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Solvent Effects on the Photoamination of 1-Amino-2,4-dibromoanthraquinone. I. Photoamination in Benzene *via* Intramolecular Charge Transfer Excited Triplet State

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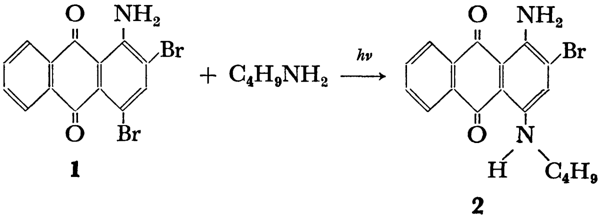
The bromine atom at the 4 position of 1-amino-2,4-dibromoanthraquinone (**1**) was substituted by butylamine and aniline by the irradiation of visible light. In ethanol the dissolved oxygen promoted the reaction and anthracene, a triplet quencher, had little effect. In benzene, the dissolved oxygen retarded the reaction and anthracene had a considerable quenching effect. Kinetic analysis indicated that in ethanol the photoamination of **1** proceeds mainly through the interaction of **1** in $S_1(^1CT)$ with the ground state oxygen, while in benzene it does through the $T_1(^3CT)$ of **1** without the aid of oxygen. The detailed reaction mechanism in benzene has been discussed and the rate constant of each process including the deactivation constant of the upper excited $T_2(^3n\pi^*)$ level evaluated.

The photochemical behavior of anthraquinone derivatives has attracted attention for a long time in relation to the photofading of vat dyes and the photosensitized oxidation. Many intensive studies have been made on the photoreduction, the photoannelation, and the photosubstitution.$^{1)}$ Anthraquinone derivatives have four $\pi\pi^*$ absorption bands in the region of the wavelength between 220 nm and 350 nm, and $n\pi^*$ band at the longer wavelength near 400 nm. When electron donating substituents such as hydroxyl, amino, and methylamino groups are introduced in to the nucleus, a new $\pi\pi^*$ absorption band, an intramolecular charge transfer band, appears in the visible region. It has been emphasized that the triplet excited $n\pi^*$ state is reactive in almost all the photochemical reactions of anthraquinones, while the excited CT state has little reactivity and the introduction of an electron donating substituent renders the excited anthraquinone extremely unreactive.$^{1)}$ However, recently a new photosubstitution reaction of aminohaloanthraquinone has been reported: the bromine atom of sodium 1-amino-4-bromoanthraquinone-2-sulfonate **3** has been substituted by ammonia and alkylamine by the irradiation of visible light.$^{2)}$ The oxygen molecule is indispensable for the photoamination and the mechanism has been postulated that the photoamination proceeds through an exciplex or an encounter complex formation between **3** in its excited ^{1}CT state and the ground sate oxygen, followed by an attack of amine to produce the aminated product as shown below.$^{3)}$

$$\begin{tikzcd} AQ^*(^1CT) + {}^3O_2 \arrow[r] & {[AQ^{\delta+}\cdots O_2^{\delta-}]} \arrow[dl] \arrow[d, "\text{Amine}"] \\ AQ + O_2 & \text{Amination} \end{tikzcd}$$

This photoamination appears to be the first example of a reaction which proceeds *via* the excited CT state of anthraquinone derivatives.

In this paper the photoamination of 1-amino-2,4-dibromoanthraquinone **1** by butylamine has been investigated. Very large solvent effects were observed between the photoamination of **1** in benzene and that in ethanol: both the reactive state of the excited **1** and the reaction mechanism changed with the nature of the solvents used.



Experimental

1-Amino-2,4-dibromoanthraquinone **1** was prepared by the bromination of sodium 1-amino-4-bromoanthraquinone-2-sulfonate **3** with bromine and was purified by repeated recrystallizations from ethanol. Shimadzu UV-200 spectrophotometer was used for the measurement of the visible and UV spectra, and Hitachi MPF-4 spectroflurometer for the measurement of the fluorescence spectra. The quantum yield of the photoamination of **1** was determined by the potassium tris(oxalto)ferrate(III) chemical actinometer according to the method recommended by Hatchard and Parker.$^{4)}$ The reaction mixture was irradiated by means of a 500 W xenon lamp (USHIO UXL-500 DXO) or a 100 W high-pressure mercury lamp (Eikosha) through the following filter system: soda glass for the irradiation of light of $\lambda > 300$ nm, a Toshiba interference filter KL-40 for monochromatic light of $\lambda = 400$ nm, and a Toshiba interference filter KL-47 and a glass filter VY-45 for monochromatic light of $\lambda = 470$ nm, respectively.

Results and Discussions

*The Photoamination of **1** in Benzene.* A solution of **1** (1.00×10^{-4} mol/dm^3) and butylamine (5.00×10^{-2} mol/dm^3) in benzene was irradiated by the light of $\lambda > 300$ nm, and a new absorption band appeared in the region between 500 and 700 nm which is characteristic of the aminated product **2**, having the isosbestic points at $\lambda = 390$ and 512 nm. TLC analysis (silica gel, eluent: 93:7 benzene–acetone) of the irradiated mixture indicated that only **2** was produced in the reaction system. From these results it was concluded that the photoreaction of **1** with butylamine in benzene gave only the aminated product **2**. After evaporating the solvent from the irradiated mixture, the aminated product **2** was seperated by silica gel column chromatography and purified by repeated recrystallizations from hexane. (Found: C, 58.02; H, 4.55; N, 7.56%).

*Solvent Effects on the Photoamination of **1**.* The solvent effects on the photoamination of **1** with butylamine are shown in Table 1. Very large solvent effects were observed. In ethanol, 1) the dissolved oxygen promoted the photoamination of **1**, but **1** had a poor reactivity under a nitrogen atmosphere, 2) a little quenching effect was observed by the addition of anthracene, and 3) the yield (%) of **2** was not equivalent to the conversion (%) of **1** and the ratio (0.79) between them was unchanged during the photoreaction. The last result suggests that the simultaneous photodecomposition of **1** accompanied by the photoamination took place as observed in the photoamination of **3** in aqueous 2-propanol. In benzene, 1) the dissolved oxygen retarded the photoamination and **1** was rather reactive under a nitrogen atmosphere, 2) a considerable quenching effect was observed by the addition of anthracene, and 3) the yield of **2** was equal to the conversion of **1**, suggesting that the photoamination of **1** proceeded quantitatively.

Table 1. Solvent effects on the photoamination of **1** by butylamine[a)]

Solvent	Φ_{N_2}[b)] / Φ_{Air}	Quenching effect by anthracene[c)]	Yield of **2** / conversion of **1**
Ethanol	0.13	△[d)]	0.79
Benzene	1.50	○[e)]	1.00

a) **1** (1.00×10^{-4} mol/dm^3); butylamine (5.00×10^{-2} mol/dm^3); in ethanol or benzene; light of $\lambda >$ 420 nm. b) Φ_{N_2} and Φ_{Air} are the quantum yield of the photoamination of **1** under nitrogen and air, respectively. c) [Anthracene] = 1.00×10^{-2} mol/dm^3. d) Little quenching. e) Considerable quenching.

*Absorption and Fluorescence Emission Spectra of **1**.* The absorption and the fluorescence emission spectra of **1** shown in Fig. 1 have two distinct characteristics. 1) The λ_{max} of the first absorption band in ethanol exibits a red shift of 5 nm compared with that in benzene and the λ_{max} of the fluorescence spectrum exibits a red shift of 21 nm. This supports the theory that **1** in the excited state has an intramolecular CT nature. 2) Contrary to the usual solvent effect,[5)] the relative intensity of the fluorescence spectrum in benzene is weaker by a factor of ten than that in ethanol under the same conditions. This suggests that **1** in its ^{1}CT state in benzene is deactivated more than ten times as effectively as in ethanol, possibly by a process such as an enhanced intersystem crossing to the triplet state.

*Energy Diagram of the Excited State of **1**.* An introduction of substituent to the anthraquinone nucleus is thought to have little effect on the position of the $n\pi^*$ level,[1b)] so that the $^1n\pi^*$ and $^3n\pi^*$ levels of **1** are supposed to lie in the neighborhood of those of anthraquinone, 280 kJ/mol and 259 kJ/mol respectively. As the absorption and the fluorescence spectra were still structureless even at 77 K, the 0-0 band in the first absorption band of **1** was estimated from the intersection of the absorption and the fluorescence spectra in a mirror image relation.[6)] The ^{1}CT level of **1** was supposed to be at 218 kJ/mol in ethanol and 228 kJ/mol in benzene, respectively.

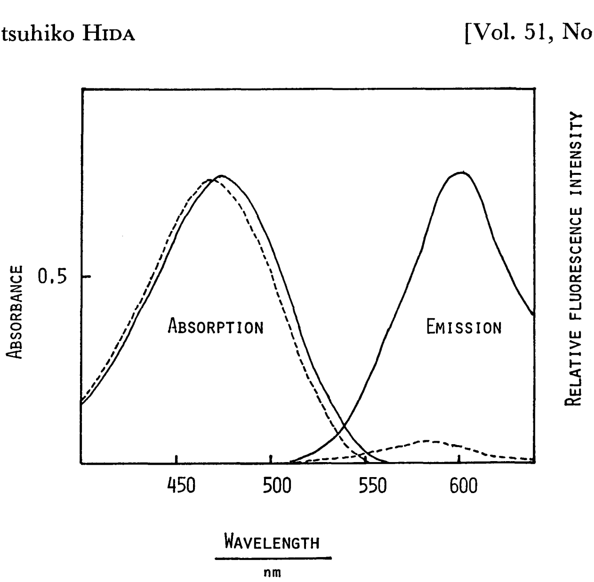
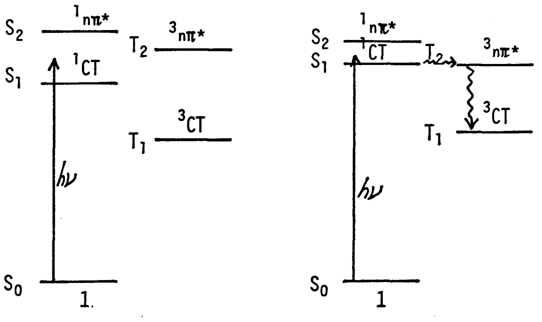


Fig. 1. Absorption and fluorescence spectra of **1**. [**1**] = 1.00×10^{-4} mol/dm^3, ——: in ethanol, ----: in benzene.



a) in ethanol b) in benzene

Fig. 2. Energy diagram of the excited state of **1**.

Thus, the ^{1}CT level of **1** in ethanol was considered to be a little lower than the $^3n\pi^*$ level as illustrated in Fig. 2a. In benzene the absorption and the fluorescence spectra indicate the ^{1}CT level of **1** being situated at a higher position than that in ethanol. Moreover, the $n\pi^*$ level of **1** in a non-polar solvent such as benzene lies in a relatively lower position than that in a polar protic solvent such as ethanol, and it may be reasonably accepted that in benzene the ^{1}CT level lies in close contiguity to the $^3n\pi^*$ level as shown in Fig. 2b. An inversion of the disposition between the ^{1}CT and the $^3n\pi^*$ levels may take place by the variation of the solvent polarity. On the basis of the energy diagram of the excited states of **1** (Fig. 2a and b), the solvent effects on the photoamination can be discussed as follows. In ethanol **1** is excited to the ^{1}CT level by an irradiation of the first absorption band of **1** and the photoamination takes place in a similar manner to the case of **3** in aqueous 2-propanol. In benzene, because of a close contiguity or an inversion of the disposition between $S_1(^1CT)$ and the $T_2(^3n\pi^*)$ levels, both levels interact more strongly with each other than in ethanol, resulting in enhancement of the intersystem crossing process. Thus the relative fluorescence intensity of **1** in benzene becomes weaker by a factor of ten compared with that in ethanol. Consequently, the $T_1(^3CT)$ level of **1** is supposed to be largely populated by the irradiation of the first absorption band of **1** in benzene by the dominant deactivation process of $S_1(^1CT)\rightsquigarrow T_2(^3n\pi^*)\rightsquigarrow T_1(^3CT)$. Then, the photoamination is supposed to proceed mainly from the $T_1(^3CT)$ without the aid of the dissolved oxygen.

Effect of Oxygen in Benzene. The quenching experiments by the dissolved oxygen in benzene gave a linear Stern-Volmer plot (Fig. 3), indicating that the dissolved oxygen acted as a quencher of the photoamination of **1** in benzene and the photoreaction proceeds through the one excited state of **1**. From the slope of the linear plot, $k_q \cdot \tau_1$ was found to be 513 dm^3/mol, where k_q denotes the quenching rate constant by oxygen and τ_1 the lifetime of the excited state quenched by oxygen, respectively.

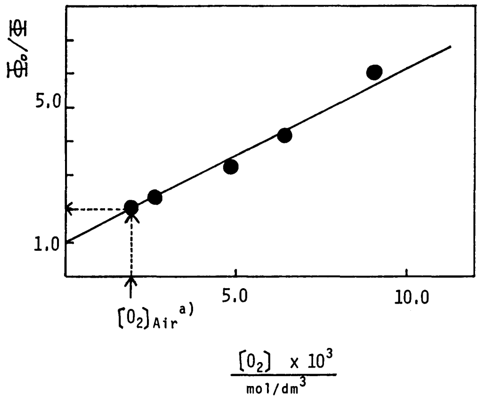


Fig. 3. Stern-Volmer plot for the quenching effect of oxygen on the photoamination of **1** (1.00×10^{-4} mol/dm^3) by butylamine (5.00×10^{-2} mol/dm^3) in benzene by the irradiation of the light of $\lambda=470$ nm.
a) The concentration of the dissolved oxygen in the air saturated benzene.

Effect of the Triplet Sensitizer in Benzene. The benzene solution of **1** (1.00×10^{-4} mol/dm^3) and butylamine (5.00×10^{-2} mol/dm^3) with or without a triplet sensitizer (1.00×10^{-2} mol/dm^3) was irradiated by monochromatic light of $\lambda=400$ nm under nitrogen. In the presence of benzil ($E_T=226$ kJ/mol) and fluorenone ($E_T=226$ kJ/mol) as triplet sensitizers the reaction was promoted by a factor of 1.8 and 10, respectively. These results indicate that the photoamination proceeds through the triplet excited state of **1**. As the triplet levels of both benzil and fluorenone are lower than the $T_2(^3n\pi^*)$ of **1**, it is supposed that the photoreaction proceeds through the $T_1(^3CT)$ level.

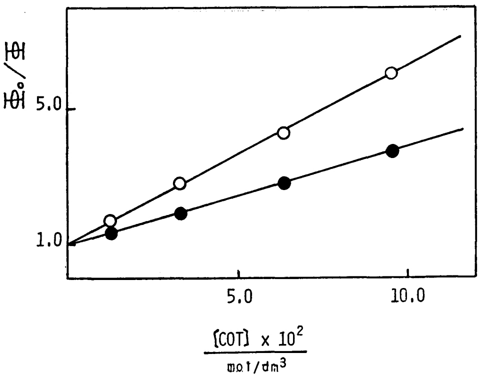


Fig. 4. Stern-Volmer plot for the quenching effect of cyclooctatetraene on the photoamination of **1** (1.00×10^{-4} mol/dm^3) by butylamine (5.00×10^{-2} mol/dm^3) in benzene by the irradiation of the light of $\lambda=470$ nm.
○: Under nitrogen, ●: under air.

Effect of the Triplet Quencher in Benzene. Cyclooctatetraene (COT) and anthracene did not affect the fluorescence intensity of **1**. Thus, they were expected to act as a triplet quencher but not as a singlet quencher. The Stern-Volmer plot was shown in Fig. 4 when COT ($E_T=163$ kJ/mol) was used as a triplet quencher. A linear relationship between Φ_0/Φ and the concentration of COT was observed and its slope was 52 dm^3/mol under nitrogen and 28 dm^3/mol in aerated solution, respectively, that is, the lifetime of the excited state of **1**, quenched by COT, depended upon the presence of the dissolved oxygen, suggesting that the dissolved oxygen may interact with the same state as that quenched by COT. These results, in addition to the above sensitizing experiments, lead to the conclusion that the photoamination of **1** proceeded through the $T_1(^3CT)$ level of **1** which can be quenched by both the dissolved oxygen and COT.

In the presence of anthracene ($E_T=176$ kJ/mol), the Stern-Volmer plot for the photoamination of **1** was also found to be linear (Fig. 5). A different result with COT was obtained. The slope of the Stern-Volmer plot was the same both under nitrogen and air, that is, the lifetime of the excited state of **1** quenched by anthracene was not affected by the presence of oxygen. This suggests that anthracene interacts in the quenching manner with the different excited state of **1** from the $T_1(^3CT)$ which is quenched by oxygen. It is been reported that the photoreduction of anthraquinone *via* the $^3n\pi^*$ level is efficiently quenched by anthracene.[7] Davies *et al.* reported the quenching of the $T_2(^3n\pi^*)$ level of 1-dimethylaminoanthraquinone by anthracene.[8] The quenching effect on the photoamination of **1** by anthracene in this study is understandable by

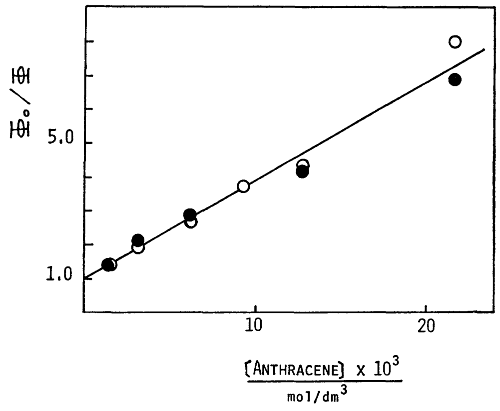


Fig. 5. Stern-Volmer plot for the quenching effect of anthracene on the photoamination of **1** (1.00×10^{-4} mol/dm^3) by butylamine (5.00×10^{-2} mol/dm^3) by the irradiation of the light of $\lambda=470$ nm.
○: Under nitrogen, ●: under air.

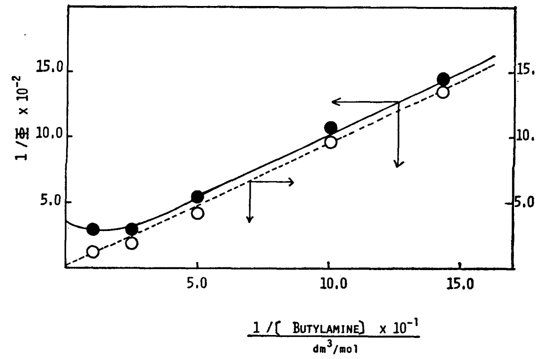


Fig. 6. Effect of the concentration of butylamine on the photoamination of **1** (1.00×10^{-4} mol/dm^3) in benzene. -●-: 1/*Φ* *vs.* 1/[Butylamine], -○-: ***f*** *vs.* 1/[Butylamine].

assuming that the $T_2(^3n\pi^*)$ level of **1** is quenched by anthracene. Thus, the $T_1(^3CT)$ level of **1** in benzene, which was quenched by COT ($E_T = 163$ kJ/mol), but not by anthracene ($E_T = 176$ kJ/mol), was supposed to lie in the range of 163—176 kJ/mol.

Effect of the Concentration of Butylamine in Benzene. The plot of the reciprocal of the quantum yield of the photoamination of **1** *versus* the reciprocal of the concentration of butylamine gave the curve as shown in Fig. 6. This curve may be explained by assuming that the amine molecule participates not only in the process leading to the aminated product **2**, but also in the quenching. Since anthraquinonesulfonic acids and aminoanthraquinones have been reported to be photoreduced *via* their $^3n\pi^*$ state by an electron transfer from amines or inorganic anions in polar solvents,[9,10] it may be possible that in non-polar benzene, butylamine as an electron donor interacts with **1** in the $T_2(^3n\pi^*)$ level in a quenching manner to the photoamination of **1** which proceeds through the $T_1(^3CT)$ level of **1**. If butylamine interacts with the $T_2(^3n\pi^*)$ level in a quenching manner to the photoamination, the lifetime of the $T_2(^3n\pi^*)$ level, τ_2, should be shortened by an increase in concentration of butylamine: the slope of the Stern-Volmer plot (Fig. 5) expressed as $k_q' \cdot \tau_2$, where k_q denotes the quenching rate constant of T_2-$(^3n\pi^*)$ by anthracene and τ_2 the lifetime of $T_2(^3n\pi^*)$, should decrease with an increase in concentration of the amine. The slope of the Stern-Volmer plot in different concentration of the amine are listed in Table 2. It is seen that the slope of the Stern-Volmer plot, $k_q' \cdot \tau_2$, decreased with an increase in concentration of the amine. Consequently, it may be concluded that butylamine interacts with **1** in the $T_2(^3n\pi^*)$ level in a quenching manner. The quenching effect by the amine may be explained by assuming an exciplex formation such as [$AQ^{\delta-} \cdots Amine^{\delta+}$] which whould not lead to the aminated product **2**, but be deactivated to the ground state of **1** and the amine in non-polar benzene.

Table 2. Effect of the concentration of butylamine on the slope of the Stern-Volmer plot in Fig. 5

[Butylamine] × 10^2 mol/dm^3	2.00	5.00	10.0
Slope ($k'_q \cdot \tau_2$) dm^3/mol	380	290	210

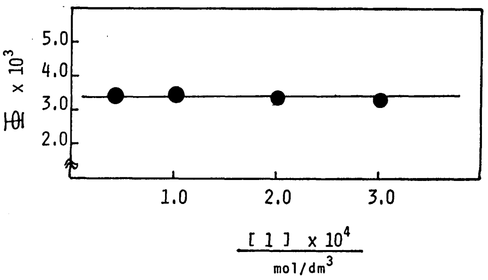


Fig. 7. Effect of the concentration of **1** on the photoamination of **1** by butylamine (5.00×10^{-2} mol/dm^3) by the irradiation of the light of $\lambda = 470$ nm.

Effect of the Concentration of 1 in Benzene. The quantum yield of the photoamination remained unchanged by the variation of the concentration of **1** (Fig. 7). This precludes the possibility that **1** participates in the photoamination as depicted below.

$$\begin{tikzcd}
AQ^* + AQ \arrow[r] & {[AQ^{\oplus} \cdots AQ^{\ominus}]} \arrow[dl] \arrow[d, "Amine"] \\
2AQ & Amination
\end{tikzcd}$$

The Reaction Mechanism of the Photoamination of 1 in Benzene. On the basis of the above experimental results, the reaction scheme for the photoamination of **1** may be depicted as Fig. 8.

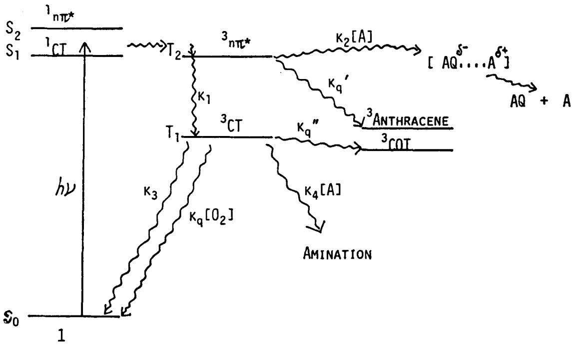


Fig. 8. Reaction scheme of the photoamination of **1** by butylamine in benzene.

The quantum yield for the production of **2** under nitrogen without a triplet quencher may be expressed by

$$\Phi = \Phi_{\rm isc} \cdot \left(\frac{k_1}{k_1 + k_2[A]}\right) \cdot \left(\frac{k_4[A]}{k_3 + k_4[A]}\right) \cdot \alpha, \tag{1}$$

where $\Phi_{\rm isc}$ = the efficiency of the intersystem crossing of $S_1(^1CT) \rightsquigarrow T_2(^3n\pi^*)$,
k_i = the rate constant of each process indicated in Fig. 8,
A = butylamine,
and α = the yield of the aminated product **2** for every collision between the amine and **1** in its $T_1(^3CT)$ level.

The reciprocal of the quantum yield is thus expressed by

$$\frac{1}{\Phi} = \frac{1}{\Phi_{\text{isc}}\cdot\alpha}\cdot\left(1+\frac{k_2[\text{A}]}{k_1}\right)\cdot\left(1+\frac{k_3}{k_4[\text{A}]}\right). \tag{2}$$

Hence, a plot of the reciprocal of the quantum yield *versus* the reciprocal of the concentration of butylamine would be expected to show the result given in Fig. 6.

With dissolved oxygen present, the Stern-Volmer equation may be expressed by

$$\frac{\Phi_0}{\Phi} = 1 + \frac{k_\text{q}[\text{O}_2]}{k_3+k_4[\text{A}]}. \tag{3}$$

When COT was used as a triplet quencher,

$$\frac{\Phi_0}{\Phi} = 1 + \frac{k_\text{q}''[\text{COT}]}{k_3+k_4[\text{A}]+k_\text{q}[\text{O}_2]} \tag{4}$$

and in the case of anthracene,

$$\frac{\Phi_0}{\Phi} = 1 + \frac{k_\text{q}'[\text{Anthracene}]}{k_1+k_2[\text{A}]}. \tag{5}$$

A plot of Φ_0/Φ *versus* the concentration of each quencher used should give a linear relationship (Figs. 3, 4, and 5). Equation 4 indicates that the slope of the plot in Fig. 4 means to be $k_\text{q}''/(k_3+k_4[\text{A}]+k_\text{q}[\text{O}_2])$, which should be dependent upon the concentration of the dissolved oxygen as discussed before. The ratio between the slope of the plot (Fig. 4) for the results under nitrogen and air (52/28=1.9), corresponding to $1+k_\text{q}[\text{O}_2]_\text{air}/(k_3+k_4[\text{A}])$, agrees with the value of $\Phi_0/\Phi=1+k_\text{q}[\text{O}_2]_\text{air}/(k_3+k_4[\text{A}])=2.0$ obtained from Fig. 3 and Eq. 3 at the air saturated oxygen concentration. Equation 5 indicates that the slope of the plot, Φ_0/Φ *versus* [Anthracene] (Fig. 5), should be independent of the concentration of the dissolved oxygen.

By combining the values of the slopes of the lines represented by Figs. 3, 4, and 5 with Eqs. 3, 4, and 5, the following rate constants relationships were obtained;

$$\frac{k_\text{q}}{k_3+k_4[\text{A}]} = 513\ \text{dm}^3/\text{mol}, \tag{6}$$

where $[\text{A}]=5.00\times10^{-2}$ mol/dm^3,

$$\frac{k_\text{q}''}{k_3+k_4[\text{A}]} = 52\ \text{dm}^3/\text{mol}, \tag{7}$$

where $[\text{A}]=5.00\times10^{-2}$ mol/dm^3, and

$$\frac{k_\text{q}'}{k_1+k_2[\text{A}]} = 210,\ 290,\ \text{and}\ 380\ \text{dm}^3/\text{mol}, \tag{8}$$

where $[\text{A}]=1.00\times10^{-1}$, 5.00×10^{-2}, and 2.00×10^{-2} mol/dm^3, respectively.

Equation 8 gave the value of $k_1/k_\text{q}'=2.1\times10^{-3}$ mol/dm^3 and $k_2/k_\text{q}'=2.7\times10^{-2}$ mol/dm^3, respectively. Assuming that the quenching rate constant of $\text{T}_2(^3\text{n}\pi^*)$ by anthracene is $k_\text{q}'=1.6\times10^{10}$ dm^3/(mol·s) which is a diffusion controlled one, k_1 and k_2 may be calculated as $k_1=3.4\times10^7$ s^{-1} and $k_2=4.3\times10^8$ dm^3/(mol·s), respectively.

If Eq. 2 is rewritten using Eq. 9, the value of f calculated by using the k_1 and k_2 obtained above, with the reciprocal of the concentration of butylamine would be expected to exibit a linear relationship.

$$f = \frac{1}{\Phi}\left(\frac{k_1}{k_1+k_2[\text{A}]}\right) = \frac{1}{\Phi_{\text{isc}}\cdot\alpha}\cdot\left(1+\frac{k_3}{k_4[\text{A}]}\right) \tag{9}$$

A plot of f *versus* the reciprocal of the concentration of butylamine gave a linear relationship as indicated by the dotted line in Fig. 6. These results support the reaction scheme shown in Fig. 8. It may be seen from Eq. 9 that the ratio between the slope and the intercept in the plot of f *versus* the reciprocal of the concentration of the amine (Fig. 6) is equal to k_3/k_4. The value of k_3/k_4 was obtained as 0.50 mol/dm^3. Supposing the quenching rate constant of $\text{T}_1(^3\text{CT})$ by oxygen k_q to be the diffusion controlled one (1.6×10^{10} dm^3/(mol·s)), k_3 and k_4 may be determined by substituting the value of k_3/k_4 into Eq. 6 as $k_3=2.8\times10^7$ s^{-1} and $k_4=5.7\times10^7$ dm^3/(mol·s), respectively. Moreover, the substitution of the value of k_3 and k_4 into Eq. 7 reveal the quenching rate constant of $\text{T}_1(^3\text{CT})$ by COT, k_q'', to be 1.6×10^9 dm^3/(mol·s), which is one order of magunitude smaller than the diffusion controlled rate. It has been reported that the quenching rate by energy transfer drops very quickly from the diffusion controlled rate when the acceptor triplet level approaches that of the donor within 13—17 kJ/mol.[11] This may be valid in the case of $\text{T}_1(^3\text{CT})$ ($E_\text{T}=163$—176 kJ/mol) of **1** as a donor level and COT ($E_\text{T}=163$ kJ/mol) as an acceptor. The rate constant in the reaction scheme of Fig. 8 determined by these kinetic analysis are tabulated in Table 3.

TABLE 3. RATE CONSTANTS IN THE REACTION SCHEME FOR THE PHOTOAMINATION OF **1** BY BUTYLAMINE IN BENZENE[a]

k_1 s^{-1}	k_2 dm^3/(mol·s)	k_3 s^{-1}	k_4 dm^3/(mol·s)	k_q'' dm^3/(mol·s)
3.4×10^7	4.3×10^8	2.8×10^7	5.7×10^7	1.6×10^9

a) They were determined on the assumption that k_q, $k_\text{q}'=1.6\times10^{10}$ dm^3/(mol·s) (diffusion controlled rate), respectively.

It is significant that these rate constants, especially the deactivation constant of the upper excited level $\text{T}_2(^3\text{n}\pi^*)$ can be determined kinetically, which is rarely possible in many cases because of the short lifetime of the upper excited level. The deactivation constant k_1 corresponding to the reciprocal of the lifetime of $\text{T}_2(^3\text{n}\pi^*)$ level was revealed to have a value of 3.4×10^7 s^{-1} comparable to that of the lowest excited triplet level $\text{T}_1(^3\text{CT})$ ($k_3=2.8\times10^7$ s^{-1}). Davies *et al.* reported the photoreduction of 1-dimethylaminoanthraquinone by hydrogen abstraction *via* its upper excited level $\text{T}_2(^3\text{n}\pi^*)$ and pointed out that anthraquinone derivatives might have a lifetime long enough to photoreact in their upper excited $\text{T}_2(^3\text{n}\pi^*)$ level.[8] This has been demonstrated in this study. That the $\text{T}_2(^3\text{n}\pi^*)$ level of **1** has such a long lifetime of *ca.* 30 ns in contrast to those of T_2 of substituted anthracenes (*ca.* 0.3 ns) and naphthalene (*ca.* 10 ps) would be unusual. These values were kinetically determined by Liu *et al.*[12,13]

Previously it has been reported that in contrast to the aliphatic amines, aromatic amines appeared not to photoreact with sodium 1-amino-4-bromoanthraquinone-2-sulfonate **3** in polar medium. As stated above, in polar solvent the photoamination proceeds through the $\text{S}_1(^1\text{CT})$ level interacting with the ground state oxygen along with the simultaneous production of the peroxide, probably derived from the superoxide ion O_2^-.[3] Consequently it was considered that the aromatic amine was oxidized predominantly by the peroxide produced in the reaction system, resulting in the suppression of the photoamination in polar solvent. These considerations suggest that aromatic amines would be expected to photoreact with **1** in benzene, in which the photoamination proceeds without the aid of oxygen. In fact, in benzene under a nitrogen atmosphere effective photoamination of **1** with aromatic amine, aniline, was observed.

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