The Dual Fluorescence Nature of Some *N*-Monosubstituted Salicylamides

Michio Kondo

Central Research Laboratories, Sankyo Co., Ltd., Hiromachi 1-2-58, Shinagawa-ku, Tokyo 140

(Received March 10, 1976)

Dual fluorescence from *N*-methylsalicylamide (**1**) in alcoholic solutions was observed under excitation by 280 nm light, and was ascribed to two different molecular species: one with and the other without intramolecular proton transfer in the lowest excited singlet state. Some related compounds having two identical chromophores showed similar dual emission spectra with weak emission bands at shorter wavelengths. This fact was explained as being due to the intramolecular energy transfer between the two chromophores in the excited state. From the temperature dependence of the intensity ratio of the two emission bands for these compounds, the difference between the activation energies for the two emissive states was estimated.

In general, fluorescence of an aromatic molecule occurs only from the lowest excited singlet state and therefore, consists of a single band.[1] However, there are a few exceptional cases in which a molecular system having only one chromophore exhibits dual fluorescence: in the cases of (i) exciplex formation (ii) acid-base equilibrium in the excited state which greatly differs from that in the ground state, and (iii) anomalous dual emission in the case of *p*-dimethylaminobenzonitrile in polar solvents.[2,3]

In this paper, the author reports that *N*-methylsalicylamide (**1**) and some related derivatives show dual fluorescence in alcoholic solvents and single fluorescence in other solvents. The origin of this dual fluorescence and its behavior, especially a possible intramolecular energy transfer for the conversion of the emitting state, are discussed.

Experimental

N-Methylsalicylamide (**1**, mp 88 °C) and *N*-benzylsalicylamide (**2**, mp 134 °C) were prepared by the reaction of methyl salicylate with aqueous methylamine in methanol and with benzylamine, respectively. *N,N'*-disalicyloylethylenediamine (**3**, mp 182 °C), -trimethylenediamine (**4**, mp 180 °C), and -hexamethylenediamine (**5**, mp 141 °C) were prepared from methyl salicylate and appropriate diamines. The products were purified by recrystallization from ethanol.

Absorption and fluorescence spectra were recorded on a Hitachi Model 356 spectrophotometer and a Hitachi Model MPF-2 fluorescence spectrophotometer, respectively.

Temperature-dependent studies of the fluorescence spectra were carried out in a quartz dewar in which the temperature can be controlled to whitin ±0.2 °C around room temperature during the period necessary for recording a fluorescence spectrum.

A slit width corresponding to a wavelength of 8 nm was chosen for both the incident and emitted light.

Results

In Table 1 are shown the peak positions of the absorption and emission bands of **1** in various solvents. The first absorption band lies at about 300 nm and is slightly blue shifted for an increase in the solvent polarity.

The fluorescence emissions of **1** in all solvents examined were very strong. This indicates that the lowest excited singlet state is a π-π^* state. The emission band with a large Stokes' shift can be explained as emission by an intramolecular proton transfer from the phenolic OH to the carbonyl group. This is accomplished through thermal relaxation from the Frank-Condon state, as Weller has proposed for methyl salicylate.[4] This explanation seems to be reasonable because it is well known that phenolic hydroxyl has an increased acidity and the carbonyl group has increased basicity in the excited singlet state.[5]

Another point of interest in Table 1 is that a new emission band with about one half of the intensity of the longer wavelength band, appears at about 338 nm when an ethanol solution of **1** is irradiated by 280 nm light (Fig. 1). (Hereafter, the emission band at about

Table 1. Peak positions of absorption and emission spectra of *N*-methylsalicylamide in various organic solvents

Solvent	Absorption		Emission	
	λ_{max}(nm)	ε_{max}	λ_{ex}: 280 nm	320 nm
Cyclohexane	306	5050	440	441
1,2-Dichloroethane	304	4850	440	440
Ethyl ether	305	5100	432	433
Dioxane	304	5000	434	434
Ethyl acetate	304	4850	433	432
Acetonitrile	303	4550	431	432
Ethanol	301	4350	423 338	423

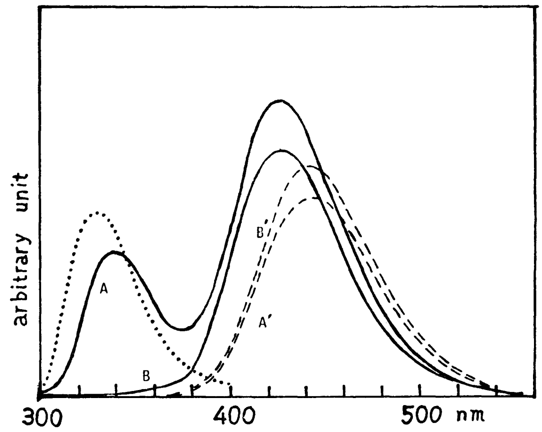

Fig. 1. Emission spectra of *N*-methylsalicylamide in ethanol (——) and in cyclohexane (----), irradiated by 280 nm (A and A') and 320 nm (B and B') light and of *N*-methyl-*o*-methoxybenzamide in ethanol (······) irradiated by 280 nm light.

TABLE 2. EMISSION SPECTRUM OF *N*-METHYLSALICYLAMIDE IN VARIOUS ALCOHOLS

Solvent		Excitation: 280 nm			320 nm	
		λ_F(max)	$I^{a)}$	I_B/I_R	λ_F(max)	$I^{a)}$
Methanol	B-band	338 nm	375	0.95	419	335
	R	420	395			
Ethanol	B	338	380	0.52	423	593
	R	423	725			
1-Propanol	B	336	410	0.48	424	715
	R	424	850			
2-Propanol	B	336	415	0.47	424	770
	R	424	890			
1-Butanol	B	336	380	0.42	424	840
	R	424	895			
Ethylene glycol	B	341	452	1.00	422	387
	R	421	452			

a) Intensity in arbitrary units.

TABLE 3. RATIOS OF THE INTENSITIES OF THE B-BAND TO THE R-BAND FOR SEVERAL SALICYLAMIDES IN METHANOL UNDER IRRADIATION BY 280 nm LIGHT AT ROOM TEMPERATURE

Compound	Concn$^{a)}$	Absorption		Emission (280 nm excitation)				
		λ_{max}	ε_{max}	B-band	$I_B{}^{b)}$	R-band	$I_R{}^{b)}$	I_B/I_R
1	4.7	300	4400	338	385	420	349	0.93
2	4.9	301	4500	341	308	422	354	0.87
3	4.5	302	8700	338	85	427	592	0.14
4	4.2	302	8900	339	85	426	695	0.12
5	4.3	301	8700	339	140	423	860	0.16

a) $\times 10^{-5}$ M. b) Intensity in arbitrary units.

338 nm is referred to as the B-band and that at about 425 nm is the R-band). Weller has observed a weak emission band around 350 nm for methyl salicylate in methylcyclohexane, together with another strong emission band at about 442 nm, but he failed to observe the corresponding emission band at shorter wavelengths for a methanol solution of methyl salicylate. The light source he used, a high-pressure mercury arc, Q-81, together with a filter system UG-11 and aqueous potassium chromate, produced almost zero intensity at wavelengths below 300 nm. This may be the reason why he missed the emission band at shorter wavelengths.

In Table 2 are displayed the relative intensity of the two emission bands of **1** in several alcohols. The intensity of the B-band is independent of the solvent, but that of the R-band distinctly increases upon changing the solvent from methanol to butanol. In ethylene glycol, the intensities of both bands are comparable to those in methanol. The ratio, I_B/I_R, is largest in methanol and ethylene glycol.

In Table 3 are summarized the ratios, I_B/I_R, of several related compounds in methanol solutions subject to 280 nm irradiation. These solutions were of about the same concentration. The molar extinction coefficients for the compounds **3**, **4**, and **5** are about twice those for **1** and **2**, reflecting the presence of the two identical chromophores in each molecule. On the other hand, the values of I_B/I_R are about 0.9 for **1** and **2**, while they are about 0.1—0.2 for **3**, **4**, and **5**. The intensities of the R-band of **3**, **4**, and **5** are clearly much larger than those of **1** and **2**, whereas those of the B-bands are much smaller for **3**, **4**, and **5** than for **1** and **2**. These observations suggest that some intramolecular interactions between the two chromophores are operative in photophysical processes in the excited state.

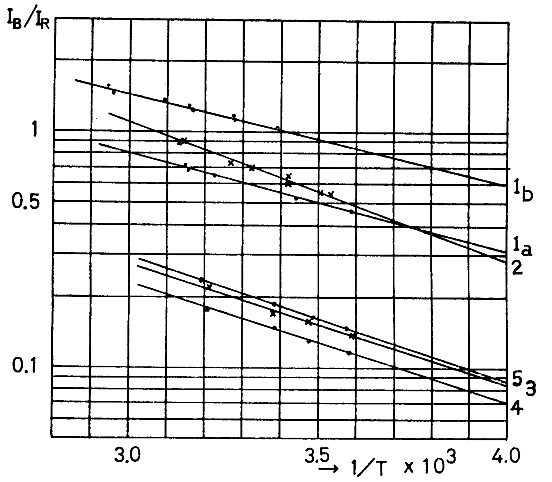

Fig. 2. Temperature variation of the intensity ratio, I_B/I_R.

The ratio, I_B/I_R, shows a temperature dependence. Plotting the quantity log (I_B/I_R) against $1/T$ for several systems resulted in good linear relationships, as is shown in Figure 2. These lines are well expressed by the following equation:

$$\log (I_B/I_R) = A - \frac{\Delta E^*}{2.303RT} \qquad (1)$$

In Table 4 are given the ΔE^* values obtained from the slopes of these lines. They are about 2.0 kcal/mol with some divergence.

TABLE 4. ENERGY DIFFERENCE (ΔE^*) BETWEEN TWO ACTIVATION ENERGIES FOR THE TWO EMISSIVE STATES

Compound	Solvent	ΔE^*(kcal/mol)
1a	Ethanol	1.76
b	Ethylene glycol	1.67
2	Ethanol	2.72
3	Methanol	2.39
4	Methanol	2.38
5	Methanol	2.41

Discussion

The Origin of the B-band. Irradiation of **1** in alcoholic solutions by 280 nm light yielded two emission bands at about 338 nm (B-band) and 425 nm (R-band). The R-band can be interpreted as emission from the lowest excited singlet state, which is characterized by intramolecular proton transfer.

As mentioned in the introduction, there are some examples showing dual emission bands under special conditions. In the case of **1**, for example, negligible concentration effects may rule out the excimer mechanism as the origin of the B-band. The emission bands from the cation, the neutral molecule, and the anion of salicylamide are located at 383, 435, and 417 nm, respectively.[6] Therefore, the B-band cannot be ascribed to ionic species in the excited state. Recently, Rotkiewicz *et al.*[3] have found new spectroscopic evidence which casts some doubt on the previous interpretation of the anomalous luminescence of *p-N,N*-dimethylaminobenzonitrile and they assigned the two emission bands to two excited species differing in polarity and in the orientation of the $-N(CH_3)_2$ group. This interpretation, however, also does not seem to be applicable to the present case.

Zadorozhnji observed two emission bands for salicylic acid and methyl salicylate but a single luminescent band for salicylamide.[7] He explained the two emission bands as transitions from the two extreme distances in the same vibrational level in the excited state to the same branch of the ground state potential curve, provided that the energy of the intramolecular hydrogen bond in the excited state is considerably higher than that in the ground state. However, this does not seem to explain the excitation-wavelength dependence of the occurrence of the B-band.

The excitation spectrum obtained by monitoring the R-band or the B-band of **1** in ethanol (1.06×10^{-5} M) has a peak at 310 or 299 nm, respectively (no correction was made for, *e.g.*, the energy distribution of the xenon lamp light source). The energy difference between these two wavelengths is 3.38 kcal/mol. The fact that the two excitation spectra were different for the two emission bands, seems to suggest the coexistence of two molecular species in the ground state. With regards to this point it has been reported from parachor measurements that salicylamide exists in an intramolecularly hydrogen bonded form in acetone, ethyl acetate, and dioxane, but this intramolecular hydrogen bond is disrupted in ethanol.[8] However, the peak position and the half width of the first absorption band of **1** in ethanol differ little from those in cyclohexane, indicating that the intramolecular hydrogen bond of **1** survives in ethanol solutions.

The relative intensity of the two emission bands showed a rather marked temperature dependence, while the absorption spectrum of **1** in ethanol, for example, showed a negligible temperature dependence over the range from 10 to 40 °C. Therefore, it is difficult to ascribe the B-band to the molecular species having no intramolecular hydrogen bond in the ground state.

Taking into consideration that the two emission bands were observed only for alcoholic solutions irradiated by 280 nm light, it is assumed that the proton exchanges between alcohol molecules and the solute molecules in the excited state play an important role in the appearance of the B-band. The B-band may originate from a molecular species having no intramolecular hydrogen bonds in the excited state, because the fluorescence band of *N*-methyl-*o*-methoxybenzamide in ethanol, which was measured for comparison, was found to be at about 330 nm, very close to the B-band in question (Fig. 1). The solute molecules excited by 280 nm light reach higher vibrational levels in the excited states. Then some molecules change conformation into species without the intramolecular hydrogen bond through intermolecular interactions with protic solvents, returning to the ground state with the resulting B-band emission. Although water is considered to be more active in proton exchange, the B-band was not observed for aqueous solutions of **1**, although a single broad emission band was observed at about 417 nm, which is ascribed to an anionic species.

Intramolecular Energy Transfer. The ratio, $I_B/I_R=0.14$ for compounds with two identical chromophores in the molecule is in sharp contrast to the values of about 0.9 for **1** and **2**. In the present case, the mean intermolecular distance of about 55 nm estimated from the sample concentration (*ca.* 5×10^{-5} M) is too great for intermolecular energy transfer *via* the exciton mechanism.[9] Furthermore, the fact that the ratios, I_B/I_R, are independent of the number of methylene groups joining the two identical chromophores conflicts with the results of the fluorescence study on a number of diphenylalkanes, where excimer fluorescences were found for diphenylpropane derivatives only.[10] Therefore, it is very likely that some intramolecular interactions are operative between the two chromophores in **3**, **4**, and **5** in the excited state.

Under irradiation by ordinary light sources, it is generally accepted that no chromophoric molecule could be brought to states for which two chromophores in the same molecule are excited by the simultaneous absorption of two photons. In other words, in an excited molecule, one chromophore has to be in the excited state while the other is in the ground state.

Since the B-band of the excited chromophore partially overlaps with the absorption band of the chromophore in the ground state, which is intramolecularly hydrogen bonded, the energy transfer between two chromophores in the same molecule may occur efficiently. The R-band, on the other hand, does not undergo this kind of energy transfer, resulting in relatively weak B-bands for compounds **3**, **4**, and **5**.

Temperature Dependence of the Ratio, I_B/I_R. Considering molecules excited by 280 nm light, some molecules break the intramolecular hydrogen bond resulting in the B-state which can emit B-band fluorescence, while other molecules undergo intramolecular proton transfer yielding the R-state which is responsible for the R-band. For simplicity, it is assumed that back processes may be neglected. Under these conditions, the relative intensity, I_B/I_R, is given by

$$I_B/I_R = \frac{k^B_f/(k^B_f+k^B_d)}{k^R_f/(k^R_f+k^R_d)} \cdot \frac{k^B}{k^R} \tag{2}$$

where the k values are the rate constants for the elementary processes represented in Scheme 1.

$S_0 + h\nu \rightarrow S^*$		absorption	(a)
$S^* \rightarrow S_1$		vibrational relaxation	(b)
$S_1 \rightarrow S_1{}^R$	k^R	intramolecular proton transfer	(c)
$S_1 \rightarrow S_1{}^B$	k^B	changing conformation into the B-state	(d)
$S_1{}^R \rightarrow S_0{}^R + h\nu^R$	k^R_t	R-band emission	(e)
$S_1{}^B \rightarrow S_0{}^B + h\nu^B$	k^B_f	B-band emission	(f)
$S_1{}^R \rightarrow S_0{}^R$	k^R_d	internal conversion	(g)
$S_1{}^B \rightarrow S_0{}^B$	k^B_d	internal conversion	(h)

Scheme 1.

Assuming the Arrhenius equations for elementary processes (c) and (d), that $k^R = A^R \exp(-E^R/RT)$ and $k^B = A^B \exp(-E^B/RT)$, and that the other processes are temperature independent, can be rewritten as

$$I_B/I_R = K \exp(-\Delta E^*/RT) \tag{3}$$

where $K = \{k^B_f(k^R_f+k^R_d)/k^R_f(k^B_f+k^B_d)\}(A^B/A^R)$ and $\Delta E^* = E^B - E^R$.

Weller has estimated the E^R value to be less than 2.6 kcal/mol for salicylic acid.[4] From this value and the ΔE^* values in Table 4, the E^B value was evaluated to be about 4.5 kcal/mol. This value seems to be reasonable for the activation energy of intramolecular hydrogen bond disruption. Recently, Shizuka *et al.* obtained a similar value for the rapid radiationless decay process of 2,4-bis-(dimethylamino)-6-(2-hydroxy-5-methyphenyl)-*s*-triazine, though the details of the process were not determined.[11]

References

1) M. Kasha, *Discuss. Faraday Soc.*, **9**, 14 (1950).

2) E. Lippert, W. Luder, and H. Boos, "Advances in Molecular Spectroscopy," Pergamon Press, London (1962), p. 443.

3) K. Rotkiewicz, K. H. Grellmann, and I. R. Grabowski, *Chem. Phys. Lett.*, **19**, 315 (1973).

4) A. Weller, *Z. Elektrochem.*, **60**, 1144 (1956).

5) A. Weller, *Z. Phys. Chem. N.F.*, **3**, 238 (1955).

6) S. G. Schulman, P. J. Kovi, and J. F. Young, *J. Pharm. Sci.*, **62**, 1197 (1973).

7) V. R. Shastry and W. V. Rhagwat, Vikram, *J. Vikram Univ.*, **7**, 33 (1963); *Cf.* CA **64**, 11886h (1966).

8) B. A. Zadorozhnji, *Zh. Prikl. Spektrosk.*, **5**, 349 (1966); *Cf.* CA **66**, 60510p (1967).

9) Th. Foerster and K. Kasper, *Z. Phys. Chem, N.F.*, **1**, 275 (1954); B. Stevens, *Adv. Photochem.*, **8**, 161 (1971).

10) F. Hirayama, *J. Chem. Phys.*, **42**, 3163 (1965).

11) H. Shizuka, K. Matsui, T. Okamura, and I. Tanaka, *J. Phys. Chem.*, **79**, 2731 (1975).