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Electronic Structures of Excited States of Benzoquinolines1)

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Measurements of the dipole moments and acidity constants in the lowest excited singlet states for benzo[*c*]quinoline, benzo[*f*]quinoline, and benzo[*h*]quinoline have been carried out by spectrophotometry. The electronic structures of excited states have been calculated by using the semi-empirical SCF-π-MO CI method, which allows for a bond order-bond length relationship at each iteration. The experimentally-determined dipole moments and acidity constants can not be correlated to the calculated electronic structures of the Franck-Condon states, but they can be correlated to the calculated structures of the equilibrium states for the lowest excited singlet states of three isomeric benzoquinolines.

Many phenomena occurring in the electronically-excited states of molecules, such as photochemical reactions, are dependent on the changes in the electronic structures. Electronic excitation in molecules leads to a new electron density distribution and, consequently, to changes in the dipole moment and in the reactivity. For example, aminonaphthalenes, which are weak bases in the ground state, lose their basic properties in the lowest excited-singlet state and become weak acids, dissociating in alkaline solutions.2) Furthermore, some unusual photochemical reactions of aromatic substitution seem to correlate with the electron-density distribution in the excited states.3,4) Numerous quantitative data are already known on the protolytic equilibria5) and on the dipole moments6) of molecules in their excited states. A comparison of the two sets of experimental data has, however, been done only exceptionally from the point of view of the electron-density distribution in the excited molecules.7)

It is the purpose of this paper to determine experimentally the acidity constants and dipole moments in the lowest excited singlet states of benzo[*c*]quinoline (I), benzo[*f*]quinoline (II), and benzo[*h*]quinoline (III) and to investigate the possible correlation between the experimental results and the theoretical π-electron indices.

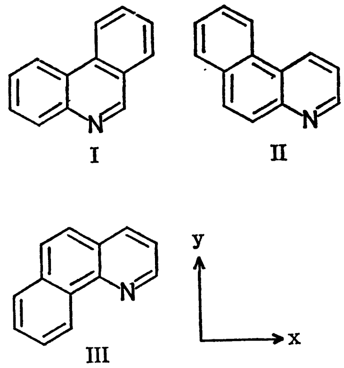

Fig. 1. Numbering of benzoquinolines and choice of axes.

Experimental

Materials. Substance I was obtained from the Dōjindō Chemicals Co. It was purified by recrystallization from light petroleum and by subsequent sublimation *in vacuo*.8) II and III were purchased from the Tokyo Kasei Co. According to the procedure described by Kanda and Shimada,9) the purification was done in the same way for both compounds. The solvents used were carefully purified according to the descriptions in Ref. 10.

Measurements. The dielectric constants were determined with a home-made resonance-method apparatus which used the electric circuit reported by Nakagawa.11) A dielectric-constant-measurement cell with cylindrical platinum electrodes was used. The refractive indices were measured by means of a Pulfrich refractometer. The static dielectric constant (ε) and the refractive index (n_D) at the sodium D line of the solvents agreed with the values cited in Ref. 10. The densities of the solutions were measured by the use of a pycnometer12) for volatile liquids.

The absorption spectra were measured with a Hitachi EPS-3T spectrophotometer. The fluorescence spectra were recorded on a Shimadzu RF-502 spectrophotometer. The wave numbers of the emission-band maxima were determined from the emission spectra, as corrected for the spectral sensitivity of the instrument. The concentration of I, II, and III was kept less than 10^{-5} mol/l for all solutions prepared, so that the system was free from any undesired concentration quenching. The measurements were made on deaerated samples at 20 °C.

Calculation

The method used in predicting the energetically most favorable nuclear arrangement for an electronically-excited state of a conjugated molecule, which is assumed to be planar, is a modified version13) of the semi-empirical SCF MO CI method used in combination with the variable bond-length technique, which has proved to be quite successful in predicting the ground-state electronic structures of a variety of conjugated molecules.14)

Assuming a certain nuclear arrangement for a conjugated molecule, we carry out the SCF MO CI calculation in the framework of the Pariser-Parr-Pople approximation.15,16) Using the wave function for an excited state obtained after the inclusion of the configuration mixing all the singly-excited states, we then calculate the bond length for the excited state by the aid of a suitable bond order-bond length relationship (*vide infra*). The new nuclear arrangement is taken as the geometrical structure for the next SCF MO calculation, and the process is repeated until the bond lengths for the excited state converge.

The one-center repulsion integrals were found from the corresponding valence-state ionization potentials, (W), and electron affinities, (E), by the Pariser-Parr method,15) the W and E being determined from the spectroscopic data using the promotion energies of Hinze and Jaffé.[17] The two-center repulsion integrals were estimated by using the Mataga-Nishimoto method.[18]

Resonance integrals were included only between nearest neighbors. These resonance integrals were estimated by using the Wolfsberg-Helmholtz overlap approximation:[19]

$$\beta_{\mu\nu} = -0.5K_{\mu\nu}(W_\mu + W_\nu)S_{\mu\nu} \tag{1}$$

where the overlap integral, *S*, was calculated from Roothaan's formulas[20] using the effective nuclear charges of 3.25 and 3.90 for carbon and nitrogen respectively.

Only the nearest-neighbor two-center integrals were allowed to change, using a bond distance calculated by the aid of this relationship:

$$r_{\mu\nu} = \alpha - 0.186p_{\mu\nu} \tag{2}$$

where p is the π-bond order. The nonbonded distances were calculated assuming the ring to be regular and were kept constant for the sake of simplicity.

The values of K in Eq. (1) and α in Eq. (2) were determined as follows.

C–N Bond. The best value of K for the C–N bond was determined from the β value so adjusted that the theoretical excitation energies and intensities of the reference molecule, *s*-triazine,[21,22] which were calculated using a bond distance obtained by the X-ray technique[23] in the framework of the SCF MO CI method, might reproduce the experimental excitation energies and intensities of this molecule. We thus obtained $K=0.97$. From the bond order of the C–N bond that was calculated by using the best value of K obtained by means of the SCF MO CI method, the bond order-bond length relationship for this bond was determined. This procedure yielded $\alpha=1.459$ Å.

C–C Bond. The value of α which had been proposed by Nakajima and Katagiri,[24] was used. The value of K for this bond was determined from the value so adjusted as to reproduce the experimental excitation energies of such reference molecules as butadiene and naphthalene.[25–27] We thus obtained $K=0.85$.

Using these values for K and α, we calculated the transition energies and intensities of pyridine and pyrazine. The calculated transition energies and intensities of these molecules are in good agreement with the experimental values.[28,29]

The dipole moments of the ground and excited states for I, II, and III are calculated by using the moment due to the C–N localized bonds, 1.77 D,[30] and the C–H moment, 0.4 D.[31]

Results and Discussion

Ground-state Dipole Moments, $\vec{\mu}_0$. The dipole moment, $\vec{\mu}_0$, of I has already been measured in benzene solutions.[8] The dipole moments, $\vec{\mu}_0$, of II and III were measured in carbon tetrachrolide by the use of the ordinary Halverstadt-Kumler method.[32] The molecular refractions, $[R_L]_D$, were obtained from this expression: $[R_L]_D = M[r_2 + (r_{12} - r_2)/\omega_1]$. Here, ω_1 is the weight fraction of the solute, whose molecular weight is M, and r_2 and r_{12} are the specific refractions of the solvent and the solution respectively. These results are summarized and compared with the calculated results in Table 1. The predicted values agree well with the experimental values.

TABLE 1. GROUND-STATE DIPOLE MOMENTS $\vec{\mu}_0$ AND MOLECULAR REFRACTIONS $[R_L]_D$ OF BENZOQUINOLINES

Molecule	$[R_L]_D$ (cm^3)	μ_0 (D)[a]	
		Calcd	Obsd
I	60.82[b]	2.74 (75°)	2.39[b]
II	60.51[c]	2.52 (93°)	2.19[c]
III	60.32[c]	2.28 (91°)	1.81[c]

a) Numbers in parenthesis represents the angle that the dipole moment makes with X-axis in the counterclockwise sense in the coordinate system of Fig. 1. b) Measured in benzene. See Ref. 8. c) Measured in carbon tetrachloride.

Excited-state Dipole Moments, $\vec{\mu}_1$. The difference between the dipole moments in the lowest singlet excited state ($\vec{\mu}_1$) and the ground state ($\vec{\mu}_0$), $|\Delta\vec{\mu}_1| = |\vec{\mu}_1 - \vec{\mu}_0|$, can be estimated by measuring the wave numbers of the band maxima of the fluorescence (ν_f^m) and the absorption (ν_a^m) spectra in various solvents and by using the following equation:[33]

$$\begin{aligned} \nu_a^m - \nu_f^m &= \text{Const.} + F(\varepsilon, n_D)\delta \\ F(\varepsilon, n_D) &= \frac{\varepsilon - 1}{\varepsilon + 2} - \frac{n_D^2 + 1}{n_D^2 + 2} \\ \delta &= \frac{2|\Delta\vec{\mu}_1|^2}{a^3hc} \end{aligned} \tag{3}$$

where a is the cavity radius in Onsager's theory[34] of the reaction field.

The observed ($\nu_a^m - \nu_f^m$) *versus* $F(\varepsilon, n_D)$ relations are shown in Figs. 2, 3, and 4. The straight lines in the figures were obtained by the least-squares method. The $\Delta\vec{\mu}_1$ values for I, II, and III were determined by using the slopes (A) of these lines.

These results are summarized and compared with the theoretical results in Table 2. Table 2 shows that the difference between the dipole moments for the equilibrium state of the lowest singlet excited state ($\vec{\mu}_E$) and for the ground state ($\vec{\mu}_0$), $|\Delta\vec{\mu}_E| = |\vec{\mu}_E - \vec{\mu}_0|$, is in better agreement with the experimental $|\Delta\vec{\mu}_1|$ value than the difference between the dipole moments for the Franck-Condon state of the lowest excited state ($\vec{\mu}_F$) and for the ground state, $|\Delta\vec{\mu}_F| = |\vec{\mu}_F - \vec{\mu}_0|$. This agreement of the experimental and computed results on the dipole moments indicates a good approximation of the electronic structures for the equilibrium states of the lowest singlet excited states.

Excited Singlet-state Acidity Constants. The pK_a values in the ground states (S_0) were previously meas-

TABLE 2. EXCITED-STATE DIPOLE MOMENTS OF BENZOQUINOLINES[a)]

Molecule	a(Å)[b)]	A (cm^{-1})	Calcd (D) $\vec{\mu}_F$	Calcd (D) $\lvert\Delta\vec{\mu}_F\rvert$	Calcd (D) $\vec{\mu}_E$	Calcd (D) $\lvert\Delta\vec{\mu}_E\rvert$	Exptl. (D) $\lvert\Delta\mu_1\rvert$
I	3.91[c)]	193	3.84 (137°)	3.51	3.34 (97°)	1.30	0.77
II	3.86[d)]	397	4.29 (127°)	2.53	3.75 (120°)	1.89	1.24
III	3.94[d)]	268	3.18 (155°)	2.99	2.66 (127°)	1.57	1.08

a) Numbers in parenthesis represent the angle that the dipole moment makes with the positive X-axis in the counterclockwise sense in the coordinate system of Fig. 1. b) Estimated from the apparent molal volume ϕ_V. The ϕ_V is defined by the relation, $\phi_V = 1000(d_2-d_{12})/(m_1 d_2 d_{12}) + M_1/d_{12}$, where d_2 and d_{12} are the densities of the solvent and the solution of molality m_1 of the solute having molecular weight M_1, respectively. c) Estimated from the tabulated data of Ref. 8. d) Measured in carbon tetrachloride.

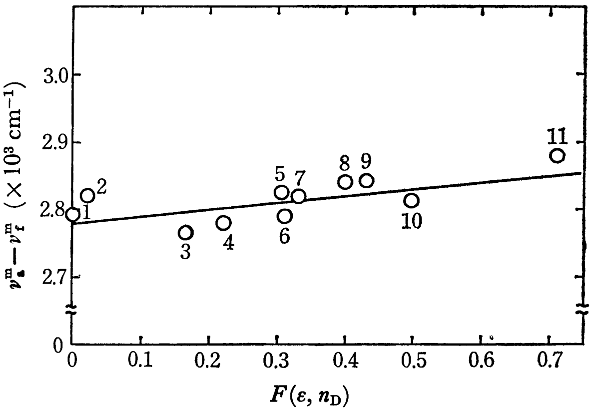

Fig. 2. The plot of $(\nu_a^m - \nu_f^m)$ against $F(\varepsilon, n_D)$ for benzo[*c*]quinoline. Here numbers denote the solvents as (1): cyclohexane, (2): carbon tetrachloride, (3): *n*-butyl ether; (4): anisole, (5): isoamyl acetate, (6): ethyl ether, (7): *n*-butyl acetate, (8): ethyl acetate, (9): methyl acetate, (10): benzonitrile, (11): acetonitrile.

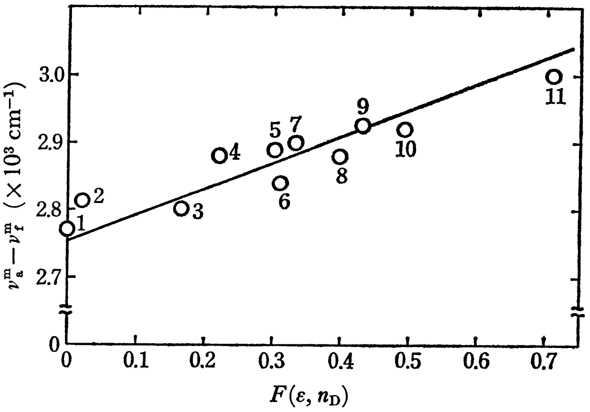

Fig. 3. The plot of $(\nu_a^m - \nu_f^m)$ against $F(\varepsilon, n_D)$ for benzo[*f*]quinoline. The numbers are the same as described in Fig. 2.

ured at 20 °C in an aqueous ethanol solution (50 vol. percent ethanol solution).[35)] The pK_a (S_1) values were estimated by means of the Förster cycle, as in the following relation:[2)]

$$\mathrm{p}K_a(S_0) - \mathrm{p}K_a(S_1) = \frac{\Delta E_{HB} - \Delta E_B}{2.303\,RT} \qquad (4)$$

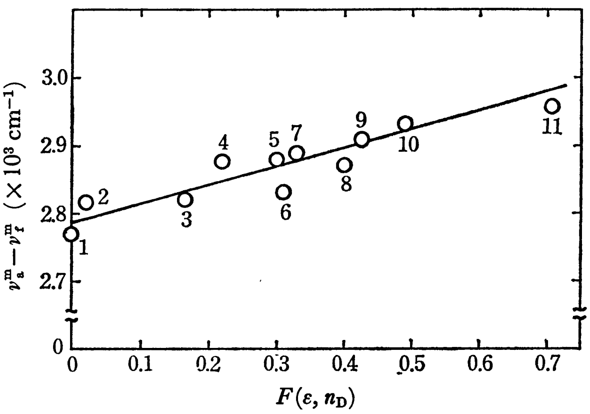

Fig. 4. The plot of $(\nu_a^m - \nu_f^m)$ against $F(\varepsilon, n_D)$ for benzo[*h*]quinoline. The numbers are the same as described in Fig. 2.

where ΔE_{HB} and ΔE_B are the energy differences between the ground and excited states of the protonated and unprotonated molecules respectively. The p$K_a(S_0)$ and p$K_a(S_1)$ denote the pK_a values in S_0 and the excited state (S_1) respectively. R and T are the gas constant and the absolute temperature respectively. In the present work, the energy difference between the S_0 and S_1 states was evaluated by means of the absorption and fluorescence spectra.

The absorption and fluorescence spectra of I, II, and III and of their conjugated acids were measured at 20 °C in an aqueous ethanol solution (50 vol. percent ethanol solution) for the unprotonated molecules (B) and in an aqueous ethanol solution with sulfuric acid added for the protonated molecules (BH$^+$). In Table 3, the p$K_a(S_1)$ values obtained by the application of the Förster cycle are collected, along with the pK_a (S_0) values.

It has been shown that there is a good correlation between the pK_a value of heterocyclic molecules containing a nitrogen atom and the electron density (q_N) of the atom.[36)] In a series of molecules where the molecular skeleton changes, the relation between pK_a and q_N is much less direct. Besides q_N, the interactions with all the π-electron charges, located at various distances from the reactive center, also influence the pK_a values.[37,38)] A large q_N value may be compensated for by the influence of positive charges located on neighboring carbon atoms. For the ground

TABLE 3. $S_1 \leftarrow S_0$ TRANSITION ENERGIES, p$K_a(S_0)$, AND p$K_a(S_1)$ VALUES

Molecule	Absorption (eV)		Fluorescence (eV)		0-0 Transition energy (eV)[a]		p$K_a(S_1)$	p$K_a(S_0)$[b]
	B	BH$^+$	B	BH$^+$	B	BH$^+$		
I	3.58	3.37	3.53	3.06	3.56	3.22	9.16	3.36
II	3.57	3.38	3.52	2.89	3.54	3.14	10.2	3.90
III	3.57	3·41	3.53	2.90	3.55	3.16	10.7	3.15

a) Evaluated by means of the absorption and fluorescence spectra. b) Measured by using the potentiometric method. See Ref. 35.

TABLE 4. CALCULATED ELECTRON DENSITIES (q_N) AND INTERACTION TERMS ($\sum_p Q_p(l_N l_N|pp)$) (eV) OF VARIOUS STATES

Molecule	S_0 state		S_1 state			
			Frack-Condon		Equilibrium	
	q_N	$\sum_p Q_p(l_N l_N|pp)$	q_N	$\sum_p Q_p(l_N l_N|pp)$	q_N	$\sum_p Q_p(l_N l_N|pp)$
I	1.234	−1.71	1.285	−2.28	1.262	−2.01
II	1.238	−1.73	1.280	−2.27	1.260	−2.05
III	1.237	−1.70	1.288	−2.33	1.263	−2.07

state, Nakajima and Pullman[37] have proposed this relationship between the pK_a values and the interactions:

$$\mathrm{p}K_a \propto \sum_p Q_p(l_N l_N|pp) + \text{Const.} \qquad (5)$$

In Eq. (5), Q_p is the formal charge on the p atom and $(l_N l_N|pp)$ is the Coulomb repulsion integral between the lone-pair electrons of the nitrogen atom and the π-electron on the p atom. The $(l_N l_N|pp)$ integral was calculated from Roothaan's formulas[20] using the effective nuclear charges of 3.25 and 3.90 for carbon and nitrogen respectively.

The calculated q_N and $\sum_p Q_p(l_N l_N|pp)$ values for the S_0 and S_1 states are listed in Table 4. From Tables 3 and 4, no relationship can be found between the q_N and the variation in the pK_a values of both the states. In the S_0 state and the equilibrium state of the S_1 state, however, it seems that there is a good correlation between the pK_a value and the first term in Eq. (5) for both the states. Such a correlation can not be found in the Franck-Condon state of the S_1 state.

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