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Ultraviolet Studies and Fluorescence Quenching of Some Aromatic Primary Amines

Samaresh Mukherjee
Department of Physical Chemistry, Indian Association for the Cultivation of Science,
Jadavpur, Calcutta 700 032, India

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The fluorescence quenching of *o*-aminobenzoic acid, 1-naphthylamine, aniline, *p*-toluidine, *m*-toluidine, and *N,N*-dimethylaniline by 2-hydroxy-5-methyl-1,3-benzenedicarbaldehyde (**VII**) was studied. The equilibrium constant of hydrogen bonding in the ground state was evaluated from the absorption spectral change for various donor–acceptor (D–A) pairs. The rate constants of hydrogen-bond formation as well as decomposition in the excited state were evaluated in the case of several donor–acceptor pairs from fluorescence intensity measurements. In addition, the mechanism of fluorescence quenching and absorption spectral shift when **VII** acted as a quencher/proton donor (D) was discussed on the basis of charge-transfer and hydrogen-bond interaction.

Light absorption brings out rather strong change in some molecular properties in the excited state and the proton dissociation, energy transfer or hydrogen-bond formation of aromatic hydroxy and amino compounds occurs far easily in the excited state than in the ground state.[1–5] Apart from spectral shift, hydrogen bonding also causes fluorescence enhancement or quenching. The phenomenon of fluorescence quenching particularly has received wide attention.[6–15] It is known that aromatic amines experience a large change in the excited state[16–18] consequently it will be of interest to investigate the effect of various influences on the ground vis-a-vis excited state properties of aromatic amines. The present investigation dealing with interaction of some aromatic primary amines, viz. *o*-aminobenzoic acid (**I**), 1-naphthylamine (**II**), aniline (**III**), *p*-toluidine (**IV**), *m*-toluidine (**V**), and *N,N*-dimethylaniline (**VI**) with a proton donor (D), viz. 2-hydroxy-5-methyl-1,3-benzenedicarbaldehyde (**VII**) in cyclohexane at 300 K was undertaken with the object to study the spectral changes in relation to hydrogen-bonding properties of the molecules in the ground and excited state and probable reaction processes leading to fluorescence quenching.

Experimental

1-Naphthylamine, *o*-aminobenzoic acid, and *p/m*-toluidines were purified by recrystallization followed by vacuum sublimation. Aniline and *N,N*-dimethylaniline were first dried over solid KOH and then distilled over zinc dust. Cyclohexane (Merck, spectroscopic grade) was dried over metallic sodium and distilled fractionally. Proton donor **VII**[19] was received as a gift from department of inorganic chemistry of this institute. All the absorption spectra were recorded with freshly prepared solutions in a Cary 17D spectrophotometer. The fluorescence spectra were recorded in a Perkin-Elmer fluorescence spectrophotometer (Model MP F-44B) using 1 cm stoppered quartz cell at 300 K. Blank runs were made with solvent alone which showed no fluorescence emission at the maximum sensitivity of the instrument in the spectral region of interest.

The fluorescence quantum yield of amines are measured from the corrected area under fluorescence curve relative to that of anthracene[20] in identical conditions. Radiative lifetimes are estimated from integrated absorption spectra using Eq. 1

$$\tau_N = \frac{1.5}{(\bar{\nu}_{\max})^2 \times f}\,, \tag{1}$$

where $f = 4.33 \times 10^{-9} \int \varepsilon \bar{\nu} d\bar{\nu}$, is the oscillator strength of the lowest electronic transition.

Results and Discussion

The change of absorption spectrum caused by hydrogen bonding is shown in Fig. 1 in the case of *o*-aminobenzoic acid (**I**)+2-hydroxy-5-methyl-1,3-benzenedicarbaldehyde (**VII**) system in cyclohexane. Frequency maxima (ν_E in cm^{-1}) and frequency shifts ($\Delta\nu_E$ in cm^{-1}) for the proton acceptor molecules **I** and **II** are given in Table 1. From the observed spectral change, the equilibrium constant K_g of hydrogen-bond formation with proton acceptor molecules for the case **I** and **II** in the ground state can be evaluated by the Ketelaar's method[21] using the Eq. 2.

$$\frac{1}{A_o - A_f} = \frac{1}{[D]} \cdot \frac{1}{A_b - A_f} \cdot \frac{1}{K_g} + \frac{1}{A_b - A_f} \tag{2}$$

In Eq. 2, A_f and A_b denotes the absorbance of free acceptor and the hydrogen-bonded complex respectively and A_o that of a solution of acceptor where the concentration D is [D]. On extrapolating the straightline obtained from $1/(A_o - A_f)$ vs. $1/[D]$ plot to the point where $1/(A_o - A_f) = 0$, K is obtained as $K = -1/[D]$. The association equilibrium constants (K_g) evaluated by linear regression analysis are given in Table 2. It is observed that with gradual increase of [D] the position of the absorption maximum shifts gradually (Fig. 1) and then tends to a constant value above a certain concentration indicating that intermolecular hydrogen bond formation is almost complete as such concentration. Another significant observation is that the oscillator strength (f_b) for

Table 1. Frequencies of Fluorescence Maxima (ν_F in cm^{-1}), Excitation Maxima (ν_E in cm^{-1}), and Measured Oscillator Strengths (f) of Free and Hydrogen-Bonded Molecules in Cyclohexane Solvent at 300 K

System	$f_f^* \times 10^3$	$f_b^* \times 10^3$	f_b^*/f_f^*	ν_F	ν_E	$\Delta\nu_F = F^{b*} - F^{f*}$	$\Delta\nu_E = E^{b*} - E^{f*}$	I_P/eV†
I	58.81	—	—	26316	29851			
I+VII	—	222.56	3.92	25641	28935	−675	−866	
II	79.21	—	—	27027	31446			
I+VII	—	292.33	3.69	26173	30303	−849	−1143	
III				32258	34728			8.64d)
III+VII				32258	34728	0	0	4.34e)
IV				31250	34247			8.14d)
IV+VII				32051	34247	801	0	3.88e)
V				32258	34965			8.27d)
V+VII				32787	34965	529	0	3.96e)
VI				30769	33557			7.14d)
VI+VII				31746	33557	977	0	2.98e)

* The sub- and superscripts "f" and "b" refer to free and bonded species respectively. † The superscripts "e" and "d" refer to I_p(eV), for acceptor molecules in the ground (obtained from NBS, 34, 1969) and excited (calculated) state, respectively.

Table 2. Equilibrium and Rate Constants of Hydrogen Bonding at 300 K

System	K_1/dm^3 mol^{-1}	$\dfrac{\tau K_1(=K_Q)}{(1+\tau' K_2)}$	K_g/dm^3 mol^{-1}	K_e/dm^3 mol^{-1}	K_1/dm^3 ml^{-1} s^{-1}	K_2/s^{-1}
I	3200	1180	265±5	1.74×10^4	2.13×10^{11}	1.22×10^7
II	2000	1106	345±3	8.71×10^4	3.36×10^{11}	0.41×10^7

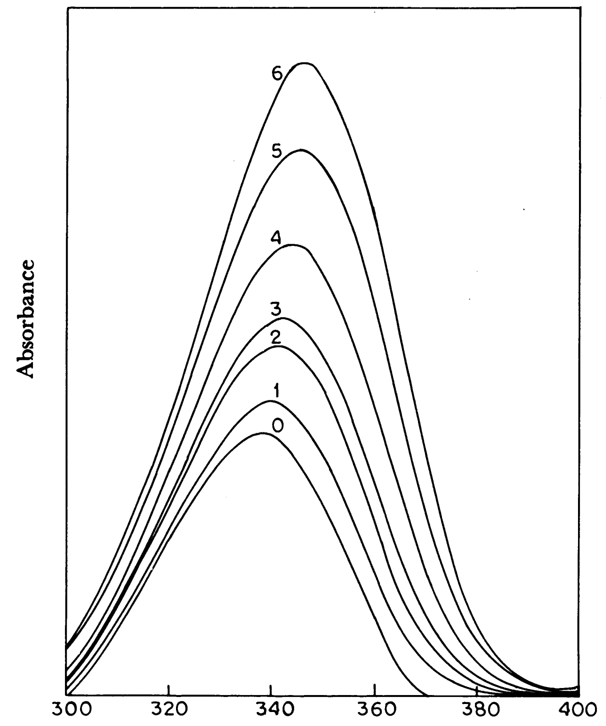


Fig. 1. Absorption spectra of *o*-aminobenzoic acid (**I**)-**VII** (D)-cyclohexane system.
[I] = 4.5×10^{-5} mol dm^{-3}; [D]/mol dm^{-3} 0: 0; 1: 2.95×10^{-5}, 2: 5.7×10^{-5} 3: 8.6×10^{-5}, 4: 1.41×10^{-4}, 5: 1.7×10^{-4}, 6: 2.95×10^{-4}.

bonded molecules is always greater than that (f_f) for free molecules in the case of both **I** and **II**. Thus we see from Table 1 that there is a correlation between the hydrogen-bond formation and the increase in f-values of transition.

The change of fluorescence spectrum caused by hydrogen bonding of the proton donor (**VII**) with aniline (**III**) and *N*,*N*-dimethylaniline (**VI**) in cyclohexane is shown in Fig. 2 and the relevant spectral data are set out in Table 1. At low concentration the quenching of fluorescence by a proton donor in solution follows the classic Stern-Volmer relationship (3)

$$f^0/f = 1 + K_Q[D], \tag{3}$$

where K_Q is called the quenching constant, f is the intensity of fluorescence at the proton donor **VII** concentration, [D], and f^0 is its value without D. The K_Q values evaluated graphically (Fig. 3) using the relation (3) are given in Table 3. By equating the bimolecular rate constant for the quenching reaction (K_1) against the rate of emission it can be shown[22] that $K_Q = K_1\tau$ where τ is the actual mean life of the fluorescence i.e., quantum efficiency (ϕ) × radiative life (τ_N) (see Table 3). Detailed quantitative study of the relative fluorescence yield and life time measurements were also carried out for all the systems. The wave number shifts $\Delta\nu_F$ and $\Delta\nu_E$ of the fluorescence

Table 3. Mean Life of the Fluorescence (τ), Radiative Lifetime (τ_N), Quenching Constant (K_Q), Bimolecular Rate Constant (K_1), and Quantum Yield (ϕ and ϕ_A) of Some Aromatic Amines Acting as Proton Acceptor (A) with Donor **VII** in Cyclohexane at 300 K

System	ϕ	ϕ_A	τ_N/s	τ/s	K_Q/dm^3 mol^{-1}	K_1/dm^3 mol^{-1} s^{-1}
I	0.36	—	2.98×10^{-8}	15.0×10^{-9}	—	—
II	0.31	—	1.92×10^{-8}	5.95×10^{-9}	—	—
III	0.12	0.13	4.92×10^{-8}	5.90×10^{-9}	8.3×10^{2}	1.4×10^{11}
IV	0.041	0.039	4.47×10^{-8}	1.83×10^{-9}	7.5×10^{2}	4.1×10^{10}
V	0.029	0.028	3.6×10^{-8}	0.9×10^{-9}	3.75×10^{2}	4.16×10^{11}
VI	0.26	0.24	3.76×10^{-8}	9.78×10^{-9}	1.20×10^{3}	1.22×10^{11}

Range of [A]: 5.7×10^{-5}—9.8×10^{-5} mol dm^{-3} and [D]: 6.1×10^{-5}—8.5×10^{-3} mol dm^{-3}; K_Q: Values are obtain from Stern-Volmer plots (Eq. 2); ϕ_A^α: Limiting quantum yields of photoreactions obtained from the intercepts of the usual Plots of ϕ_A^{-1} vs. $[D]^{-1}$ (in case where K_Q $[D]<1$) where, ϕ_A is quantum yields for disappearance of amines (see Ref. 11).

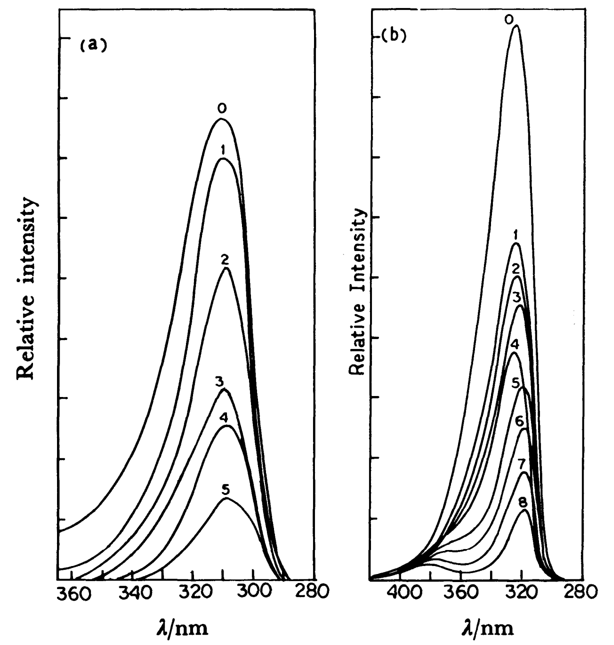


Fig. 2. Fluorescence spectra of (a) aniline (**III**), (b) *N*,*N*-dimethylaniline (**VI**) in mixed **VII** (D)-cyclohexane system.

(a): [**III**] = 1.05×10^{-4} mol dm^{-3}; [D]/mol dm^{-3} 0: 0, 1: 1.14×10^{-4}, 2: 1.71×10^{-4}, 3: 2.28×10^{-4}, 4: 2.85×10^{-4}, 5: 5.02×10^{-4}.

(b): [**VI**] = 1.21×10^{-4} mol dm^{-3}; [D]/mol dm^{-3} 0: 0, 1: 0.65×10^{-4}, 2: 1.06×10^{-4}, 3: 1.48×10^{-4}, 4: 2.13×10^{-4}, 5: 3.19×10^{-4}, 6: 3.48×10^{-4}, 7: 7.5×10^{-4}, 8: 8.5×10^{-4}.

and excitation spectrum respectively due to hydrogen-bond formation are given in Table 1. Of all the proton acceptor studied the spectral shift on hydrogen-bond formation in the excited state $\Delta\nu_f=\nu_b-\nu_f$ (b and f referring to bonded and free molecules respectively) is found to be towards longer wavelength for **I** and **II** (i.e., $\Delta\nu<0$) for **IV** to **VI** towards shorter wavelength. For **III**, however, $\Delta\nu=0$.

While K_g is evaluated by Eq. 2 from the absorption spectral change, the corresponding quantity in the

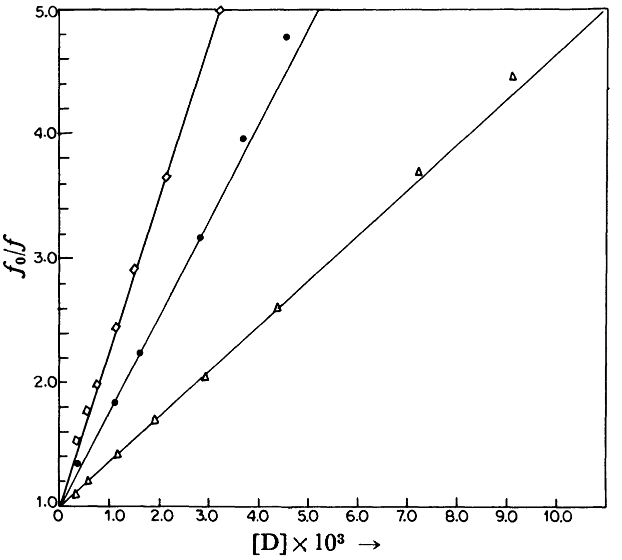


Fig. 3. Stern-Volmer plots for the quenching of acceptor molecules (△) **V**; (●) **IV**; (□) **VI**, by donor **VII**.

excited state, K_e (for **I** and **II**) can be estimated approximately by Eq. 4 assuming the same entropy change due to hydrogen-bond formation in the excited state as well as in the ground state[5]

$$\log K_e = \log K_g + \frac{0.625}{T}\cdot\Delta\nu_a\,. \tag{4}$$

In Eq. 4 $\Delta\nu_a$ is the limiting wave number shift of the absorption spectrum caused by hydrogen bonding and T is the absolute temperature. The values of K_g and K_e estimated in this way at ≈300 K are given in Table 2. It is important to point out here that in all of the systems under consideration quenching occurred, but the spectral shift observed in the ground state and excited state did not occur in the same way. When **I** and **II** were used as acceptor molecules, spectral shift occurred both in the ground and excited states. On the other hand, in the cases of **IV** and **VI**, spectral shift was observed only in the excited state. However, for **III** no

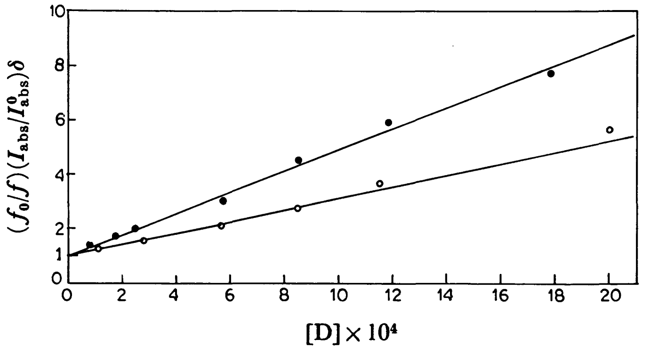


Fig. 4. $(f^0/f)(I^0_{abs})\delta$ vs. [D] relation for (●) **I—VII** and (○) **II—VII** systems in cyclohexane.

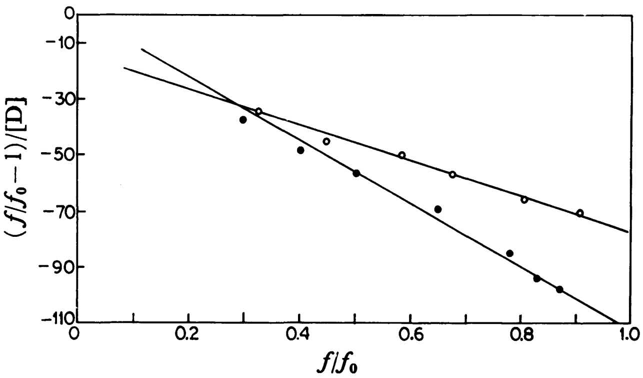


Fig. 5. $(f/f^0-1)/[D]$ vs. $(f/f^0))$ relation for (●) **I—VII** and (○) **II—VII** systems in cyclohexane.

spectral shift occurred both in ground as well as excited state.

Qualitatively speaking, the observed difference between the hydrogen-bonding effect on the fluorescence and absorption spectrum may indicate that, the equilibrium shifts more or less to the side of hydrogen-bond formation during the life time of fluorescence state. To treat quantitatively the very rapid reaction which occurs during the life time of excited state Mataga et al.[5] has derived the general equation considering the probable reaction scheme and from the general equation they have derived several special cases also assuming the stationary state. For simplicity two approximate relationship can be used here

$$(f_0/f)(I_{abs}/I^0_{abs})\cdot\delta = 1 + K_1\tau[D]\,, \tag{5}$$

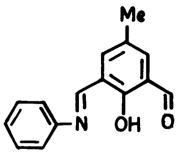
$$(f/f_0-1)/[D] = K'_f\tau' K_1/K_f(1+K_2\tau') - [\tau K_1/(1+K_2\tau')]f/f_0\,. \tag{6}$$

In these expressions I_{abs} is the total light quanta absorbed by solution when D is present, δ is the fraction of A* and is given by $\delta=1/\{1+(\varepsilon_c/\varepsilon_A)K_g[D]\}$, ε_A and ε_c are the molar extinction coefficients of acceptor (A) and donor acceptor complex (DA) respectively, at the wavelength of exciting light. K_1 is the bimolecular rate constant of hydrogen-bonding reaction and K_2 is the unimolecular rate constant of dissociation of DA*. I^0_{abs} is the total light quanta absorbed by the solution when D is absent and f_0 is the fluorescence intensity in that case. Using Eqs. 5 and 6 one can evaluate $K_1\tau$ and $\tau K_1/(1+K_2\tau')$. Figures 4 and 5 shows that for **I** and **II** these equations are approximately satisfied. The values of τK_1 and $\tau K_1/(1+\tau' K_2)$ obtained in this way are collected in Table 2. Using the values of given in Table 3, K_1 can be easily estimated. From the K_1 values and by means of the relation $K_2=K_1/K_e$, K_2 values may be estimated, if K_e values obtained by Eq. 3 are used. Practically, when no hydrogen-bonded complex exists in the ground state, $\delta=1$. The change of molar extinction coefficient caused by hydrogen-bonding is very small at the wavelengths of exciting light (288, 292, 286, and 298 nm for **III** to **VI** respectively) used, which mean I_{abs} is practically equal to I^0_{abs}. Moreover, because the fluorescence quenching was almost complete in the concentration range studied here, but practically no change in the absorption spectrum was observed, Eq. 6 therefore reduces to $f^0/f=1+K_1\tau[D]$, which incidentally is the simple Stern-Volmer Eq. 3.

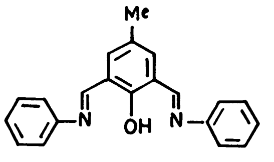
One point to note here is that the values of the bimolecular quenching rate constant K_1 given in Tables 2 and 3 are rather high in comparison to diffusion controlled rate constant. A possible explanation may be presumed as follows. As the singlet energy level of **VII** lies below that of the primary aromatic amine, it is quite logical that the observed quenching rate constant K_1 may be composed of two rate constant: viz. (i) for strong hydrogen bond formation by which CT state is produced which may be somewhere below the S_1 state of aromatic amines, and internal conversion (IC) rate from this CT state to the ground state of aromatic amines may be enhanced due to lowering of energy gap between these two states (CT and ground state); (ii) for intermolecular energy transfer from singlet of aromatic amine to singlet of electron acceptor **VII**.

The fluorescence spectral shifts of aniline (**III**), *p*-toluidine (**IV**), *m*-toluidine (**V**), and *N*,*N*-dimethylaniline (**VI**) on interaction with **VII** are given in Table 1. It may be noted that in the case of aniline no spectral shift occurs, but the following decreased order of band shift takes place with the other amines: **VI**>**V**>**IV**. This trend is rather expected because the electron density on the nitrogen atom of the substituted anilines have increased by the electron releasing methyl group attached to the nitrogen atom itself or to the aromatic ring. The ionization potentials (I_P) (Table 1) of these compounds (**VI**>**V**>**III**) also clearly indicate that hydrogen bonding of **VII** will occur most easily with **VI** and least readily with **III**. The considerable blue shift of **IV**, **V**, and **VI** in the excited state (Table 1) can be related to the more basic character of these amines in the excited state. This can be appreciated by taking into consideration the I_P of these molecules in the excited state (Table 1). It may also be noted in Table 2 that $K_e \gg K_g$ which indicates stronger proton acceptor ability (that is more basic character) of the molecules in their electronically excited state. The fluorescence quenching observed in the present study may be interpreted as due to the charge-transfer interaction via hydrogen bonding and seems to be followed by a very rapid nonradiative vibronic interaction process.

Another significant observation is that for certain proton acceptor molecules (**III** to **V**) quenching reaction appears as positive curvature in Stern-Volmer plots at high quencher concentrations.[27–29] Deviations from the Stern-Volmer equation in certain quenching reaction may be explained by a compound formation. In fact it has been observed that proton donor **VII** from Schiff's bases with aniline of the types **VIII** and **IX** at higher concentration of aniline at an elevated temperature.[30]



VIII



IX

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