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Substitution and Hydrogen Bonding Effects on Fluorescence and Intersystem Crossing in Naphthaldehydes and Their Derivatives

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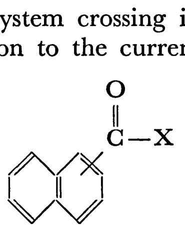
Absorption and fluorescence spectra, fluorescence and phosphorescence quantum yields and lifetimes of 1- and 2-naphthaldehyde and their derivatives have been measured in rigid glass solution at 77 K. Naphthaldehydes and acetonaphthones are non-fluorescent, whereas naphthoyl chlorides and methyl naphthoates are fluorescent. Upon formation of a hydrogen bond with ethyl alcohol, 2-naphthaldehyde and 2-acetonaphthone become fluorescent, and 1-naphthoyl chloride increases in fluorescence quantum yield by a factor of about 65. The rate constants for intersystem crossing in these three molecules decrease by about two orders of magnitudes as a result of hydrogen bonding. The decrease of the rate constants is attributed to elevation of the (n, π^*) level and the resulting change in its position relative to the (π, π^*) level. The experimental results are discussed in relation to the current theories of radiationless transition, and are found to conform to the theory in which both spin-orbit coupling and nuclear kinetic-energy operators are treated as the perturbation causing intersystem crossing.

Molecules possessing low-lying (n, π^*) states, such as aromatic carbonyls and nitrogen heterocyclics, are in general non-fluorescent or only very weakly fluorescent but strongly phosphorescent.[1,2] These phenomena have been extensively discussed by taking into account the relative positions of (n, π^*) and (π, π^*) levels and their role in intersystem crossing.[3–9]

Recently, Henry and Siebrand formulated a general rate expression for intersystem crossing by treating both spin-orbit coupling and nuclear kinetic-energy operators as the perturbation which causes the non-radiative transition.[10] The rate expression of these authors is very different from that of Lin[11] and Bixon and Jortner.[12] As has been noted by Azumi,[13] these two types of theories may predict different fluorescence characteristics for molecules with (n, π^*) states. At the present stage of the theory of intersystem crossing, therefore, a systematic study on the fluorescence characteristics of molecules of this kind is desirable to clarify the nature of the perturbation for the intersystem crossing.

In the present study, the absorption spectra and fluorescence characteristics of the simplest carbonyl substituted naphthalenes, 1- and 2-naphthaldehyde (1-, 2-NA), and their respective three derivatives have been examined in detail at 77 K with particular regard to substitution and hydrogen bonding effects. The derivatives used are as follows: acetonaphthones (1-, 2-AN), naphthoyl chlorides (1-, 2-NC), and methyl naphthoates (1-, 2-MN). On the basis of rate constants estimated for intersystem crossing and other pertinent results obtained, the mechanism of the intersystem crossing in these molecules is discussed in relation to the current theories mentioned above.



1-, 2-NA: X=H
1-, 2-AN: X=CH_3
1-, 2-NC: X=Cl
1-, 2-MN: X=OCH_3

Experimental

1-Substituted compounds were purified by distillation under reduced pressure, and 2-substituted compounds were recrystallized twice from *n*-hexane. Isopentane and methylcyclohexane were purified by chromatography using a column of silica gel. Spectro-grade ethyl alcohol (EtOH) was refluxed for five hours over calcium oxide and distilled. A mixture of isopentane and methylcyclohexane (4 : 1 by volume, abbreviated to PM hereafter) was used as solvent.

Absorption and fluorescence spectra, quantum yields and lifetimes were obtained at 77 K by the same methods as described in previous papers.[7,14] The correction of fluorescence and excitation spectra was made by the relative method.[7]

Sample solutions for quantum yield and lifetime measurements were degassed by freeze-thaw cycles. Unusual absorption and emission bands, probably due to aggregated species, appeared at concentrations higher than (6—7)$\times 10^{-5}$ M. For this reason, concentrations of the sample solutions were chosen as $\sim 5\times 10^{-5}$ M for 1-substituted compounds and $\sim 3\times 10^{-5}$ M for 2-substituted compounds.

Results and Discussion

Substitution Effects on Fluorescence Characteristics and Positions of (n, π^*) Levels. The fluorescence quantum yields (Φ_F) and observed fluorescence lifetimes (τ_F) of 1- and 2-NA and their derivatives in PM at 77 K are shown in column (a) of Table 1. NA and AN do not fluoresce. The chloro or methoxy

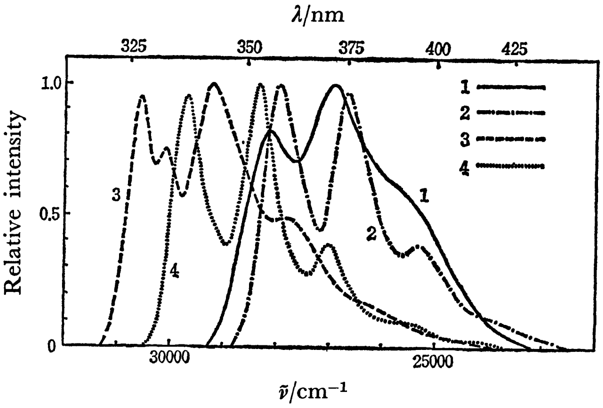


Fig. 1. Fluorescence spectra of naphthoyl chlorides and methyl naphthoates in PM at 77 K. The relative intensity represents relative quanta per unit frequency interval. (1) 1-NC; (2) 2-NC; (3) 1-MN; (4) 2-MN.

TABLE 1. FLUORESCENCE DATA ON NAPHTHALDEHYDE SERIES AT 77 K

Compound	(a) Free molecule				(b) H-bonded molecule			
	Φ_F	τ_F (ns)	k_F (s^{-1})	k_{ISC} e) (s^{-1})	Φ_F	τ_F (ns)	k_F (s^{-1})	k_{ISC} e) (s^{-1})
1-Naphthaldehyde	~ 0 a)	—	$\sim 5\times10^{5}$ c)	$>5\times10^{10}$	~ 0 a)	—	$\sim 5\times10^{5}$ c)	$>5\times10^{10}$
1-Acetonaphthone	0 a)	—	$\sim 5\times10^{5}$ c)	$>5\times10^{10}$	~ 0 a)	—	$\sim 5\times10^{5}$ c)	$>5\times10^{10}$
1-Naphthoyl chloride	0.002	—	$\sim 4\times10^{7}$ c)	$\sim 2\times10^{10}$	0.13	(~ 3) b)	4.3×10^{7} d)	2.9×10^{8}
Methyl 1-naphthoate	0.08	~ 2	4.0×10^{7} d)	4.6×10^{8}	0.08	~ 2	4.0×10^{7} d)	4.6×10^{8}
2-Naphthaldehyde	~ 0 a)	—	$\sim 5\times10^{5}$ c)	$>5\times10^{10}$	$\sim 10^{-2}$	—	$\sim 10^{7}$ c)	$\sim 10^{9}$
2-Acetonaphthone	~ 0 a)	—	$\sim 5\times10^{5}$ c)	$>5\times10^{10}$	0.05	—	$\sim 10^{7}$ c)	$\sim 2\times10^{8}$
2-Naphthoyl chloride	0.19	17.4 (16.1) b)	1.1×10^{7} d)	4.7×10^{7}	0.37	(17.8) b)	2.1×10^{7} d)	3.6×10^{7}
Methyl 2-naphthoate	0.32	38.4	0.8×10^{7} d)	1.7×10^{7}	0.29	32.5	0.9×10^{7} d)	2.2×10^{7}

a) Fluorescence emission could not be detected by the spectrofluorometer used in this study; Φ_F is estimated to be $<10^{-5}$. b) Obtained for a sample solution without degassing. (1- and 2-NC react with EtOH during degassing.) c) Calculated from absorption spectra. d) Calculated by the relation, $k_F=\Phi_F/\tau_F$. e) Calculated by the relation, $k_{ISC}=k_F\times(1-\Phi_F)/\Phi_F$.

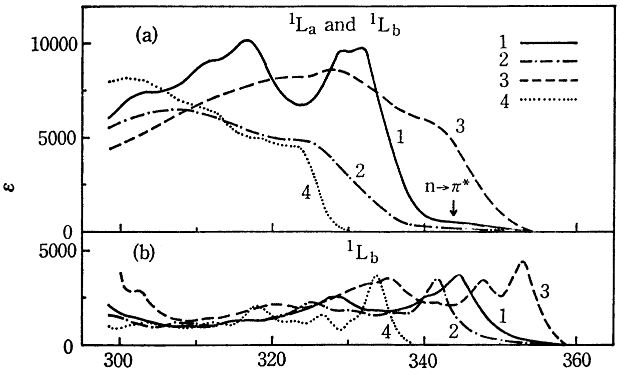


Fig. 2. Absorption spectra of 1-naphthaldehyde series (a) and 2-naphthaldehyde series (b) in PM at 77 K. The Platt notation is used for designation of electronic transitions. (1) NA; (2) AN; (3) NC; (4) MN.

TABLE 2. PHOSPHORESCENCE LIFETIMES AND YIELDS AND ENERGIES OF $T_1(\pi, \pi^*)$ LEVELS FOR NAPHTHALDEHYDE SERIES IN PM AT 77 K

Compound	τ_P (s)	Φ_P	ν_P(0-0) (cm^{-1})
1-Naphthaldehyde	0.048	0.01	19610
1-Acetonaphthone	0.093	0.01	19610
1-Naphthoyl chloride	0.25	0.04	19490
Methyl 1-naphthoate	1.05	0.02	19960
2-Naphthaldehyde	0.34	0.02	20700
2-Acetonaphthone	0.84	0.03	20700
2-Naphthoyl chloride	0.94	0.07	20410
Methyl 2-naphthoate	2.18	0.02	20660

substitution increases the fluorescence yield in that order in both 1- and 2-compounds. The fluorescence spectra of NC and MN in PM at 77 K are shown in Fig. 1. The fluorescence spectra of 1-MN and 2-MN are very similar to those of 1- and 2-naphthoic acid monomers, respectively.[14)]

As is well known, the $n\rightarrow\pi^*$ absorption band of saturated carbonyl compounds such as acetaldehyde is shifted to the blue by an electron-donating substituent.[15,16)] The magnitude of the blue shift increases with increasing electron-donating power of the substituent, *i.e.*, in the order CH_3, Cl, and OCH_3. Roughly speaking, the fluorescence quantum yield of the molecules in Table 1 increases in the same order.

Absorption spectra of 1- and 2-NA and their derivatives in PM at 77 K are shown in Figs. 2(a) and (b). The $n\rightarrow\pi^*$ bands of these molecules cannot easily be distinguished from $\pi\rightarrow\pi^*$ bands. Absorption spectra of 1-NA and 1-AN in Fig. 2(a) show a weak band as a long tail in the region from 340 to 350 nm. It was found that this band was shifted to the blue on addition of a small amount of EtOH (~0.1%, v/v). The weak band is therefore most likely an $n\rightarrow\pi^*$ band, which is known to be blue-shifted by hydrogen bond formation.[17,18)] The S_1 state in these molecules is then an (n, π^*) state at 77 K, as well as at 20 °C.[19)] On the other hand, absorption spectra of 1-NC and 1-MN do not show such an $n\rightarrow\pi^*$ band. For 2-NA and 2-AN in Fig. 2(b), the $\pi\rightarrow\pi^*$ (^1L_b) band is situated at longer wavelengths than that of the corresponding 1-substituted compounds, and consequently the $n\rightarrow\pi^*$ band is not clearly resolved. However, an $n\rightarrow\pi^*$ transition is likely to contribute to the tail which appears at the longest wavelength portion of the absorption spectra of these molecules. On close inspection, it is found that such a tail is absent in 2-NC and 2-MN. On the assumption that the location of the (n, π^*) level is not greatly affected by the position of the substituent (1- or 2-position of the naphthalene nucleus), and on the basis of the spectral shape described above, the S_1 state at 77 K of 2-NA and 2-AN can be assigned to an (n, π^*) state, in agreement with the assignment at 20 °C.[19)] The S_1 state at 77 K of 1-, 2-NC and 1-, 2-MN can be assigned to a (π, π^*) state from the substitution effect and spectral shape mentioned above.

When the phosphorescent triplet state (T_1) in a molecule possessing (n, π^*) states is of the (π, π^*) type, the radiative lifetime of T_1 is known to increase with the elevation of the (n, π^*) levels.[20)] Accordingly, the position of a ^{1}(n, π^*) level relative to the T_1 (π, π^*)

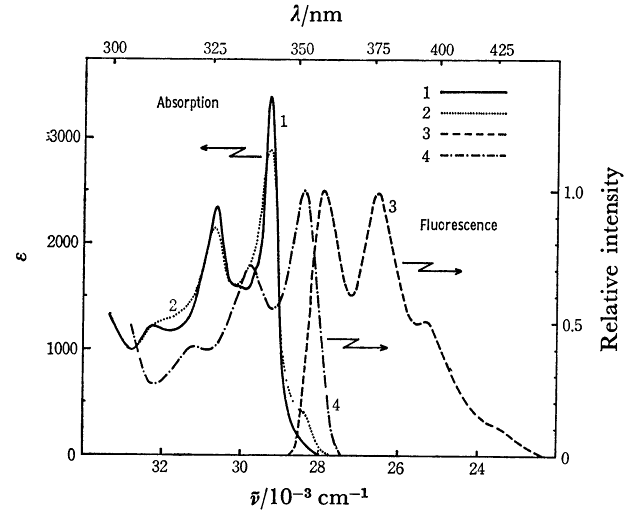


Fig. 3. Absorption, fluorescence, and excitation spectra of 2-acetonaphthone at 77 K. (1) absorption spectrum, [EtOH] = 0; (2) absorption spectrum, [EtOH] = 0.05% (v/v); (3) fluorescence spectrum, [EtOH] = 0.05% (v/v); (4) excitation spectrum, [EtOH] = 0.05 % (v/v).

level may be inferred from the data on the phosphorescence lifetimes. Observed phosphorescence lifetimes (τ_P) and quantum yields (Φ_P) are shown in Table 2, together with the energies of the $T_1(\pi, \pi^*)$ levels expressed by the frequency of the 0—0 band of phosphorescence ν_p (0—0). For 1- or 2-substituted compounds, the T_1 energies and the phosphorescence quantum yields are fairly constant regardless of the substituent, so that the lifetime data would reflect to some extent the differences in position of the $^1(n, \pi^*)$ levels. It may then be said from Table 2 that the $^1(n, \pi^*)$ levels are located at higher energies in the order NA, AN, NC, and MN. This is consistent with the results obtained from the absorption-spectral data.

Hydrogen Bonding Effects on Fluorescence and Intersystem Crossing. Figure 3 shows changes in the absorption spectrum of 2-AN in PM due to addition of a very small amount of EtOH (0.05%, v/v). The band intensity at 341.5 nm slightly decreases with the addition of EtOH, and at the same time a new, weak band grows at about 350 nm. These spectral changes may safely be attributed to the formation of a hydrogen bond between 2-AN and EtOH.

Although 2-AN in PM is not fluorescent, the addition of EtOH drastically changes its emission characteristics, making 2-AN fluorescent owing to the hydrogen bond. The fluorescence and excitation spectra of the hydrogen(H)-bonded 2-AN are also shown in Fig. 3. The longest wavelength band at 351 nm in the fluorescence excitation spectrum corresponds to the absorption band at about 350 nm of the H-bonded 2-AN.

As described before, the S_1 state of 2-AN in PM is of an (n, π^*) type. Since in general an $n \rightarrow \pi^*$ transition shifts to the blue by about 1000—2000 cm^{-1} as a result of hydrogen bond formation,[18] the 350 nm absorption band of the H-bonded 2-AN cannot be assigned to the $n \rightarrow \pi^*$ transition. The overall shape of the excitation spectrum resembles that of the absorption spectrum due to the ^1L_b transition in the free molecule. From these facts, the excitation spectrum, or the corresponding absorption spectrum including the 350 nm band, can be assigned to the ^1L_b transition in the H-bonded 2-AN. Thus, when 2-AN forms a hydrogen bond with EtOH, the S_1 state must change from an (n, π^*) to a (π, π^*) state.

Changes in absorption and fluorescence characteristics of 2-NA by hydrogen bond formation are similar to those of 2-AN described above. On the other hand, hydrogen bonding does not induce fluorescence in 1-NA and 1-AN. The fluorescence quantum yields and observed fluorescence lifetimes of the molecules forming hydrogen bonds with EtOH at 77 K are shown in column (b) of Table 1. It can be seen that the fluorescence quantum yields of the H-bonded 2-NA and 2-AN are at least 1000 times higher than those of the corresponding free molecules, whereas the yields of 2-NC, 1-MN, and 2-MN, which show relatively strong fluorescence in PM, are not affected significantly by hydrogen bonding. The fluorescence quantum yield of 1-NC increases by a factor of about 65 on hydrogen bond formation. Changes in fluorescence characteristics similar to those observed in 2-NA, 2-AN, and 1-NC have been reported for other molecules possessing (n, π^*) states such as pyrene-3-aldehyde,[21] acridine, quinoline, and isoquinoline.[22,23]

To explain the changes in fluorescence characteristics by hydrogen bonding, radiative rate constants for fluorescence (k_F) and rate constants for intersystem crossing (k_{ISC}) were estimated from the intensities of $S_0 \rightarrow S_1$ absorption transitions and the fluorescence quantum yields and lifetimes; the results are shown in Table 1. The values of k_F for molecules with the S_1 state of (n, π^*) type were tentatively estimated from the intensity of the $n \rightarrow \pi^*$ absorption of benzaldehyde, since the $n \rightarrow \pi^*$ transition in these molecules is hardly separated from the neighboring transition (see Fig. 2).

In the estimates of k_{ISC} values the rate constants for the internal conversion $S_1 \rightsquigarrow S_0$ processes (k_{FQ}) were tentatively neglected, as usually done.[24] This procedure is supported by the fact that efficient intersystem crossing is considered to take place in non-fluorescent carbonyls.[1,2] For example, the quantum yield of intersystem crossing (Φ_{ISC}) of 2-AN, which gives no fluorescence in PM, has been reported to be 0.84 in benzene at room temperature.[25] However, even in the non-fluorescent molecules such as NA and AN the phosphorescence emission was relatively weak ($\Phi_P \approx 10^{-2}$). To confirm the validity of our procedure, we measured triplet–triplet absorption at 77 K. All the molecules showed at least the same absorption intensity as naphthalene. The Φ_{ISC} value for naphthalene has been reported to be 0.25[26] in a mixture of 30% *n*-butanol and 70% isopentane at 77 K, and 0.40[25] in benzene at room temperature. Thus, in the naphthaldehyde series studied, even if internal conversion from S_1 to S_0 should occur, k_{FQ} would be of comparable magnitude to k_{ISC} at the greatest. We may therefore reasonably neglect k_{FQ} in the following discussion, where we are concerned with the order of magnitude of k_{ISC}. As the detection limit of the spectrofluorometer used in this study was 10^{-5} in quantum yield, the k_{ISC} values for non-fluorescent molecules were estimated by assuming Φ_F to be smaller than 10^{-5}.

To begin with, 2-NA and 2-AN will be discussed in comparison with 1-NA and 1-AN. As is seen in Table 1, the k_{ISC} values for 2-NA and 2-AN decrease with hydrogen bonding by about two orders of magnitude, while those for 1-NA and 1-AN remain unchanged. For the 2-substituted compounds, the energy separation between $S_1(n, \pi^*)$ and $S_2(\pi, \pi^*)$ (^1L_b) states is $\sim$400 cm^{-1} (see Fig. 2(b)). The (n, π^*) states in aromatic carbonyls have singlet–triplet intervals of about 2000 cm^{-1}.[27,28] This implies that the $S_2(\pi, \pi^*)$—$T_j(n, \pi^*)$ energy gaps in 2-NA and 2-AN are $\sim$2400 cm^{-1}. The $^1A \rightarrow {}^1L_b$ transition shifts to the red by about 800 cm^{-1} with hydrogen bond formation (see Fig. 3), while the $n \rightarrow \pi^*$ transition to the blue, as described before. The estimated k_{ISC} values and relatively small $S_2(\pi, \pi^*)$—$T_j(n, \pi^*)$ energy gaps suggest that in 2-NA and 2-AN a reversal of the S_1 state from the (n, π^*) to the (π, π^*) type and elevation of the $T_j(n, \pi^*)$ level above the resulting $S_1(\pi, \pi^*)$ level are likely to occur simultaneously as a result of hydrogen bonding. On the other hand, in 1-NA and 1-AN the energy separation between $S_1(n, \pi^*)$ and $S_2(\pi, \pi^*)$ (^1L_b) states is $\sim$1500 cm^{-1} (see Fig. 2(a)), and hence the $S_2(\pi, \pi^*)$—$T_j(n, \pi^*)$ energy gaps are $\sim$3500 cm^{-1}. In this case, the magnitude of the red shift due to hydrogen bonding of the ^1L_b transition is difficult to obtain because of the broadness of absorption bands. It is generally known that the red shifts of the $^1A \rightarrow {}^1L_b$ transitions due to hydrogen bonding are smaller in 1-substituted naphthalenes such as 1-naphthol than in the corresponding 2-substituted ones.[29,30] Thus, the elevation of the $T_j(n, \pi^*)$ level above the ^1L_b level is not likely to occur in the case of 1-NA and 1-AN.

The relative positions of the energy levels for both the free and H-bonded molecules of 1-NA and 1-AN and for the free molecules of 2-NA and 2-AN are schematically represented by Fig. 4(a), while those for the H-bonded 2-NA and 2-AN by Fig. 4(b). In the former group of molecules, the efficient spin-orbit coupling between $^1(n, \pi^*)$ and $^3(\pi, \pi^*)$ states should result in the fast rate of intersystem crossing.[3] However, in the H-bonded 2-NA and 2-AN, the spin-orbit interaction between the singlet and triplet (π, π^*) states is vanishingly small,[3] so that the rate of the direct intersystem crossing $^1(\pi, \pi^*) \rightsquigarrow {}^3(\pi, \pi^*)$ would be low enough for fluorescence emission to compete with the intersystem crossing.

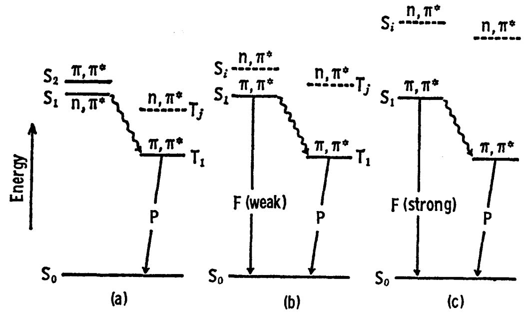


Fig. 4. Electronic energy level diagrams showing differences in fluorescence and intersystem-crossing characteristics among naphthaldehyde series. Broken lines represent the energy levels which are assumed to exist.

Next, the case of 1- and 2-MN will be discussed. According to the substitution effects described before, the $^1(n, \pi^*)$ state of these molecules is probably situated at a relatively high level, as shown in Fig. 4(c). Further elevation of the (n, π^*) level by hydrogen bonding will not greatly affect the intersystem crossing, and leave the fluorescence characteristics essentially unchanged.

Finally, the case of 1-NC and 2-NC will be considered. The fluorescence characteristics of 1-NC are changed by hydrogen bonding as in the case of 2-NA and 2-AN, while those of 2-NC are not changed significantly as in the case of MN. The S_1 states of the free and H-bonded NC are of (π, π^*) type, as previously mentioned. Although the definite positions of (n, π^*) levels are not known, the experimental data for 1-NC and 2-NC suggest that the $T_j(n, \pi^*)$ level should be higher than the $S_1(\pi, \pi^*)$ level. It follows from Fig. 2 that the $S_1(\pi, \pi^*)$ level of 1-NC is higher than that of 2-NC. This implies that the magnitudes of energy separations between $T_j(n, \pi^*)$ and $S_1(\pi, \pi^*)$ levels for 1- and 2-NC are different from each other, provided the (n, π^*) levels of these molecules are situated at approximately the same position. We assume that the $T_j(n, \pi^*)$ level of 1-NC in PM lies closely above the $S_1(\pi, \pi^*)$ level, as shown in Fig. 4(b). The free molecule of 1-NC will then show weak fluorescence. When 1-NC forms a hydrogen bond with EtOH, the $^3(n, \pi^*)$ level rises and the fluorescence intensity increases. From the fact that the energy separation between $T_j(n, \pi^*)$ and $S_1(\pi, \pi^*)$ levels is larger in 2-NC than in 1-NC, the relative positions of the energy levels for 2-NC are thought to be similar to Fig. 4(c). Further elevation of the (n, π^*) level of 2-NC by hydrogen bonding would not change greatly the fluorescence characteristics, as has been shown for MN.

On the Mechanism of Intersystem Crossing. Three different rate expressions have been theoretically derived so far for intersystem crossing. El-Sayed[3] first obtained a rate expression, based on the theory of Robinson and Frosch,[31] by considering the spin-orbit coupling operator (H_{SO}) as the perturbation (H') which causes the non-radiative transition. Lin[11] and Bixon and Jortner[12] independently formulated an expression by treating the nuclear kinetic-energy operator (T_N) alone as the perturbation. On the other hand, Henry and Siebrand[10] and Lawetz, Orlandi, and Siebrand[32] recently formulated a rate expression by including both H_{SO} and T_N in the perturbation.

The matrix element, H'_{mn}, in the expressions by El-Sayed and Siebrand *et al.* involves the first-order term $\langle {}^3\Psi_m | H_{\mathrm{SO}} | {}^1\Psi_n \rangle$. Here, $^1\Psi_n$ and $^3\Psi_m$ stand for pure-spin Born-Oppenheimer wave functions of singlet and triplet states, respectively; they are written as products of an electronic wavefunction (Φ) and a vibrational wavefunction (Λ), *i.e.*, ${}^1\Phi_n \cdot \Lambda_n$ and ${}^3\Phi_m \cdot \Lambda_m$ respectively. Such a first-order term does not appear in the formulation by Lin *et al.* As is well known, the electronic matrix element of H_{so} between ${}^{1,3}(\mathrm{n}, \pi^*)$ and ${}^{3,1}(\pi, \pi^*)$ states, *e.g.*, $\langle {}^3\Phi(\pi, \pi^*) | H_{\mathrm{so}} | {}^1\Phi(\mathrm{n}, \pi^*) \rangle$, is far larger than that between ${}^1(\pi, \pi^*)$ and ${}^3(\pi, \pi^*)$ states, $\langle {}^3\Phi(\pi, \pi^*) | H_{\mathrm{so}} | {}^1\Phi(\pi, \pi^*) \rangle$. According to the theory of El-Sayed or Siebrand *et al.*, therefore, in molecules possessing (n, π^*) states, the rate of intersystem crossing depends strongly on whether or not ${}^3(\pi, \pi^*)$ and ${}^3(\mathrm{n}, \pi^*)$ levels are located below $\mathrm{S}_1(\mathrm{n}, \pi^*)$ and $\mathrm{S}_1(\pi, \pi^*)$, respectively, and the fluorescence characteristics are expected to be changed drastically by a reversal of the relative positions of (n, π^*) and (π, π^*) levels. On the other hand, the theory by Lin *et al.* does not predict such changes in fluorescence, as noted recently by Azumi.13,33)

As has been mentioned, the fluorescence characteristics and intersystem crossing rates in the naphthaldehyde series, particularly in 2-NA and 2-AN, vary markedly, depending upon the relative positions of (n, π^*) and (π, π^*) levels. In other words, the experimental results suggest that the intersystem crossing is caused by the perturbation including H_{so}.

The experimental results show also that there is a distinct difference in fluorescent behavior between molecules related to Fig. 4(b) and those to 4(c) (cf. Table 1). In either case the $\mathrm{S}_1(\pi, \pi^*)$ and $\mathrm{T}_j(\mathrm{n}, \pi^*)$ states are arranged in the same order of energy, so that the above-mentioned difference cannot be explained in terms of the theory including only H_{so} in the perturbation.

The matrix element H'_{mn} in the rate expression by Siebrand *et al.* involves second-order terms such as

$$\sum_i [\langle {}^3\Psi_m | H_{\mathrm{SO}} | {}^1\Psi_i \rangle \langle {}^1\Psi_i | T_{\mathrm{N}} | {}^1\Psi_n \rangle / (\mathrm{E}_i - \mathrm{E}_n)]$$

and

$$\sum_i [\langle {}^3\Psi_m | T_{\mathrm{N}} | {}^3\Psi_i \rangle \langle {}^3\Psi_i | H_{\mathrm{SO}} | {}^1\Psi_n \rangle / (\mathrm{E}_i - E_n)]$$

where the subscript i refers to intermediate states, and E_i and E_n represent the energies of ${}^{1,3}\Psi_j$ and ${}^1\Psi_n$, respectively. Similar terms appear also in the rate expression by Lin *et al.* From these second-order terms it follows that an increase in energy difference between initial and intermediate states (see Figs. 4(b) and (c)) may lead to a distinct change in the intersystem crossing rate and hence in the fluorescence characteristics, in agreement with the experiment.

Thus, the present experimental results are best explained in terms of the theory in which both H_{so} and T_{N} are treated as the perturbation causing intersystem crossing.

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