# *The Quenching Action of Pyridine and Quinoline on the Fluorescence of Naphthalene Derivatives*

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The influence of the hydrogen bond on the fluorescent properties of aromatic compounds has been studied by seveval authors, including Mataga and Koizumi,[1] Kasha[5] and Weller.[6] Mataga particularly has performed some systematic studies using various combinations of acceptor and donor.[1-4] One of his most interesting findings is that an aromatic fluorescer is strongly quenched when it is hydrogen-bonded directly with another $\pi$-electronic system. Thus, for example, the fluorescence of naphthol and acridine is largely quenched by, respectively, pyridine and phenol. He has proposed, as a mechanism for such a quenching process, that the charge transfer from quencher to fluorescer or from fluorescer to quencher via the hydrogen bond occurs, followed by the vibronic energy dissipation. In connection with this hypothesis, it seemed interesting to extend the study to systems in which the possibility of an electronic energy transfer via the hydrogen bond is conceivable. In such cases there is also a possibility that the quenching efficiency depends on the wavelength of the exciting light. Very few examples of such systems have ever been studied, perhaps because the complicated character of such systems is supposed to make the analysis of the results very troublesome.

We have sttempted such an experiment using naphthol and naphthylamine as hydrogen-donating fluorescers and quinoline, as a hydrogen-accepting quencher; for the sake of comparison, we have also studied the effect of quinoline on the fluorescence of 2-naphthylmethylether and *N, N*-dimethyl-2-naphthylamine, both of which are unable to form hydrogen bonds. We have found appreciable quenching, even in the latter cases. In connection with these rather unexpected results, therefore, some experiments have been made with the use of pyridine as a quencher, and, further, the solvent effect has been studied to some extent.

1) N. Mataga, Y. Kaifu and M. Koizumi, *Nature*, **175**, 731 (1955); This Bulletin, **29**, 115 (1956); N. Mataga and S. Tsuno, ibid., **30**, 368, 711 (1957).
2) N. Mataga, ibid., **31**, 481 (1958).
3) N. Mataga, ibid., **31**, 487 (1958).
4) N. Mataga, Y. Torihashi and Y. Kaifu, *International Symposium on Molecular Structure and Spectroscopy, September 1962, Science council of Japan*, D. 113-1~4; *Z. Phys. Chem., N. F.*, **34**, 379 (1962); N. Mataga and Y. Kaifu, *J. Chem. Phys.*, **36**, 2804 (1962).
5) M. Ashraf El-Bayoumi and M. Kasha, ibid., **34**, 2181 (1961).
6) A. Weller, *Naturwiss.*, **7**, 175 (1955); *Z. Elektrochem.*, **60**, 1144 (1956). A. Weller and K. H. Grellmann, ibid., **64**, 145 (1960).

## Experimental

**Materials.**—*2-Naphthylamine.* — A G. R. sample was dissolved in dilute hydrochloric acid, filtered, and neutralized by soduim hydroxide. The precipitate obtained, after being filtered and dried, was submitted to repeated crystallization from a water-ethanol mixture and to sublimation in vacuo.

*N, N-Dimethyl-2-naphthylamine.* — The mixture of methyl iodide and 2-naphthylamine, with sodium hydroxide added, was heated for ten hours at 120°C in a sealed vessel. The product was extracted by chloroform, and the raw crystal was obtained by evaporating the solvent. For further purification, recrystallization from methanol and sublimation under reduced pressure were repeated several times (m. p. 43.2°C).

*2-Naphthol.*—A G. R. sample was recrystallized from a water-ethanol mixture and sublimed in vacuo.

*2-Naphthylmethylether.* — A concentrated sulfuric acid solution of 2-naphthol and methyl alcohol was refluxed for four hours at 125°C. The product was extracted by benzene and washed with an aqueous alkaline solution until no existence of a phenolic hydroxy group was detected by a Millon test. The crystal obtained by evaporating the solvent, after several recrystallizations from ethanol, was dried in a calcium chloride desiccator (m. p. 72.1°C).

*Quinoline.* — Synthesized quinoline manufactured by Tokyo Kasei was dried over barium oxide for more than a week and was twice distilled in vacuo.

*Pyridine.*—A G. R. reagent of Wako-Junyaku was dehydrated by making the azeotrope with benzene. Ordinary distillation, fractional distillation with a packed column and vacuum distillation were performed in succession.

*n-Hexane.*—After being shaken for a long time with fuming sulfuric acid diluted with concentrated sulfuric acid, this was washed with water, neutralized with an aqueous alkaline solution, treated with alkaline potassium permanganate, washed again with water, and then dried over calcium chloride. It was further distilled from over sodium metal or phosphorous pentoxide. The fraction (67.5~68.5°C) was used.

*Benzene.*—A G. R. sample of Wako-Junyaku was shaken with concentrated sulfuric acid, treated with an aqueous alkaline solution, washed with water, and then dried over calcium chloride. Three recrystallizations in a ice bath and fractional distillation through a packed column were performed.

*Ethanol.*—A G. R. sample of Wako-Junyaku was fractionally distilled through a column packed with stainless spirals.

*Anthracene.*—A sample of a high purity was kindly supplied by Professor Shimpachiro Kato of the University of Tokyo.

The purity of 2-naphthylmethylether and of *N*, *N*-dimethyl-2-naphthylamine was checked by I. R., while that of pyridine and quinoline was checked by gas chromatography.

**Apparatus.**—A block diagram of fluorometer is shown in Fig. 1.

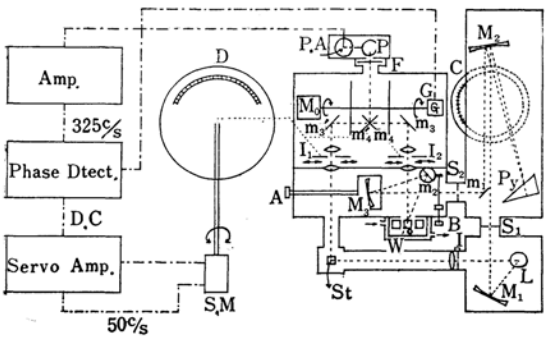



Fig. 1. Fluorometer.
A, B: screw for adusting focus, C: wavelength disk, D: intensity disk, F: filter, G: generator, I, $I_1$, $I_2$: iris, L: light source, $M_0$: synchronous motor, $m_1$, $m_2$, $m_3$, $m_4$, $m_3'$, $m_4'$: mirror, $M_1$, $M_2$, $M_3$: concave mirror, o: sample, P: photomultiplier, P. A: priamplifier, Py: prism. $S_1$, $S_2$: slit, S. M: reversible motor, St: standard material, W: water jacket

This apparatus is constructed in such a way that the solution is illuminated obliquely from the front, the exciting light being focused close to the cell. The fluorescent light coming out from the same front is compared with a standard beam taken through another path from the same light source; by mechanically balancing the intensity of the two beams, the ratio of the two can be read directly on a scale-disk. The apparatus is suitable for systems with a large optical density. The exciting light from a 500W Xenon lamp of Ushio Kogyo was made monochromatic by a prism monochromator. A RCA 1P28 photomultiplier was used. The absorption spectra were measured by means of a Hitachi spectrophotometer, and the fluorescence spectra, by the same apparatus with its fluorescence attachments.

**The Procedure, the Calibration of the Apparatus and an Outline of the Analysis.**—The measurement was made in the following way. The relative intensity against the standard light beam was measured with a solution containing only a fluorescer and with a solution containg the same concentration of fluorescer and various amounts of quencher at the same time. From these measurements the ratio of the former, $F_0$, to the latter, $F$, was calculated. The measurement was made at constant temperatures and at various wavelengths in the region from 260 to 350 m$\mu$. The concentration was $10^{-3}$ M for 2-naphthylamine and *N*, *N*-dimethyl-2-naphthylamine, and $2.5\times10^{-3}$ M for 2-naphthol and 2-naphthylmethylether. The concentration of quencher was varied over a suitable range according to the situations.

After the scale of the intensity ratios and of the wavelengths had been calibrated in a suitable way, the depth effect or the effect of the optical density of the system on the measured fluorescence intensity was examined. This effect is, of course, mainly due to the quantity of the absorption of light, but it is expected that the effect partially depends on the geometric condition characteristic of the apparatus. Thus, the emitting position varies according to the optical density of the solution, thereby affecting the measured intensity. This effect is expected to be especially large when the optical density is rather small and when the exciting beam penetrates into the inner part of the solution. This is the reason why the experimental calibration is desirable.

To examine this effect quantitatively, the solution of anthracene in *n*-hexane was used as a sample for calibration, since it has been well established by many investigations[7-9,10] that its fluorescence

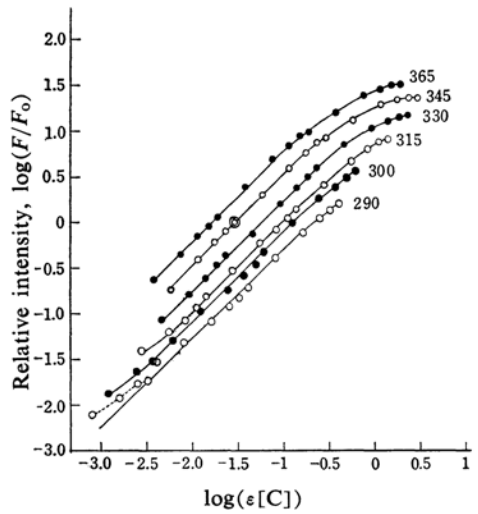



Fig. 2. Relation between fluorescence intensity and optical density for the solution of anthracene in *n*-hexane. All the $(F/F_0)$ values are the relative ones, the value for $10^{-5}$ M anthracene solution at 345 m$\mu$ being taken as a standard (denoted by ◎ in the figure). The number is exciting wavelength (m$\mu$).

7) Cf., for example, W. H. Melhuish, *J. Phys. Chem.*, **65**, 229 (1961); W. R. Ware, ibid., **66**, 455 (1962).
8) G. Weber and F. W. J. Teale, *Trans. Faraday Soc.*, **54**, 640 (1958). J. Ferguson, *J. Mol. Spectroscopy*, **3**, 177 (1959).
9) E. J. Bowen and A. Norton, *Trans. Faraday Soc.*, **35**, 45 (1939).
10) A. Dammers-de Klerk, *Mol. Phys.*, **1**, 141 (1958).

quantum yield is independent of the wavelength[8] and that, further, its concentration quenching is practically of no importance up to about $10^{-3}$ M.[9] Moreover, the experimental conditions quite similar to those for the systems to be studied can be chosen. Actually the concentration of anthracene in *n*-hexane was varied from $2\times10^{-6}$ M to $10^{-3}$ M. The relations obtained between the optical density of the solution and the measured fluorescence intensity are shown in Fig. 2.

The dependence of the position of the curves on the frequency is no doubt due to the intensity distribution of the exciting light. In the region of low optical density, all the curves have the same unit slope, while they tend to constant values characteristic for each frequency. The latter phenomena are mainly due to the situations approaching the complete absorption of exciting light. In fact, the plot of $\log(F/F_0)$ against $\log(1-e^{-2.303\varepsilon[C]})$ gives a straight line, with a unit slope for each frequency. From the results in Fig. 2 one can estimate the intensity distribution of the exciting light. In most of the experiments the optical density was so high that the intensity of the fluorescence was believed to be independent of it, but in a few cases where the optical density was lower, the correction factor for the incomplete absorption of light was estimated from Fig. 2.

To interpret the relation between $F_0/F$ and the concentration of the quencher, it is necessary in general to take into account the inner filter effect of the absorption of the quencher, the effect of hydrogen bond formation in the ground state, and lastly, the genuine quenching effect. As has been shown by Mataga[4] and by one of the present authors[11] (M. K.), the quenching effect via the hydrogen bond formation must be treated in just the same way as in the case of dynamical quenching, in contradistinction to the case of the enhancement of fluorescence intensity. The prerequisite for the method of analysis, that is, the complete suppression of fluorescence by hydrogen bonding, is supported by the fact that the fluorescence spectra of naphthylamine and naphthol are not affected by the addition of enough pyridine or quinoline to effect an appreciable change in the absorption spectra of the fluorescer. This fact enables us further to disregard the possibility of the reabsorption of the fluorescence by a quencher due to the slight overlapping of the fluorescence spectra and the absorption spectra of the quencher. In addition, the fluorescence intensity of quinoline is so weak that it can be disregarded in comparison with the fluorescence of 2-naphthylamine and 2-naphthol. Thus, it is most plausible to analyze the experimental results on the basis of the assumption that only free fluorescer molecules can emit fluorescence and that the pyridine or quinoline molecules which attack the excited fluorescer molecules cause the quenching phenomenon. In some cases, however, the influence on the fluorescence due to the inner filter effect of the quencher and the influence of the existence of a hydrogen-bonded complex are so great that it is very difficult to obtain the exact value of the quenching constant. It is desirable that any particular device is, if possible, used case by case.

11) M. Koizumi, Symposium on the Electronic States of Molecules, held by the Chemical Society of Japan, October, 1961.

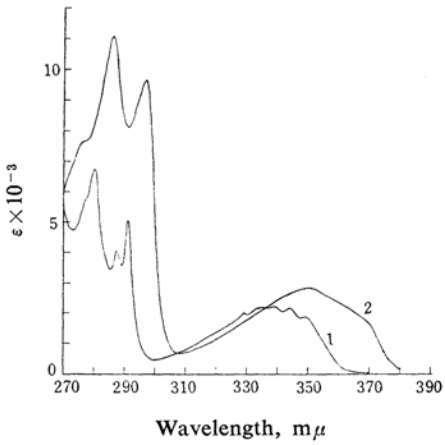



Fig. 3a. Absorption spectra in *n*-hexane.
1; 2-Naphthylamine
2; *N*, *N*-Dimethyl-2-naphthylamine

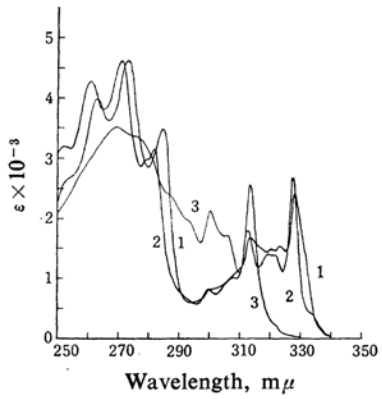



Fig. 3b. Absorption spectra in *n*-hexane.
1; 2-Naphthol, 2; 2-Naphthylmethylether, 3; Quinoline

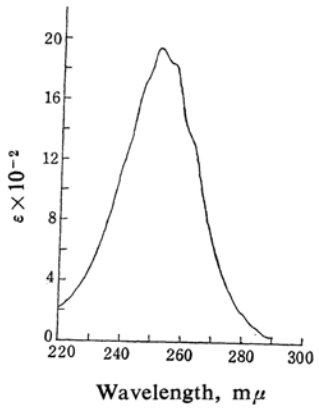



Fig. 3c. Absorption spectrum of pyridine in *n*-hexane.

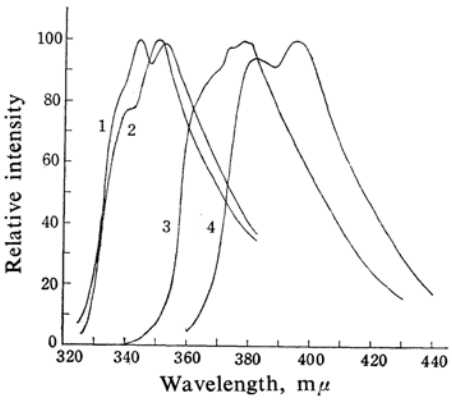



Fig. 3d. Fluorescence spectra (arbitrary unit).
1; 2-Naphthylmethylether $5\times10^{-4}$ M/l. in *n*-hexane
2; 2-Naphthol $2\times10^{-4}$ M/l. in *n*-hexane
3; 2-Naphthylamine $10^{-3}$ M/l. in *n*-hexane
4; *N*, *N*-Dimethyl-2-naphthylamine $10^{-3}$ M/l. in *n*-hexane

## Results

**Absorption Spectra and Fluorescence Spectra.**—The absorption spectra of some fluorescers and quenchers and the fluorescence spectra for the former are shown in Fig. 3, a, b, c and d.

**The Equilibrium Constant of the Hydrogen Bond Formation in the Ground State.**—This was obtained spectroscopically by the usual method. Changes in the absorption spectra in the case of 2-naphthol—pyridine and in the case of 2-naphthol—quinoline, both in *n*-hexane, are shown in Fig. 4, a and b.

The equilibrium constant was evaluated by using the following equation:

$$\frac{d^{\lambda}-d_{o}^{\lambda}}{[A]}=\varepsilon'^{\lambda}K[D_o]-Kd^{\lambda} \qquad (1a)$$

$$K=\frac{[A]\,(d_{o}^{\lambda}-d'^{\lambda})+[A']\,(d^{\lambda}-d_{o}^{\lambda})}{[A]\,[A']\,(d'^{\lambda}-d^{\lambda})} \qquad (1b)$$

where [A] or [A'] and [$D_o$] denote, respectively, the total concentration of quencher and the total concentration of fluorescer, where $d^{\lambda}$ or $d'^{\lambda}$ and $d_{o}^{\lambda}$ are the optical densities at the wavelength $\lambda$ in the presence and in the absence of a quencher respectively, and where $\varepsilon'^{\lambda}$ is the molar extinction coefficient of the hydrogen-bonded complex at $\lambda$. As Fig. 5 shows, the 1a relation holds quite satisfactorily.

The values obtained from 1a are given in Table I, together with the pertinent data published in the literature. The values from 1a are in good agreement with the average values obtained numerically from 1b.

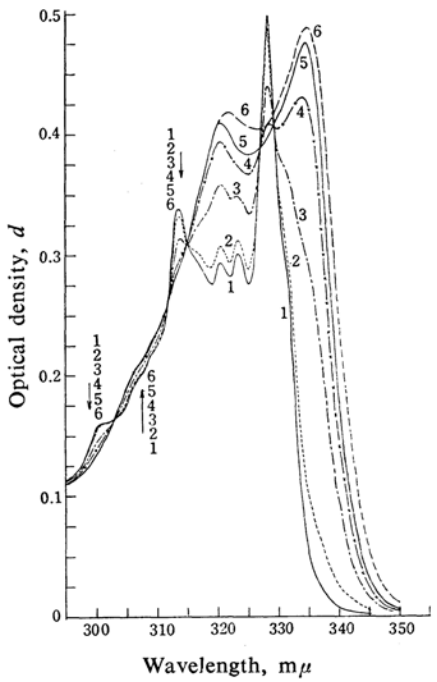



Fig. 4a. Absorption spectra of 2-naphthol ($2\times10^{-4}$ M/l.)—pyridine in *n*-hexane at 21°C. The contribution by pyridine is eliminated by substracting the absorption of pyridine solution of corresponding concentration. Concentration of pyridine (M/l.).
1; 0, 2; $9.943\times10^{-4}$, 3; $9.943\times10^{-3}$, 4; $4.972\times10^{-2}$, 5; $2.486\times10^{-1}$, 6; 2.486

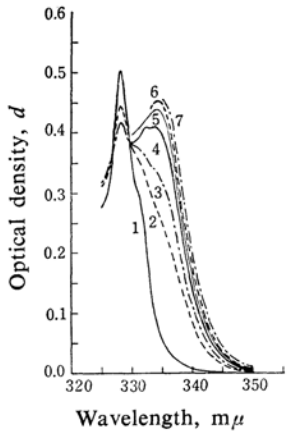



Fig. 4b. Absorption spectra of 2-naphthol ($2\times10^{-4}$ M/l.)—quinoline in *n*-hexane at 21°C. The contribution by quinoline is eliminated by substracting the absorption of quinoline solution of corresponding concentration.
Concentration of quinoline (M/l.).
1; 0, 2; $6.767\times10^{-3}$, 3; $1.353\times10^{-2}$, 4; $3.384\times10^{-2}$, 5; $6.767\times10^{-2}$, 6; $1.353\times10^{-1}$, 7; $3.384\times10^{-1}$

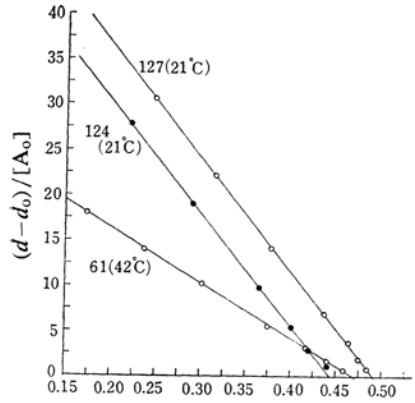



Fig. 5. The procedure for obtaining the hydrogen bonding formation constant $K$. The numbers represent the value of $K$ at the given temperature.
○ : 2-Naphthol—Pyridine in *n*-hexane at 334 mμ.
● : 2-Naphthol—Quinoline in *n*-hexane at 336 mμ.

TABLE I. THE EQUILIBRIUM CONSTANT $K$ OF THE HYDROGEN BOND FORMATION

| System | Solvent | Temp. °C | $K$ |
|---|---|---|---|
| 2-Naphthol—Pyridine | *n*-Hexane | 21 | 125 |
| | | 42 | 61 |
| | Benzene[2] | 14 | 41 |
| 2-Naphthol—Quinoline | *n*-Hexane | 21 | 125 |
| 2-Naphthylamine—Pyridine | Cyclohexane[4] | 15 | 12 |
| | Benzene[2] | 13 | 0.2 |

**2-Naphthylamine and *N*, *N*-Dimethy-2-naphthylamine in *n*-Hexane.**—In the case of *N*, *N*-dimethyl-2-naphthylamine—quinoline which has no ability to act as a hydrogen donor, there are two factors which must be taken into account: (i) the genuine quenching effect and (ii) the inner filter effect due to the absorption of quinoline. On this basis, $F_0/F$ is expressed as follows:

$$F_0/F=\frac{1-e^{-\alpha_D[D]d}}{1-e^{-(\alpha_D[D]+\alpha_A[A])d'}}\left(\frac{\varepsilon_D[D]+\varepsilon_A[A]}{\varepsilon_D[D]}\right)\times(1+k[A])=\frac{1-e^{-\alpha_D[D]d}}{1-e^{-(\alpha_D[D]+\alpha_A[A])d'}}\times\left\{1+\left(k+\frac{\varepsilon_A}{\varepsilon_D[D]}\right)[A]+k\frac{\varepsilon_A}{\varepsilon_D[D]}[A]^2\right\} \quad (2)$$

where [D] and [A] are the concentrations of fluorescer and of quencher respectively, where $\alpha_D$, $\alpha_A$, $\varepsilon_D$ and $\varepsilon_A$ are, respectively, the molar absorbancy of fluorescer and quencher and the molar extinction coefficient of fluorescer and quencher, and where $k$ is the quenching constant. The first term on the right side concerns the absorption of light, and its denominator can always be well approximated by 1, while for the numerator this is not always possible in the region where $\alpha_D$ is rather small. The value was estimated from the calibration curves of Fig. 2. $F_0/F$ divided by this value will be denoted as $(F_0/F)_{corr.}$. It is to be added that there is no overlapping of the fluorescence spectra and the absorption spectra of quinoline, even in such a high concentration of the latter as 0.388 M. As required by Eq. 2, the plot of $(F_0/F)_{corr.}-1$ against [A] gives a concave curve upward, while the plot of $((F_0/F)_{corr.}-1)/[A]$ against [A] gives a good straight line, as is shown in Fig. 6.

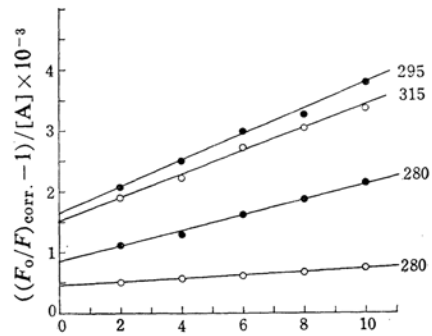



Fig. 6. Plot of $((F_0/F)_{corr.}-1)/[A]$ against the concentration of quinoline [A]. The number is the exciting wavelength (mμ).
● : 2-Naphthylamine ($10^{-3}$ M/l.)—Quinoline in *n*-hexane at 20°C.
○ : *N*, *N*-Dimethyl-2-naphthylamine ($10^{-3}$ M/l.)—Quinoline in *n*-hexane at 20°C.

From the slope and intercept one gets $k\varepsilon_A/\varepsilon_D[D]$ and $k+\varepsilon_A/\varepsilon_D[D]$; $k$ can be evaluated if the values of $\varepsilon_A$ and $\varepsilon_D$ under the experimental conditions are estimated. In this system, however, the absorption spectra of quinoline do not overlap with those of the fluorescer in the region >335 mμ, and so the correct value of $k$ can be obtained from the linear plot of $(F_0/F)_{corr.}-1$ against [A] at these wavelengths. Thus, in this case,

$$(F_0/F)_{corr.}-1=k[A] \quad (3)$$

The values obtained are $k=90$ (20°C) and $k=100$ (40°C).

This is a result somewhat unexpected, since Mataga[2] found previously that pyridine, the basicity of which is quite similar to quinoline, does not quench the fluorescence of *N*, *N*-dimethyl-2-naphthylamine at all (see Discussion).

In the case of 2-naphthylamine—quinoline, the hydrogen bond is formed with quinoline. However, the equilibrium constant of its formation, as has already been mentioned, is quite small, and under the experimental conditions the change in the absorption spectra due to the hydrogen bond formation is negligible. Therefore, all the effects of hydrogen bond formation such as (i) the increase in the reabsorption of fluorescence, (ii) the decrease in the fluorescence due to the reduced number of free molecules, and (iii) the change in the inner filter effect can be disregarded. Hence Eq. 2 is equally well applicable in this case. In fact, the plot of $(F_0/F)_{corr.}-1$ against [A] gives a concave curve upward, while the plot of $((F_0/F)_{corr.}-1)/[A]\sim[A]$ gives a good straight line (Fig. 6). As in the case of *N*, *N*-dimethyl-2-naphthylamine—quinoline, however, a more exact value of $k$ can be obtained from the results in the $\sim$335 m$\mu$ region, where the absorptions of the two substances do not overlap and where Eq. 3 satisfactorily holds. The values obtained are $k=120$ (20°C) and $k=140$ (40°C).

**The Frequency Effect on the Quenching Constant in the Cases of 2-Naphthylamine—Quinoline and *N*,*N*-Dimethyl-2-naphthylamine—Quinoline.**—Since there is some difficulty in obtaining the correct value of $k$ at various frequencies on the basis of Eq. 2, the dependence of $k$ on the frequency was examined in the following way. From Eq. 2 one can calculate $\varepsilon_D/\varepsilon_A$ if $k$ is assumed to be constant, irrespective of the frequency, and to have the same value as that at 335 m$\mu$, where there is no overlapping of absorptions. If the values of $(\varepsilon_A/\varepsilon_D)$ at various frequencies obtained from the calculation coincide with those from the observed $\varepsilon_A$ and $\varepsilon_D$ values, one may conclude that there is no frequency effect on $k$. In the opposite case, one will have to recognize the dependence of $k$ on the frequency. The result is, as Figs. 7 and 8 show, that there is a very good correspondence between the two.

Thus there is no doubt that $k$ is constant, independent of the frequency.

**2-Naphthylmethylether and 2-Naphthol in *n*-Hexane.**—In the case of 2-naphthylmethylether—quinoline, the absorption spectra of the two substances overlap over the whole wavelength region. Therefore, $\varepsilon_A/\varepsilon_D$ values were estimated from the molar extinction coefficient and $k$ was calculated for various frequencies on the basis of Eq. 2. The value is $k=53$ (21°C), irrespective of the wavelength.

In the case or 2-naphthol—quinoline, there are three kinds of effects which reduce the fluorescence intensity: (i) the genuine quenching action, (ii) the inner filter effect, and

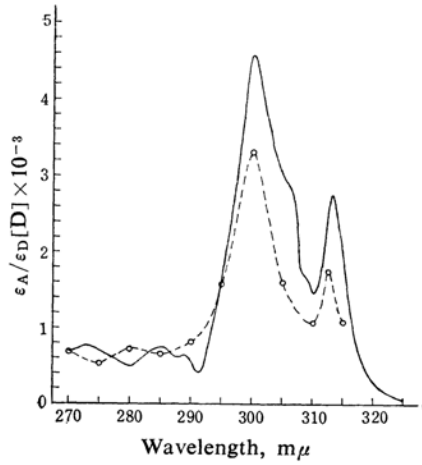



Fig. 7. Inner filter effect for 2-naphthylamine—quinoline in *n*-hexane. Full line and dotted line represent respectively the calculated value $\varepsilon_A/\varepsilon_D[D]$ and the observed value.

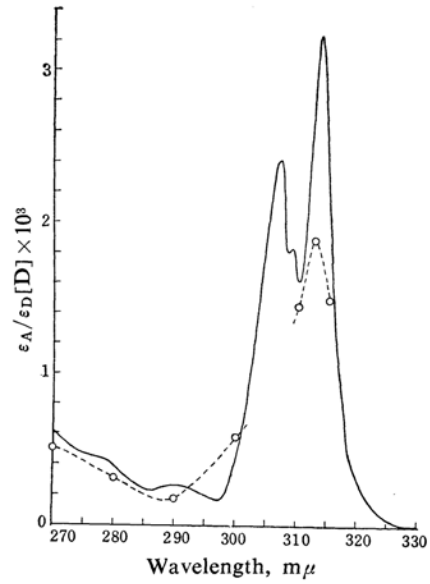



Fig. 8. Inner filter effect for *N*, *N*-dimethyl-2-naphthylamine—quinoline in *n*-hexane. Full line and dotted line represent respectively the calculated value $\varepsilon_A/\varepsilon_D[D]$ and the observed value.

(iii) the formation of the nonfluorescent hydrogen-bond complex in the ground state. Taking these three effects into account, one can derive the following equation:

$$(F_0/F)_{corr.}=(1+k[A])\times\left(1+\frac{\varepsilon_A[A]}{\varepsilon_D[D]}+\frac{\varepsilon_{DA}K}{\varepsilon_D}[A]\right)$$

where $K$ is the equilibrium constant of the

hydrogen bond formation. The above equation is further changed as follows by putting $[D] = [D_o]/(1+K[A])$:

$$(F_o/F)_{corr.} - 1 = \left(k + \frac{\varepsilon_A + K[D_o]\,\varepsilon_{DA}}{\varepsilon_D[D_o]}\right)[A] + \left(k\frac{\varepsilon_A + K[D_o]\,\varepsilon_{DA}}{\varepsilon_D[D_o]} + \frac{K\varepsilon_A}{\varepsilon_D[D_o]}\right)[A]^2 + k\frac{K\varepsilon_A}{\varepsilon_D[D_o]}[A]^3 \quad (4)$$

As Fig. 9 shows,

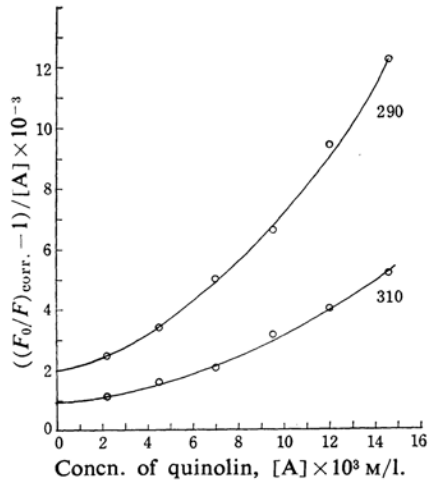



Fig. 9. Plot of $((F_o/F)_{corr.}-1)/[A]$ against the concentration of quinoline [A] for 2-naphthol ($10^{-3}$ M/l.)—quinoline in *n*-hexane at 21°C. The number is exciting wavelength (mμ).

the plot of $((F_o/F)_{corr.}-1)/[A]$ against [A] gives a concave curve upward and so Eq. 4 is considered to fit the experimental results. However, the exact value of $k$ could not be obtained because the other two effects are considerably larger than the genuine quenching action and made the treatment erroneous. It was roughly estimated that $k \approx 100$ irrespective of the wavelength.

It is to be added here that in these two cases, quinoline has absorption spectra the long wavelength part of which overlaps slightly with the fluorescence spectra and that, moreover, there is some possibility that the nonfluorescent hydrogen-bonded complex reabsorbs the fluorescence to some extent. Of course, the above treatment does not take any account of these possibilities.

**Pyridine as a Quencher.** — All the above results, which concern cases where quinoline acts as a quencher, are rather unexpected in view of the results and the proposed mechanism by Mataga,[2] because 2-naphthylmethylether and *N, N*-dimethyl-2-naphthylamine, which are both incapable of forming a hydrogen bond, are appreciably quenched by quinoline. Therefore, the quenching action of pyridine was reexamined.

*N, N-Dimethyl-2-naphthylamine and 2-Naphthylmethylether.*—In the case of these two substances, the effect, if it exists, must be due to the genuine quenching action. The result reconfirmed Mataga's observation[2] that there was not any slight quenching action of pyridine.

*2-Naphthylamine and 2-Naphthol.* — Taking into account the genuine quenching action and the effect due to the formation of a nonfluorescent hydrogen-bonded complex in the ground state, the following equation can be derived:

$$(F_o/F)_{corr.} - 1 = \left(k + \frac{\varepsilon'}{\varepsilon}K\right)[A] + k\frac{\varepsilon'}{\varepsilon}K[A]^2 \quad (5)$$

where $\varepsilon'$ and $\varepsilon$ are, respectively, the molar extinction coefficient of the hydrogen-bonded complex and the free fluorescer, $k$ and $K$ are, respectively, the quenching constant and the equilibrium constant of the hydrogen-bond formation.

In the case of 2-naphthylamine, the plot of $(F_o/F)_{corr.}-1$ against [A] gives a good straight line. This is because the quilibrium constant of the hydrogen-bond formation in the gound state is so small in this case that it can safely be disregarded. From the slope one gets $k=116$ (23°C) and $k=133$ (40°C).

In the case of 2-naphthol, $(F_o/F)_{corr.}-1 \sim [A]$ gives a concave curve upward, while $((F_o/F)_{corr.}-1)/[A] \sim [A]$ gives a good straight line and from its slope one gets $kK\varepsilon'/\varepsilon$. At the wavelength where $\varepsilon' \approx \varepsilon$, one gets $k=117$ (21°C) by using the value $K=125$ (21°C).

**The Quenching Phenomena in Ethanol and Benzene.**—To get a better insight into the mechanism of quenching, analogous experiments for several systems were made in ethanol and benzene. The results for benzene were qualitatively similar to those in *n*-hexane except that the quenching constants in all cases are somewhat less than those in *n*-hexane. In the case of ethanol, however, some extraordinary results were obtained. Thus, pyridine was found slightly to quench the fluorescence of *N,N*-dimethyl-2-naphthylamine.[3] The quenching constant evaluated by applying the Stern-Volmer equation (Eq. 3) is $k=15$ (25°C). However, the fluorescence of 2-naphthylmethylether was not affected at all by the addition of pyridine.* In the case of 2-naphthylamine

* This result contradicts Mataga's remark that this compound shows considerable quenching (see Ref. 3).

—pyridine, the plot of $(F_0/F)_{corr.}-1$ against [A] gives a good straight line and from the slope one gets $k=16$ (25°C). These findings can be comprehended if one considers that both fluorescer and quencher are hydrogen-bonded with ethanol almost completely (see Discussion). When quinoline was used as a quencher, treatment similar to that used in the case of *n*-hexane can be applied, and for 2-naphthylamine and *N*,*N*-dimethyl-2-naphthylamine, quite reliable *k*-values were obtained. No reliable value for 2-naphthylmethylether could be obtained.

The quenching constants so far obtained are tabulated in Table II.

## Discussion

In such non-polar solvents as *n*-hexane and benzene, pyridine can be a quencher only when hydrogen bond formation is possible; thus 2-naphthylamine and 2-naphthol are quenched remarkably, while *N*,*N*-dimethyl-2-naphthylamine and 2-naphthylmethylether are not quenched at all. In such cases, therefore, there is no doubt that the hydrogen bond plays an important role in the quenching process. However, the fact that *N*,*N*-dimethyl-2-naphthylamine and 2-naphthylmethylether are quenched to some extent by quinoline indicates that hydrogen bonding is not always necessary for quenching. Particularly, the result that *N*,*N*-dimethyl-2-naphthylamine is quenched by quinoline to almost the same extent as 2-naphthylamine strongly suggests that quite a different molecular process than hydrogen bonding is participating in these quenching phenomena, although it seems natural to consider that hydrogen bond formation plays a role of another type or makes it easy for the afore-mentioned molecular process to occur.

As to the nature of the molecular process which causes quenching in our cases, it seems that all the results are consistent with the mechanism involving a charge transfer from fluorescer to quencher. Thus, firstly, the finding that *N*,*N*-dimethyl-2-naphthylamine is quenched more than 2-naphthylmethylether by quinoline (in *n*-hexane) may be attributed to the larger electron-releasing power of the dimethylamino group than that of the methoxy group and, secondly, the difference between the quenching action of pyridine and quinoline may be due to the difference in their electron-accepting power, though this is not conclusive because of the lack of data on electron affinity. The results obtained in ethanol also favor this view. Thus, in this solvent both pyridine and quinoline, as well as fluorescers, form the hydrogen bond, mainly with ethanol, and the hydrogen bonding between quencher and fluorescer is almost completely suppressed. Now, if one makes the plausible assumption that the effect of the hydrogen bonding between fluorescer and ethanol is of less significance than that of the hydrogen bonding between quencher and ethanol, then, for example, 2-naphthylamine and *N*,*N*-dimethyl-2-naphthylamine may be expected to be affected equally by pyridine and by quinoline. The results are quite consistent with this expectation, since the quenching constants of pyridine and quinoline are about the same for both substances. Further, the fact that *N*,*N*-dimethyl-2-naphthylamine is quenched by pyridine, but not in non-polar solvents, may be interpreted by supposing that pyridine in ethanol gets a larger electron-accepting power because of the hydrogen bond formation with ethanol. Lastly, the finding that 2-naphthylmethylether, unlike *N*,*N*-dimethyl-2-naphthylamine, is not quenched by pyridine in ethanol may again be attributed to the lower electron-releasing power of the methoxy group compared with the dimethylamino group. Thus, it is very tempting to attribute the present quenching phenomena to the charge transfer from fluorescer to quencher. However, it seems somewhat peculiar that quinoline and pyridine act as electron-accepting agents; further studies will be necessary to confirm the above view.

Next, let us discuss the rate-determining step of the quenching process. As Table II shows, the temperature coefficient of the quenching constant is positive in all cases, irrespective of whether hydrogen bonding occurs or not. Besides, in similar systems, such as 2-naphthylamine—pyridine and 2-naphthol—pyridine, or in 2-naphthylamine—quinoline and 2-naphthol—quinoline in non-polar solvents, the quenching constant is of the same order, although the equilibrium constant of the hydrogen bonding in the ground state is quite different.[2,4] From these facts it is very plausible that the rate-determining step in quenching is the process of diffusion. To confirm this view, the quenching constant, $k$, was calculated by the well-known formula $k_q=4\pi N(D_A+D_B)(r_A+r_B)/1000$; it was then compared with the experimental values. In this equation $D_A$ and $D_B$ are the diffusion coefficients of fluorescer and quencher which were calculated from the experimental formula of Thakar;[12] $r_A+r_B$ was assumed to be 7.5 Å,[13] and $\tau$ was set as equal to $10^{-8}$ sec. The results are given in Table III, while the

12) P. E. Othmar and M. S. Thakar, *Ind. Eng. Chem.*, **45**, 589 (1939).
13) A. Weller, *Z. Elektrochem.*, **64**, 55 (1960).

TABLE II. QUENCHING CONSTANTS

| Quencher / Solvent / Fluorescer | Quinoline | | | Pyridine | | |
|---|---|---|---|---|---|---|
| | *n*-Hexane | Benzene | Ethanol | *n*-Hexane | Benzene* | Ethanol |
| 2-Naphthylamine | 120(20°C)[1]<br>140(40°C)[2] | 70(30°C)[7] | 75(28°C)[10]<br>85(50°C)[11] | 116(25°C)[15]<br>133(40°C)[16] | 60(23°C)[21] | 16(25°C)[23] |
| *N*, *N*-Dimethyl-2-naphthylamine | 90(20°C)[3]<br>100(40°C)[4] | 73(30°C)[8]<br>78(50°C)[9] | 87(25°C)[12]<br>100(50°C)[13] | 0(25°C)]17]<br>0(40°C)[18] | 0(23°C)[22] | 15(25°C)[24] |
| 2-Naphthol | 100(21°C)[5] | | | 117(21°C)[19] | | 2(21°C)[25] |
| 2-Naphthylmethyl-ether | 53(25°C)[6] | | 60(21°C)[14] | 0(21°C)[20] | | 0(21°C)[26] |

The number [*i*] corresponds to that in Fig. 10.
* N. Mataga, This Bulletin, **31**, 484 (1958).

TABLE III. THE VALUES OF $k$ CALCULATED FROM $k_q=4\pi N(D_A+D_B)(r_A+r_B)/1000$

| Quencher / Solvent / Fluorescer | Quinoline | | | Pyridine | | |
|---|---|---|---|---|---|---|
| | *n*-Hexane | Benzene | Ethanol | *n*-Hexane | Benzene | Ethanol |
| 2-Naphthylamine | 234(20°C)[1] | 140(30°C)[7] | 80(30°C)[10] | 266(20°C)]15] | 158(30°C)[21] | 91(30°C) |
| | 334(40°C)[2] | 191(50°C) | 119(50°C)[11] | 378(40°C)[16] | 216(50°C) | 135(50°C) |
| *N*, *N*-Dimethyl-2-naphthylamine | 218(20°C)[3] | 131(30°C)[8] | 75(30°C)[12] | 250(20°C)[17] | 149(30°C)[22] | 85(30°C)[24] |
| | 305(40°C)[4] | 178(50°C)[9] | 111(50°C)[13] | 348(40°C)[18] | 204(50°C) | 127(50°C) |
| 2-Naphthol | 238(20°C)[5] | 142(30°C) | 81(30°C) | 268(20°C)[19] | 160(30°C) | 92(30°C)[25] |
| 2-Naphthyl-methylether | 227(20°C)[6] | 136(30°C) | 78(30°C)[14] | 258(20°C)[20] | 154(30°C) | 89(30°C)[26] |

The number [*i*] corresponds to that in Fig. 10.

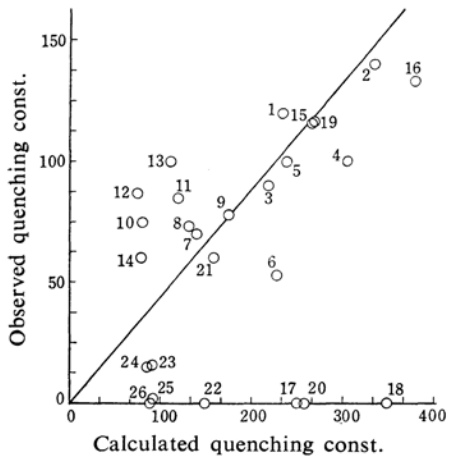



Fig. 10. Plot of the calculated quenching constants against the observed ones. The numbers in the figure correspond to the systems listed in Tables II and III.

comparison between the experimental and calculated values is shown in Fig. 10.

Broadly speaking, the correlation between the experimental and calculated values is rather good.

Thus, 2-naphthylamine—pyridine, 2-naphthol—pyridine, 2-naphthylamine—quinoline and *N*, *N*-dimethyl-2-naphthylamine—quinoline, all in nonpolar solvents, are close to the drawn line. It is clear that the difference between benzene and *n*-hexane is mainly due to the difference in viscosity, which affects the *D*-value. For all cases where the quenching constants are conspicuously small, such as *N*, *N*-dimethyl-2-naphthylamine—pyridine ($k=0$), 2-naphthylmethylether—pyridine ($k=0$) and 2-naphthylmethylether—quinoline, all in nonpolar solvents, there is no question that the genuine quenching process is rate-determining, completely or, at least, partially.

The feature in ethanol is somewhat anomalous. Thus, in the cases of 2-naphthylamine—quinoline and *N*, *N*-dimethyl-2-naphthylamine—quinoline, the observed values are appreciably larger than those which would be expected from the calculated values. Perhaps the calculated values are incorrect because of the improper estimation of $\tau$, $D_A$, $D_B$, $r_A$ and $r_B$. For *N*, *N*-dimethyl-2-naphthylamine—pyridine and 2-naphthylamine—pyridine, the observed $k$-values are less than the calculated values; this is certainly because the genuine quenching process is rate-determining.

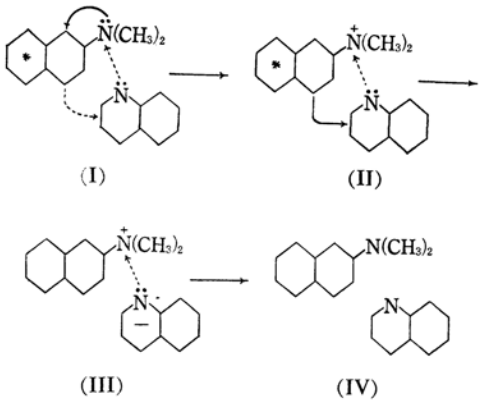
At any rate, it is clear that in nonpolar solvents the quenching process is in many cases so rapid that it is determined by the process of diffusion, irrespective of the molecular mechanism of quenching. Thus, in the case of 2-naphthylamine—pyridine or 2-naphthol—pyridine in nonpolar solvents, $k$ is considered to depend on the rate with which two molecules encounter one another with a mutual

orientation suitable for forming the intermolecular hydrogen bond. It is remarkable that the quenching in *N*, *N*-dimethyl-2-naphthylamine—quinoline seems to be diffusion rate-determining.

To summarize the above discussion, it is certain that the molecular process essential for quenching in the present systems is something other than hydrogen bonding, although it is clear that the latter plays an impotant role. According to Mataga,[4] charge transfer via the hydrogen bond makes the vibronic energy transfer feasible.

According to the view of the present authors, however, the main cause of the quenching is the charge transfer from fluorescer to quencher; the hydrogen bonding is considered, at least partly, to make it easy for this process to occur by increasing the electron density on the amino or hydroxy groups. The following fact might also have to be taken into account. If charge migration occurs from the electron-releasing group, such as a methoxy or amino group, to a ring in the excited state of the fluorescer, then a lone-pair on the hetero-atom in a quencher molecule will be able to act as a donor to these groups in a somewhat electron-deficient state. This will then make it easier for the charge transfer from fluorescer to quencher through $\pi$-$\pi$ interaction to occur.

To sum up, our model of quenching process may be written schematically as follows:




The essential point for quenching is I→II→III; the mechanism for III→IV is rather indifferent.

To verify the above speculation, the role of the quencher as an electron acceptor and the role of the hetero-atom in the quencher, which possibly acts as a donor, are the key-points which further studies should attack.

In concluding the discussion, brief comment should be made on the frequency effect of the quenching constant and on the experiment for the depth effect using anthracene.

The finding that quenching is independent of the frequency in 2-naphthylamine—quinoline and in *N*, *N*-dimethyl-2-naphthylamine—quinoline is quite natural and self-evident if one considers the conclusion obtained in the present paper, i. e., the fact that the rate-determining step of quenching is diffusion, since in such a situation the excited fluorescer molecule is sure to attain the equilibrium condition with regard to vibration and rotation and from the standpoint of interaction with the solvent molecules before the quenching process commences.

As to the effect of concentration on the fluorescence of anthracene, some anomalous results have recently been reported by Dammers-de Klerk.[10] According to him, the concentration quenching in *n*-hexane begins in a rather low concentration region, the fluorescence quantum yield at $10^{-3}$ M being about 1/5 that of the extreme dilute solution. Our present results do not show any such decrease in this concentration but conform quite well with the data of other authors.[9] Although our experiment was made in the presence of oxygen, Damers-de Klerk's results seem to be very doubtful. Förster[14] has also expressed this same opinion recently.

## Summary

The quenching constants ($k$) of quinoline for the fluorescence of several substances in *n*-hexane have been determined. The values obtained are as follows; they are independent of the frequency of the exciting light.

| | | |
|---|---|---|
| 2-Naphthylamine | 120 (20°C) | 140 (40°C) |
| *N*, *N*-Dimethyl-2-naphthylamine | 90 (20°C) | 100 (40°C) |
| 2-Naphthol | 100 (21°C) | |
| 2-Naphthylmethyl-ether | 53 (21°C) | |

The results clearly show that the hydrogen bond is not necessary for the quenching to occur, in contradiction to the mechanism proposed by Mataga[4] for the case in which pyridine is used as a quencher.

To elucidate the mechanism, the quenching phenomena in the fluorescence of the above substances have been further studied in benzene and ethanol, using pyridine and quinoline as quenchers. The most notable finding has been that, in ethanol, pyridine can quench the fluorescence of 2-naphthylamine and *N*, *N*-

14) E. Döller and Th. Förster, *Z. Phys. Chem., N. F.*, **31**, 274 (1962).

dimethyl-2-naphthylamine equally well, the $k$ value for 25°C being, respectively, 16 and 15.

A mechanism has been proposed which involves the charge transfer from fluorescer to quencher. When the quenching is considerable, the rate-determining step is the diffusion process, irrespective of the molecular mechanism for the quenching.

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