The Quenching Action of Benzoic Acid and Methyl Benzoate on the Fluorescence of Naphthalene Derivatives

By Takuji MIWA and Masao KOIZUMI

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In a previous paper,[1] the present authors investigated the quenching action of pyridine and quinoline on the fluorescence of naphthylamine and naphthol and their related compounds, in connection with the effect of intermolecular hydrogen bonding on the fluorescence power. A high degree of quenching was observed in the system consisting of naphthylamine or naphthol as a fluorescer and pyridine or quinoline as a quencher; this was just what had been expected from Mataga's finding[2] that a fluorescer loses its emissivity when hydrogen-bonded directly with another conjugated system. A notable result then found was that a rather large quenching was observed in the system consisting of *N*, *N*-dimethyl-2-naphthylamine or 2-naphthyl methyl ether (fluorescer) and pyridine or quinoline (quencher), where no hydrogen bonding is conceivable. These phenomena were explained by assuming an intermolecular charge transfer between the excited fluorescer and the quencher. Although analogous mechanisms of quenching have long been postulated, no confirmative evidence had been presented until recently, when Weller,[3] by means of a flash photolytic technique, succeeded in providing strong support for this mechanism holding in the perylene - amine system. However, from the standpoint of a charge-transfer mechanism, there seems to be very little work which has succeeded in correlating the quenching constants with such properties of fluorescers and quenchers as the ionization potential or electron affinity. Among recent articles, the works

1) T. Miwa and M. Koizumi, This Bulletin, **36**, 1619 (1963).

2) E. g. N. Mataga, ibid., **31**, 481 (1958).

3) H. Leonhardt and A. Weller, *Z. Phys. Chem., NF*, **29**, 277 (1961); "Luminescence of Organic and Inorganic Materials," Ed. by Kallman and Spruch, John Wiley and Sons, New York (1962), pp. 74—82; *Ber. Bunsges. Phys. Chem.*, **61**, 791 (1963).

of Weller[4] and Majumder et al.[5] are prominent. The former compared the quenching action of various aliphatic amines on the fluorescence of an aqueous acridine solution, while the latter investigated the fluorescence power of some condensed aromatic compounds, such as anthracene, dissolved in benzene, toluene, xylene, and mesitylene. Still fewer have been the systematic studies of various systems undertaken from this point of view.

We became interested in undertaking such a study in the expectation that it would make our proposed mechanism more concrete. In this paper, the first in a series devoted to the above study, we will describe the quenching action of benzoic acid and its methyl ester, both chosen as weak electron acceptors, on the fluorescence of naphthalene derivatives, including *N,N*-dimethylnaphthylamine and naphthyl methyl ether.

It will be shown that the benzoic acid dimer has a rather large quenching action on the above-mentioned compounds; the molecular mechanism will also be discussed.

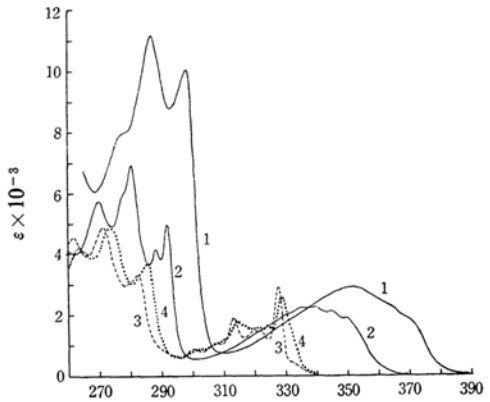


Fig. 1. Absorption spectra in cyclohexane.
1 *N,N*-Dimethyl-2-naphthylamine
2 2-Naphthylamine
3 2-Naphthyl methyl ether
4 2-Naphthol

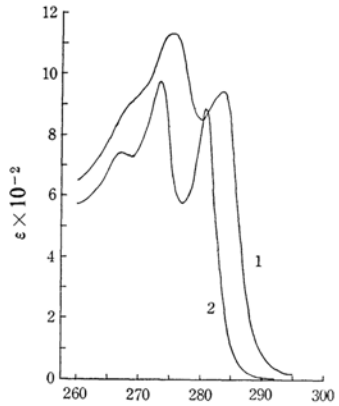


Fig. 2. Absorption spectra in cyclohexane.
1 Benzoic acid: 5×10^{-4} M
2 Methyl benzoate: 6.4×10^{-4} M

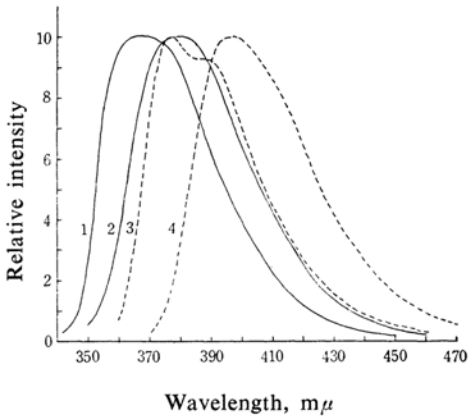


Fig. 3. Fluorescence spectra.
1 2-Naphthylamine 10^{-4} M/l. in cyclohexane
2 2-Naphthylamine 10^{-4} M/l. in benzene
3 *N,N*-Dimethyl-2-naphthylamine 10^{-4} M/l. in cyclohexane
4 *N,N*-Dimethyl-2-naphthylamine 10^{-1} M/l. in benzene

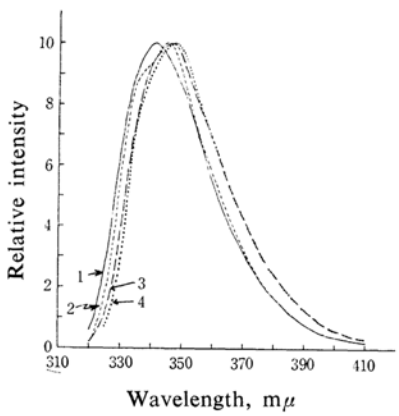


Fig. 4. Fluorescence spectra.
1 2-Naphthyl methyl ether 2×10^{-4} M/l. in cyclohexane
2 2-Naphthol 2×10^{-4} M/l. in cyclohexane
3 2-Naphthyl methyl ether 2×10^{-4} M/l. in benzene
4 2-Naphthol 2×10^{-4} M/l. in benzene

4) A. Weller, "Reaction Kinetics," Vol. I, Ed. by G. Porter, Pergamon Press, New York (1961), p. 195.
5) D. K. Majumdar and S. Basu, *J. Chem. Phys.*, **33**, 1199 (1960).

Experimental

Materials.—*Benzoic Acid.*—The standard sample for calorimetry, obtained from the Shigen Gijutsu Shikenjo (Natural Resources Institute), was recrystallized three times from benzene.

Methyl Benzoate.—Commercial material was treated twice with a concentrated aqueous potassium carbonate solution to remove the free acid, dehydrated over potassium carbonate (for more than a week), and finally distilled twice under reduced pressure.

Cyclohexane and Other Materials.—The procedure for purification was the same as that described in a previous paper.[1]

Apparatus and Procedure.—The absorption spectra were measured with a Hitachi EPS or EPU spectrophotometer. The fluoresecence intensity was measured with a fluorometer made by the Narumi Shokai (the details of the apparatus were given in the previous paper[1]) or an Aminco-Bowman spectrophotofluorometer. In the former apparatus, only the exciting light is monochromatized by a prism while the entire (not monochromatized) fluorescence or a part of it (through a filter) is caught by a photomultiplier. Intensities were measured on a photometer. In the latter apparatus both the exciting light and the fluorescence are monochromatized with a diffraction monochromator. The action spectra as well as the fluorescence spectra can be recorded automatically. The fluorescence intensity of the sample solution containing a quenching substance was compared with that of the reference solution, measurement of which was performed immediately before and after the measurement of the sample solution. All the measurements were made at room temperature without degassing. Integrated fluorescence spectra or the height of the maxima in the fluorescence spectra were used for the analysis. A suitable correction was made when necessary, for example, when the addition of a quenching substance changed the optical density at the exciting wavelength or affected the fluorescence spectra to an appreciable extent. The absorption spectra and the fluorescence spectra of the substances employed are given in Figs. 1—4. The error in wavelength is about $\pm 0.5\ m\mu$ for absorption and about $\pm 3\ m\mu$ for fluorescence spectra.

Results

Quenching Action of Methyl Benzoate.—*N, N-Dimethyl-2-naphthylamine in Cyclohexane.*—Upon the addition of 0.2 M of quencher, the absorption spectra undergo a distinct red shift, which increases with the concentration of the quencher and which, at the same time, causes a broadening of all the features of the spectra. This phenomenon may be attributed to the so-called solvent effect. The fluorescence spectra show similar changes in the concentration range 0—2 M of the quencher. The fluorescence intensity decreases only a little with the addition of 0.2 M of quencher. In the region 0—2 M, the $F_0/F-1$ vs. [Q] (Q=quencher) plot does not obey the Stern-Volmer relation, but resembles the curve of the second degree, as Fig. 5 shows. The quenching constant was estimated to be $k<0.8$ from the tangent at $[Q]\rightarrow 0$.

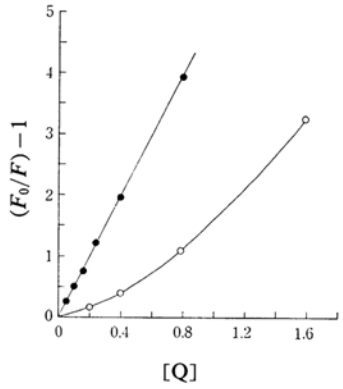


Fig. 5.

○ *N,N*-Dimethyl-2-naphthylamine (1.00×10^{-4} M/l.) - methyl benzoate in cyclohexane
● *N,N*-Dimethyl-2-naphthylamine (1.00×10^{-4} M/l.) - methyl benzoate in benzene
Q Methyl benzoate

N, N-Dimethyl-2-naphthylamine in Benzene.—This solution shows qualitative features similar to those of the cyclohexane solution, but the Stern-Volmer relation holds exactly in the range 0—2 M of [Q], as Fig. 5 shows. The value of the quenching constant is 5.

2-Naphthyl Methyl Ether in Cyclohexane.—With the addition of the quencher, the absorption spectra become a little diffused and suffer a slight red shift. The fluorescence spectra show a similar change, but the intensity is not practically affected, even by the addition of as much as 8 M of quencher (i.e., $k\approx 0$).

2-Naphthylamine in Cyclohexane.—With the addition of the quencher, the absorption spectra show a change characteristic of intermolecular hydrogen bonding, as Fig. 6 shows. The results can be analyzed by using the well known Eq. 1, where K is the equilibrium constant, where $[Q_0]$ and $[A_0]$ denote the total concentrations of quencher and fluorescer respectively, where d and d_0 are the optical densities at a certain wavelength in the presence and in the absence of the quencher respectively, and where ε is the molar extinction coefficient of the hydrogen-bonded species at the same wavelength:

$$\frac{d-d_0}{[Q_0]}=\varepsilon K[A_0]-Kd \qquad (1)$$

The value of K obtained is 0.7. Thus, the strength of the hydrogen bond is so weak that its effect on the absorption spectra may be

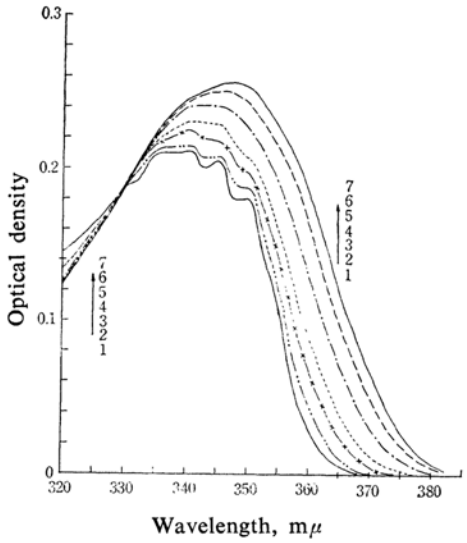


Fig. 6. Absorption spectra of 2-naphthylamine (0.998×10^{-4} M/l.) - methyl benzoate in cyclohexane. The concentrations of methyl benzoate are; 1) 0 M/l.; 2) 1.60×10^{-1} M/l.; 3) 4.00×10^{-1} M/l; 4) 8.01×10^{-1} M/l.; 5) 2.40 M/l.; 6) 4.80 M/l.; 7) 8.00 M/l.

considered to be of the same degree as the solvent effect. In such situations, the change in the absorption spectra cannot be attributed only to hydrogen bonding, and hence, the above value may be an underestimation.

The fluorescence spectra do not change essentially with the addition of the quencher up to 0.2 M; beyond this value, they do show a slight red shift, but the intensity becomes so weak that one cannot say much about the spectral features. In any case, the hydrogen-bonded species is considered to be completely or almost completely non-fluorescent. The quenching constant obtained from the Stern-Volmer formula, which holds in this case up to 10^{-2} M (Fig. 7a), is 84. Beyond 1.6×10^{-2} M, the $(F_0/F-1)/[Q]$ vs. [Q] plot becomes linear, as Fig. 7b shows. This indicates that the hydrogen-bonded species is non-fluorescent or negligibly fluorescent. It may be concluded that the quenching mechanism obeys the following scheme:

$$\begin{array}{ccc} A^* + Q & \underset{k_{-Q}}{\overset{k_Q}{\rightleftharpoons}} & A^*Q \\ k_f + k_d \;\downarrow\uparrow & & \uparrow\downarrow\; k_f' + k_d' \\ A + Q & \overset{K}{\rightleftharpoons} & AQ \end{array} \qquad (2)$$

with $k_d' \gg k_{-Q},\ k_f'$

From this scheme, the following relation can easily be derived:

$$\{(F_0/F)-1\}/[Q]=\left\{k+\left(\frac{\varepsilon'}{\varepsilon}\right)K\right\}+k\left(\frac{\varepsilon'}{\varepsilon}\right)K[Q];$$

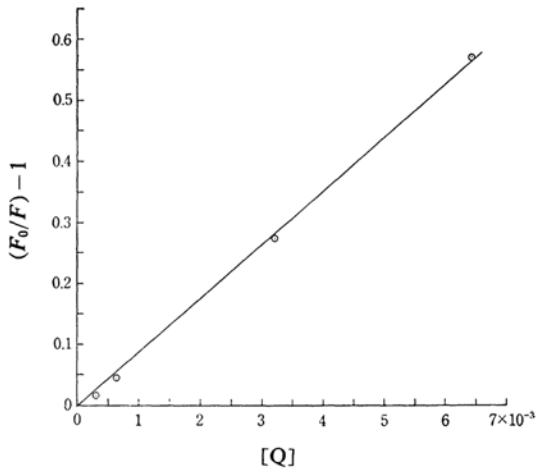


Fig. 7a. 2-Naphthylamine (0.998×10^{-4} M/l.) - methyl benzoate in cyclohexane.
Q: Methyl benzoate

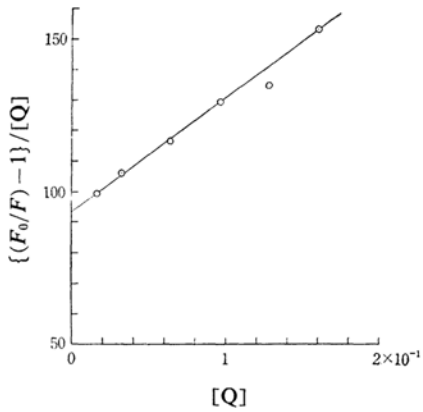


Fig. 7b. 2-Naphthylamine (0.998×10^{-4} M/l.) - methyl benzoate in cyclohexane.
Q: Methyl benzoate

$$k=\frac{k_Q}{k_f+k_d+k_Q}$$

where ε and ε' are, respectively, the molar extinction coefficient of the free species and of the hydrogen-bonded species at the exciting wavelength. It should be noted that actually the exciting wavelength was chosen at the position where $\varepsilon=\varepsilon'$. From the inclination and the intercept of the plot in Fig. 7b, one gets the quenching constant k of 89, while the equilibrium constant K for the hydrogen bonding (in the ground state) is 4. The former value agrees well with the quenching constant obtained from the inclination at $[Q]\to0$, and the latter value is consistent with the view that the hydrogen-bonding equilibrium constant obtained from the absorption spectra was underestimated.

2-Naphthol in Cyclohexane.—The absorption spectra show a typical change due to hydrogen bonding with isosbestic points at 315 and 330 mμ. From measurements of the optical densities at a fixed wavelength (334 mμ) of solutions of various compositions and by analyzing the data with Eq. 1, one gets the hydrogen-bonding equilibrium constant K in the ground state of 11.5 (at 22.6°C).

The fluorescence spectra are scarcely affected at all by the addition of the quencher up to 5×10^{-1} M, and at higher concentrations the fluorescence intensity is too weak for the spectra to be measured. By the application of the Stern-Volmer equation, which holds for quencher concentrations up to 8.0×10^{-3} M, the quenching constant, k, was found to be 87 (Fig. 8a). At higher concentrations, the $\{(F_0/F)-1\}/[Q]$ vs. [Q] plot shows a linear relation, as may be seen in Fig. 8b. The values of k and K as determined from both the intercept and the slope were found to be 78 and 15 respectively. These data are quite consistent with one another, and there is no doubt that the hydrogen-bonded species is non-fluorescent or very poorly fluorescent and that the fluorescence phenomena obey Scheme 1.

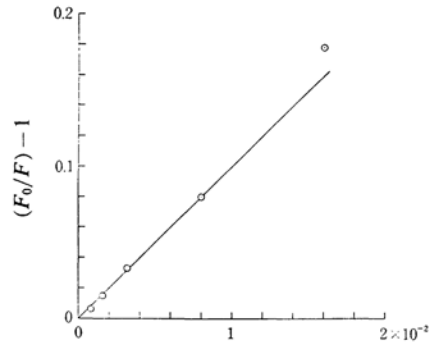


Fig. 8a. 2-Naphthol (1.99×10^{-4} M/l.) - methyl benzoate in cyclohexane.
Q: Methyl benzoate

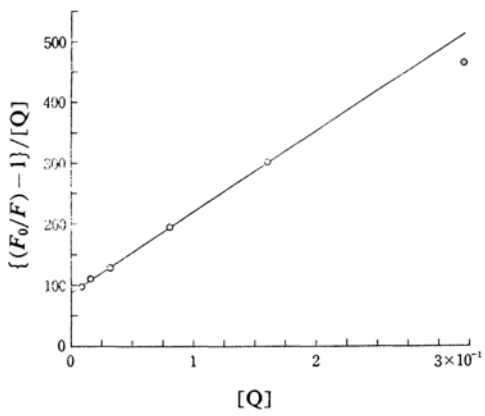


Fig. 8b. 2-Naphthol (1.99×10^{-4} M/l.) - methyl benzoate in cyclohexane.

Quenching Action of Benzoic Acid.—*i) N, N-Dimethyl-2-Naphthylamine in Cyclohexane: ii) N, N-Dimethyl-2-Naphthylamine in Benzene: iii) 2-Naphthyl Methyl Ether in Cyclohexane: iv) 2-Naphthyl Methyl Ether in Benzene.*—In none of these systems are either the absorption or the fluorescence spectra essentially affected by the addition of benzoic acid within the region of the concentrations used. An appreciable quenching of fluorescence occurs, and it is well reproduced by the Stern-Volmer relation. The quenching constants obtained for

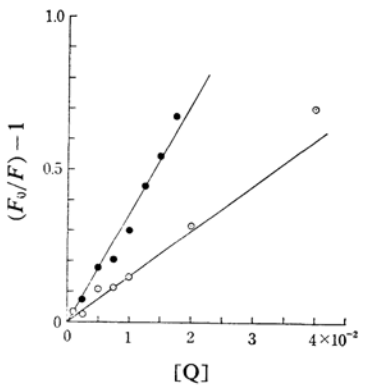


Fig. 9a.

○ 2-Naphthyl methyl ether (2.01×10^{-4} M/l.) - benzoic acid in cyclohexane
● *N,N*-Dimethyl-2-naphthylamine (1.00×10^{-4} M/l.) - benzoic acid in cyclohexane

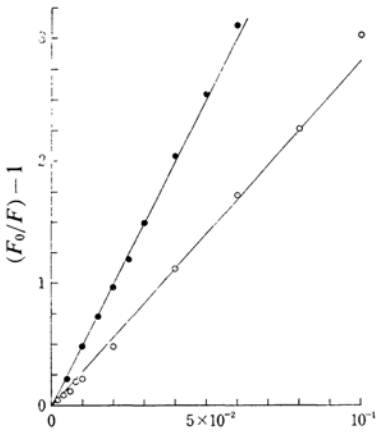


Fig. 9b.

○ 2-Naphthyl methyl ether (2.00×10^{-4} M/l.) - benzoic acid in benzene
● *N,N*-Dimethyl-2-naphthylamine (1.00×10^{-4} M/l.) - benzoic acid in benzene
Q: Benzoic acid

the systems i, ii, iii and iv are, respectively, 36, 50, 16 and 32 with reference to the monomer unit. Some examples are shown in Fig. 9.

v) 2-Naphthylamine in Cyclohexane. — The addition of the quencher causes a slight blue shift of the absorption spectra. The fluorescence are not essentially affected, and the quenching obeys the Stern-Volmer relation, from which one gets $k=52$.

vi) 2-Naphthylamine in Benzene.—The absorption spectra show a clearer blue shift than in cyclohexane. The fluorescence spectra are scarcely affected at all. The Stern-Volmer relation holds up to 5×10^{-2} M of the quencher.

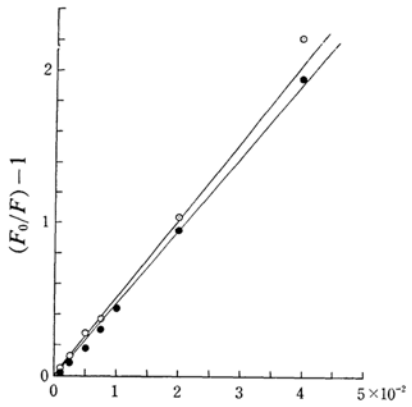


Fig. 10a.

○ 2-Naphthylamine (0.998×10^{-4} M/l.) - benzoic acid in cyclohexane
● 2-Naphthol (1.99×10^{-4} M/l.) - benzoic acid in cyclohexane

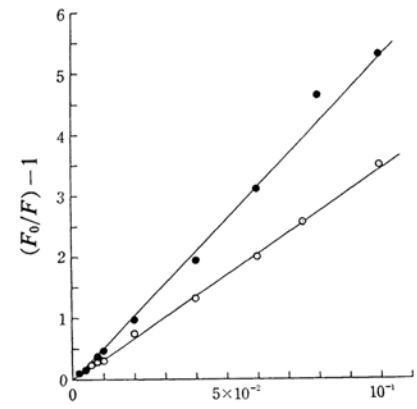


Fig. 10b.

● 2-Naphthylamine (1.00×10^{-4} M/l.) - benzoic acid in benzene
○ 2-Naphthol (2.00×10^{-4} M/l.) - benzoic acid in benzene
Q: Benzoic acid

In the higher concentration region the $\{(F_0/F)-1\}/[Q]$ vs. [Q] plot is linear and one gets $k=48$.

vii) 2-Naphthol in Cyclohexane: viii) 2-Naphthol in Benzene.—In these systems, neither the fluorescence nor the absorption spectra show any essential change. Quenching occurs and is well reproduced by the Stern-Volmer equation in both cases. The quenching constants k are, respectively, 39 and 35. Some examples for v, vi, vii and viii are shown in Fig. 10.

Discussion

A summary of the above results is given in Tables IA, IB and IC. The results in Table IA can be interpreted, for the most part, on the basis of hydrogen bonding. Thus, a remarkable difference in the magnitude of quenching between naphthylamine and naphthol, on the one hand, and their methyl derivatives, on the other, is without doubt due to the existence of intermolecular hydrogen bonding in the former case and the non-existence of it in the latter case.

The results conform quite well to Mataga's view-point, and one can say that such a compound as benzoic acid ester, which has a conjugated system of π-electrons extended to the side chain, can act as a quencher by forming a hydrogen bond with the fluorescer at the side-chain oxygen atom. The finding that a slight quenching occurs in the *N,N*-dimethyl-2-naphthylamine - benzoic acid ester system, but not in the 2-naphthyl methyl ether - benzoic acid ester system, may be interpreted by means of the charge transfer mechanism proposed in the previous paper, because naphthylamine derivatives are expected to act as stronger donors than naphthol derivatives.

Tables IB and IC contain the results for the systems in which benzoic acid is used as a quencher. They all show quenching phenomena to some extent. It is well-known that benzoic acid has a strong tendency to dimerize in non-polar solvents, and since the dimerization constant is so large,[6] practically all the molecules of benzoic acid are considered to exist as dimers under the present experimental conditions. Hence, there is no doubt that the quenching action of benzoic acid is phenomenologically to be attributed to its dimer. As for the detailed mechanism, however, no definite picture can be given at the present stage of investigation. Discussion of possible mechanisms will, however, be given below: the fluorescers being classified into two

6) For example, according to M. Ito (*J. Mol. Spectry*, 4, 144, (1960)) the value is of the order of 10^4.

TABLE IA. QUENCHING ACTION OF METHYL BENZOATE (Q)

Solvent	Fluorescer	Absorption spectra		Fluorescence spectra		
		[Q] M/l.	Spectra	[Q] M/l.	Spectra	Quenching constant
Cy	$-NC(CH_3)_2$	0—8.01	Red shift $\Delta\tilde{\nu}=630$	0—2	Red shift	<0.8
B	$-NC(CH_3)_2$	0—8.01	Red shift $\Delta\tilde{\nu}=160$	0—2	Red shift	5
Cy	$-NH_2$	0—8.01	Red shift $\Delta\tilde{\nu}=680$ H.B.; $K>0.7$	0—8.01	Ambiguous	86
Cy	$-OCH_3$	0—8.01	Red shift $\Delta\tilde{\nu}=190$	0—8.01	Red shift	~0
Cy	-OH	0—8.01	Red shift $\Delta\tilde{\nu}=390$ H.B.; $K=11.5$ (22.5°C)	0—8.01	Ambiguous	87

Cy: Cyclohexane, B: Benzene, $-NC(CH_3)_2$: *N*,*N*-Dimethyl-2-naphthylamine, $-NH_2$: 2-Naphthylamine, -OCH: 2-Naphthyl methyl ether, -OH: 2-Naphthol, H.B.: Hydrogen bond formation, *K*: H.B. formation constant.

TABLE IB. QUENCHING ACTION OF BENZOIC ACID (Q)

Solvent	Fluorescer	[Q] M/l.	Absorption spectra	Fluorescence spectra	Quenching constant
Cy	$-NC(CH_3)_2$	$0—1.75\times10^{-2}$	No change	No change	36
B	$-NC(CH_3)_2$	$0—4\times10^{-1}$	No change	No change	50
Cy	$-OCH_3$	$0—4\times10^{-2}$	No change	No change	16
B	$-OCH_3$	$0—4\times10^{-1}$	No change	No change	22

Abbreviations are the same as before. Quenching constants are referred to a monomer unit.

TABLE IC. QUENCHING ACTION OF BENZOIC ACID (Q)

Solvent	Fluorescer	[Q] M/l.	Absorption spectra	Fluorescence spectra	Quenching constant
Cy	$-NH_2$	$0—4\times10^{-2}$	Slight blue shift	No change	52
B	$-NH_2$	$0—4\times10^{-1}$	Blue shift H.B.; $K=11$	No change	48
Cy	-OH	$0—4\times10^{-2}$	No change	No change	39
B	-OH	$0—4\times10^{-1}$	No change	No change	35

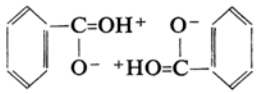
Abbreviations are the same as before. Quenching constants referred to a monomer unit.

groups: B; the fluorescers that cannot act as hydrogen donors; and C; those that can act as hydrogen donors.

It seems plausible to attribute the quenching phenomena observed in group B entirely to a charge transfer mechanism in which the fluorescer acts as an electron donor and the benzoic acid dimer acts as an acceptor.

The reason will be given below. Firstly, the possibility of hydrogen bonding in this group is limited to the case in which a fluorescer and a quencher act, respectively, as a hydrogen acceptor and a donor. However, since a rather strong intermolecular hydrogen bonding is present in the benzoic acid dimer, the dimer itself is expected to have little or no power to act as a hydrogen donor. In fact, no significant change is observed in the absorption spectra of systems made up of this group. Moreover, the formation constant of hydrogen bonding of this type is expected to be smaller in the excited state than in the ground state. In accord with this, there is, in fact, no change in the fluorescence spectra. Hence, one may safely rule out the possibility of hydrogen bonding between the excited fluorescer and the ground-state benzoic acid dimer. Thus, the mechanism of quenching must be of another type, and a charge-transfer mechanism, with charge transfer taking place between the fluorescer and benzoic acid dimer, seems to be the most plausible alternative. If charge transfer

were to take place between the benzoic acid monomer and the fluorescer, then the quenching constants for free acid and the CH_3-ester should be of the same order of magnitude, since the accepting powers of these two substances are not very different. The present result, however, shows that the quenching constant for free acid is far greater than that for the methyl ester. This may be interpreted as follows. According to the general view, the effect of hydrogen bonding on the π-electronic configuration is somewhat similar, though to a lesser extent, to that of acid dissociation, which in the present case is represented as follows*:



In other words, the delocalization of π-electrons in the carboxyl group is increased to some extent in the hydrogen-bonded system. Hence, the vacant level of this group is lowered, and a dimer is expected to be a better electron acceptor than a monomer. Furthermore, the following results can be easily comprehended on the basis of the above point of view: a) The quenching constant for *N*, *N*-dimethyl-2-naphthylamine is larger than that for 2-naphthyl methyl ether. This is because the dimethyl-amino group has a larger electron-releasing power than the methoxy group. b) The fluorescence of *N*, *N*-dimethyl-2-naphthylamine and 2-naphthyl methyl ether is quenched by benzoic acid much more than by methyl benzoate. The reason for this has already been stated above.

Turning to group C, the fluorescer is now free amine or free acid. In these cases there are two types of hydrogen bonding conceivable. One is type-a, in which the fluorescer is a donor and the quencher is an acceptor, and the other is type-b, in which their roles in the hydrogen bonding are reversed.

However, if one assumes that type-b hydrogen bonding is of no importance in the quenching phenomenon, as has been established already, then only type-a remains to be considered. However, in this connection it should be noted that the absorption spectra of naphthylamine display a slight blue shift after the addition of benzoic acid and that such a blue shift is usually related to type-b hydrogen bonding. This might imply that the formation constant of the hydrogen bond between naphthylamine and benzoic acid is large enough to compete with the dimerization of the acid. However, it is still open to question whether this is really true or whether the phenomenon is due to other unknown causes. On the other hand, the fluorescence spectra still display either a red shift or no change at all, which suggests the existence of type-a hydrogen bonding in the excited state. This is consistent with the expectation that this type of hydrogen bonding will become stronger in the excited state. Thus, one may safely assume that type-b does not take part in the quenching phenommena, whereas it is plausible that the hydrogen bond of type a participates in the quenching to some extent. However, there is a question about how the hydrogen bond is formed in this case; thus it is quite unknown whether such a hydrogen bond is formed between the fluorescer and benzoic dimer as it is, or whether the hydrogen bond formation is accompanied by a partial or a complete dissociation of the dimer molecules. The view that quenching really occurs through hydrogen bonding is supported by the fact that the quenching constant for naphthylamine and naphthol is somewhat larger than that for their methyl derivatives. However, on the basis of the discussion of group B, there is no doubt that the charge transfer mechanism also takes part in the quenching. The view that both the mechanisms are taking part in this group is supported by the following findings: a) The quenching constant of benzoic acid is larger for naphthylamine than for naphthol, while the quenching constant of methyl benzoate is of the same magnitude for naphthylamine and naphthol. This can be interpreted by taking account of the charge transfer mechanism in the former case, since the hydroxyl group is a stronger hydrogen donor than the amino group, while the amino group is a stronger electron-releasing group than the hydroxyl group. b) Benzoic acid quenches the fluorescence of naphthylamine more than it does that of dimethylnaphthylamine, and that of naphthol more than that of naphthyl methyl ether. This can be interpreted as being due to hydrogen bonding in the cases of the free amine and phenol. c) Methyl benzoate is a stronger quencher than benzoic acid toward naphthylamine and naphthol. This may be due to the fact that benzoic acid is a weaker hydrogen accepter than the ester, as has already been stated. It should be noted, however, that the quenching constants of benzoic acid in Tables 7B and 7C are given in terms of the monomer unit. If they are expressed in terms of the dimer unit, the values become twice as large and the statement in c) is not so decisive.

To summarize, only the charge transfer

* The contribution of this structure is inferred from the charge-transfer mechanism of the hydrogen bonding.[7]

7) S. Nagakura and M. Gouterman, *J. Chem. Phys.*, **26**, 881 (1957).

mechanism need be considered for group B, while the charge transfer mechanism and the hydrogen-bonding mechanism simultaneously take place in group C. It is apparent, however, that more confirming evidence is necessary before the charge transfer mechanism can be fully accepted.

Summary

1) The quenching action of benzoic acid (dimer) (BA) and methyl benzoate (MB) on the fluorescence of 2-naphthol (I), 2-naphthylamine (II), 2-naphthyl methyl ether (III) and *N*, *N*-dimethyl-2-naphthylamine (IV) in benzene and in cyclohexane has been studied.

2) MB has little or no quenching effect on the fluorescence of III and IV, whereas it shows a significant quenching action on I and II. The latter is due to the intermolecular hydrogen bonding between the fluorescer and the quencher (the H.B. mechanism).

3) BA shows quite a large quenching action on III and IV. All the results can be interpreted on the basis of a charge transfer mechanism for quenching (the C.T. mechanism).

4) The quenching action of BA is larger on I than on III, and larger on II than on IV, except for benzene solutions of II and IV, in which case the magnitudes are equal within the range of experimental error. These results has been discussed on the basis of a simultaneous occurrence of the C.T. and H.B. mechanisms.

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Department of Chemistry
Faculty of Science
Tohoku University
Katahira-cho, Sendai