psi_0\rangle, \quad M = \sum_t e_t\, r_t \tag{12}$$

where e_t and r_t are the charge and the position vector of t-th particle, respectively. The calculated values of $\Delta\vec{\mu}$ are ~ 0.69 D in the case of approximation (a) and ~ 2.43 D in the case of approximation (b). These values are fairly close to the observed $\Delta\vec{\mu}$ value and the approximation (a) seems to be more satisfactory in the present case.

Thus, the $\Delta\vec{\mu}$ value of carbazole is rather small, although the probability density of χ_{87} is much larger in Ψ_1 than in Ψ_0. This fact is in a satisfactory agreement with the observed results.

Indole. In order to make a similar calculation to the case of carbazole, it is necessary to have the wave functions of styrene. An analogous calculation to the case of biphenyl, using the Hückel MO's can interpret satisfactorily the general feature of the observed spectra of styrene, as indicated in the Appendix. However, the calculation using the simple Hückel MO's in this case seems to be not so good approximation as in the case of carbazole. Therefore, we do not attempt here to make a similar calculation for indole. Nevertheless, we can make a plausible interpretation on the electronic structure of the excited indole molecule as follows.

The calculation of the energy of the lowest CT configuration χ_{85} gives 5.3 eV, using approximation (a). This value is quite close to both of the observed and the calculated excitation energy of styrene from the ground state to the ^1L_a state (see Appendix). Accordingly, the contribution of χ_{85} in the ^1L_a state of indole seems to be very large. Furthermore, the interaction with the surrounding polar solvent molecules probably increases the probability density of χ_{85} in ^1L_a state during the lifetime of the excited state, and this probability density may be larger than that of ^1L_a of styrene, in the excited equilibrium state of indole in solution.

Appendix

The calculated and observed spectra of styrene (singlets)

State Function	$E_{calc.}$ (eV)	f	$E_{obs.}$ (eV)	obsd. intensity
$\Psi_0 = \chi_0$	0	—	0	—
$\Psi_1\,(L_b) = (\chi_{46} - \chi_{35})/\sqrt{2}$	4.789	0	4.21	weak
$\Psi_2\,(L_a) = \chi_{45}$	4.844	1.07	5.1	strong
$\Psi_3\,(B_b) = (\chi_{46} + \chi_{35})/\sqrt{2}$	5.998	0.56	5.8	strong
$\Psi_4\,(B_a) = \chi_{35}$	6.573	0.62	7.2	strong

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