 © 1984 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 57, 2261—2265 (1984)

Intramolecular Interactions in the Ground and Excited States of 1,3-Bichromophoric Propanes in the Aqueous Cyclodextrin Solutions

Michiya ITOH* and Yoshihisa FUJIWARA
Faculty of Pharmaceutical Sciences, Kanazawa University, Takara-machi, Kanazawa 920
(Received March 12, 1984)

The enhanced fluorescence of several 1,3-bichromophoric propanes in aqueous cyclodextrin solutions has been investigated by the steady-state fluorescence spectra and fluorescence lifetimes. 1-(9,10-Dicyano-2-anthryl)-3-(1- and 2-naphthyl)propanes exhibit the intramolecular charge transfer complex fluorescence generated in the ground state in the presence of γ-cyclodextrin. Two bichromophoric propanes, 1,3-di-2-naphthylpropane and 1-(1-naphthyl)-3-(2-naphthyl)propane, in the aqueous β- and γ-cyclodextrin solutions show not only the intramolecular excimer but also the ground state complex fluorescences, though the ground state complex formation of dinaphthylpropane has never been observed in the homogeneous solution even at low temperature. The intramolecular interactions in the ground and excited states seem to be attributable to their intramolecularly geometrical restriction in the extraordinary nonpolar cavity of the cyclodextrins.

The photochemical and photoinduced interactions of organic molecules have been recently studied in the cyclodextrin inclusion systems. Ueno *et al.*[1] reported one host-two guest complex between γ-cyclodextrin (γ-CDx) and sodium 1-naphthylacetate exhibiting excimer fluorescence. The large cavity of γ-CDx is capable of including two molecules of 1-naphthylacetate which shows the characteristic excimer fluorescence, whereas the cavity of α- and β-CDx is too small to accomodate two guest molecules. Recently, Turro *et al.*[2] reported the enhanced intramolecular excimer formation of 1,3-bichromophoric propanes (BC) in the aqueous β- and γ-CDx solutions. They suggested that a stable CDx and BC complex is formed exhibiting excimer fluorescence in cases where the correspondence of the size and shape of the eclipsed conformation of BC system and the cavity of CDx is high and the ratio of excimer and monomer fluorescence intensities is much greater in these cases than in homogeneous solutions. In these so called excimer fluorescence, however, no information of the dynamic process of the excimer formation in the CDx cavity was presented; whether the fluorescence is attributable to the real excimer or to the excited state of the ground state complex in the CDx cavity is not obvious.

This paper presents the intramolecular ground state complex fluorescence of 1-(9,10-dicyano-2-anthryl)-3-(1- and 2-naphthyl) propanes (βα- and ββ-DCAN),[3] and the ground state complex fluorescence as well as the excimer of 1,3-dinaphthylpropanes in the aqueous CDx solutions. The ground state complex formation in the CDx cavity is prevailing to the intramolecular excimer in 1,3-di-2-naphthylpropane (ββ-DNP), while the excimer formation is significant in 1-(1-naphthyl)-3-(2-naphthyl)propane(βα-DNP)[4,5] The intramolecular ground state complex and excimer formations are discussed in terms of the dynamic process of the intramolecular interaction of BC moieties in the CDx cavity both in the ground and excited states.

Experimental

Cyclodextrins (Nakarai Chem.) were recystallized three times from water. The 1,3-bichromophoric compounds were prepared and purified by the methods reported in the previous papers.[3-5] Ion exchanged and distilled water was used. An aqueous CDx solutions of BC compounds were prepared by filtration through a micropore filter (Fuji Film Co. pore size 0.22 μm) after sonification for about 10 min. Absorption and fluorescence spectra were measured by a Hitachi 323 and MPF-4 spectrophotometers, respectively. Fluorescence decay curves were obtained by using the Ortec Single Photon Counting system with the PRA 510 nanosecond light pulser. The triple or double exponential decay was analyzed by the following equation,

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + (1-A_1-A_2)\exp(-t/\tau_3), \quad (1)$$

where A_i and t_i are pre-exponential factor and fluorescence lifetime, respectively. The data analysis for the above equation was performed by a computer simulated deconvolution.[6] The criterion for the "best fit" was the minimum sum (Q) of the squares of the difference between observed (D_i) and calculated (D_i') data; an actual allowance was $Q<0.0001$. $Q=\sum_i^n (D_i-D_i')^2/n$, where n is the number of data, D_i and D_i' were normalized to 1.

Results and Discussion

The Ground State Complex Formation of DCAN in the Aqueous CDx Solution. Two 1,3-bichromophoric compounds, ββ- and βα-DCAN are completely insoluble in aqueous solution exhibiting no fluorescence. By adding γ-CDx in the aqueous solution, the

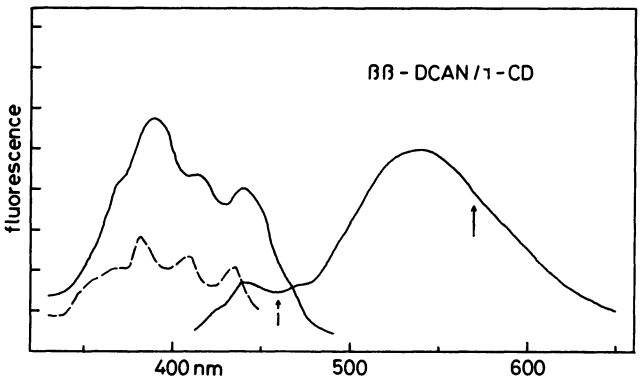

Fig. 1. Fluorescence (uncorrected, excited at 360 nm) and excitation spectra of the γ-CDx solution (10^{-2} mol dm^{-3}) of ββ-DCAN (1.8×10^{-7} mol dm^{-3}) at room temperature. The excitation spectra were monitored at 570 nm (——) and 460 nm (------).

fluorescence spectra were observed as shown in Fig. 1, where the solution was filtrated by micropore filter for removing microcrystals. However, no fluorescence was detected in the α- and β-CDx solutions. The fluorescence spectrum of this γ-CDx solution of ββ-DCAN exhibits a long wavelength fluorescence at 500—570 nm in addition to the 9,10-dicyanoanthryl moiety (DCA moiety) fluorescence at 430—500 nm at room temperature. The excitation spectrum of the former fluorescence is different from that of the latter and from the absorption spectrum of an ethanol solution of this compound. The excitation spectrum of the former long wavelength fluorescence is very similar to that of the ground state complex fluorescence observed in the 3-methylpentane (MP) solution at low temperature reported previously.[3] The MP solutions of ββ- and βα-DCAN show the ground state complex fluorescence at 500—570 nm at low temperature as well as the exciplex fluorescence at room temperature.[3] Further, the absorption spectra of the MP solution confirmed the ground state complex formation at low temperature. Therefore, the long wavelength fluorescence of the aqueous γ-CDx solution of ββ-DCAN may be ascribed not to the exciplex but to the ground state complex in the CDx cavity, though the ground state complex formation cannot be confirmed by the absorption spectra because of too weak absorption intensity. The similar ground state complex fluorescence was observed in the γ-CDx solution of βα-DCAN, whose fluorescence and excitation spectra are shown in Fig. 2. If the ≈550 nm fluorescence consists of the ground state complex and the exciplex fluorescence superimposed, the decay curve might be expressed by four or three components of exponential. However, the double exponential decay was observed throughout 450—580 nm region, though the ratio of the short lifetime component to the long was much larger at 430—530 nm than >530 nm. Therefore, the long wavelength and long lifetime fluorescence may be attributable mostly to the ground state complex mentioned above, even if a possibility of the small contribution of the exciplex fluorescence cannot entirely be removed at the present stage. The fluorescence lifetimes obtained in the aeration and deaeration are summarized in Table 1.

The fluorescence intensity ratio of the complex and

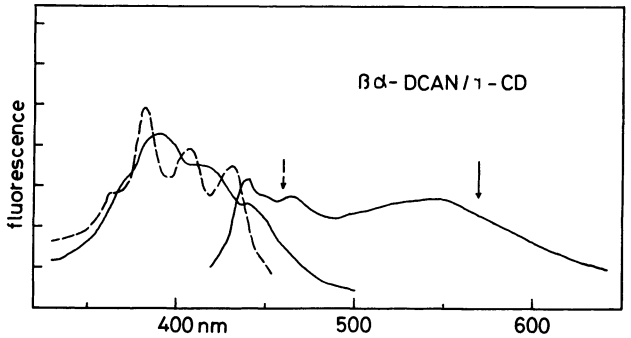

Fig. 2. Fluorescence (uncorrected, excited at 360 nm) and excitation spectra of the γ-CDx solution (10^{-2} mol dm^{-3}) of βα-DCAN (1.5×10^{-7} mol dm^{-3}). The excitation spectra were monitored at 570 nm (——) and at 460 nm (------).

DCA moiety is greater in ββ- than βα-DCAN. Further, the intensity ratio of the long lifetime component to the short one shows also a similar trend (Table 1). These facts suggest that the ground state complex formation is more significant in the former. The different fluorescence behavior between two compounds in γ-CDx solutions is well consistent with that of the enthalpy change of the complex formation in the MP solution at low temperature ($-\Delta H$=3.8 kcal mol^{-1} for ββ-DCAN and 2.6 kcal mol^{-1} for βα-DCAN, 1 kcal mol^{-1}=4.184 kJ mol^{-1}).[3] As mentioned above, these bichromophoric compounds form the ground state complex only in the nonpolar solvent such as MP at low temperature. Then, the experimental results obtained in the aqueous CDx solutions demonstrate that the inner cavity of CDx provide us with an extraordinary nonpolar and structurally restricted environment for the intramolecular interactions. The difference of the fluorescence behavior of the intramolecular ground state complex formation between ββ- and βα-DCAN may be attributable to the conformational difference of the complex formation in the CDx cavity as well as their inherent enthalpy change for the complex formation. The fluorescence lifetimes of the complex and the DCA moiety are almost invariant in the aeration and deaeration of the CDx solution, as summarized in Table 1. It seems that the excited state of the ground state complex in the CDx cavity are protected from the oxygen quenching as suggested by Turro *et al.*[2]

Intramolecular Excimer and Ground State Complex Formations of DNP in the CDx Solutions. The aqueous β- and γ-CDx solutions of ββ-DNP show the long wavelength fluorescence in addition to the naphthyl moiety. The former fluorescence excitation spectra shown in Fig. 3 is in longer wavelength region than that of the naphthyl moiety and also the longest wavelength absorption band of DNP.[5] Therefore, it seems that the 400 nm fluorescence is ascribed to the intramolecular ground state complex of ββ-DNP in the CDx cavity. Further, the γ-CDx solution of ββ-DNP shows a similar fluorescence to that of β-CDx solution, as shown in Fig. 3(b). However, the excitation spectrum of this fluorescence shows only a faint red shift from that of the naphthyl moiety. The red shifted excitation spectrum seems to suggest that the ≈400 nm fluorescence consists of the superimposed spectra of the intramolecular excimer and ground state complex in the β-CDx solution. The fluorescence decay curves of 370—450 nm of ββ-DNP in the β- and γ-CDx solutions are shown in Figs. 4 and 5. The decay curve with-

Table 1. Fluorescence lifetimes (collected at ≈550 nm) of DCAN in γ-CDx solutions at room temperature (τ, ns)

	Aerated		Deaerated	
	τ_1	τ_2	τ_1	τ_2
ββ-DCAN	11 (82%)	43	14 (83%)	51
βα-DCAN	8 (90%)	37	10 (89%)	42

$I(t)=A\exp(-t/\tau_1)+(1-A)\exp(-t/\tau_2)$.
Data in bracket are fraction (A) of components.
Errors are approximately ±5%.

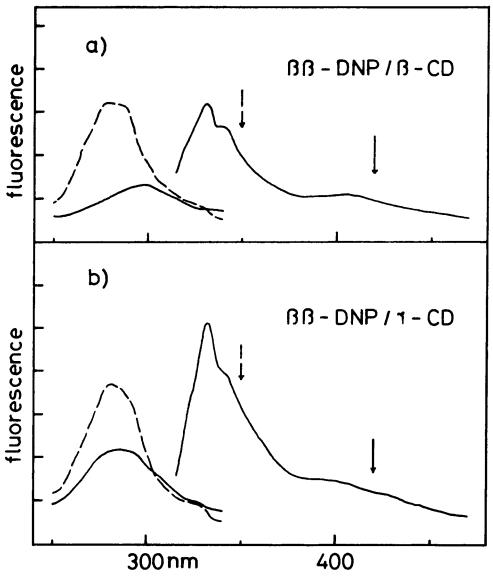

Fig. 3. Fluorescence (uncorrected, excited at 305 nm) and excitation spectra of the β- and γ-CDx solution (5×10^{-3} mol dm^{-3}) of $\beta\beta$-DNP (3.7×10^{-6} mol dm^{-3}) at room temperature. The excitation spectra were monitored at 420 nm (——) and at 350 nm (------).

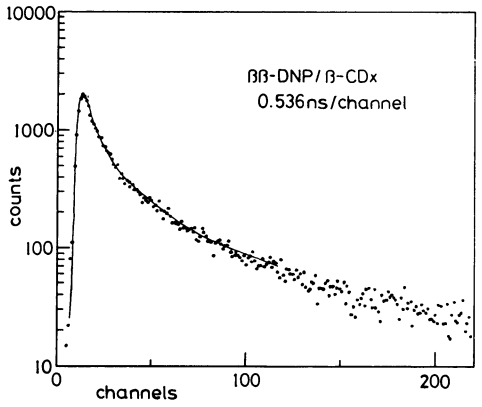

Fig. 4. Fluorescence decay curve of the long wavelength fluorescence (collected at 370—450 nm) of the β-CDx solution of $\beta\beta$-DNP (3.7×10^{-6} mol dm^{-3}) at room temperature. The curve shows the calculated decay based on the data shown in Table 2.

out fluorescence rise cannot be analyzed as a double exponential by any combination of parameters (τ_1, τ_2, A_1, and A_2 in Eq. 1), though decay curves look like a double exponential decay. The decay curves shown in Figs. 4 and 5 were analyzed as a triple exponential decay by the computer simulation, whose decay times are two short lifetimes and a long one as summarized in Table 2.

The aqueous β- and γ-CDx solutions of $\beta\alpha$-DNP exhibit remarkably enhanced fluorescence as shown in Fig. 6. A weak fluorescence ($\lambda_{max}\approx400$ nm) in β-CDx solution and a rather strong fluorescence (≈375 nm) in γ-CDx solution were observed in addition to the naphthyl moiety fluorescence. These fluorescence excitation spectra of both solutions shows rather similar to that of the naphthyl moiety fluorescence. Therefore, it seems that these fluorescence are mostly attributable to the intramolecular excimer of these compounds. The flurescence rise in the long wavelength fluores-

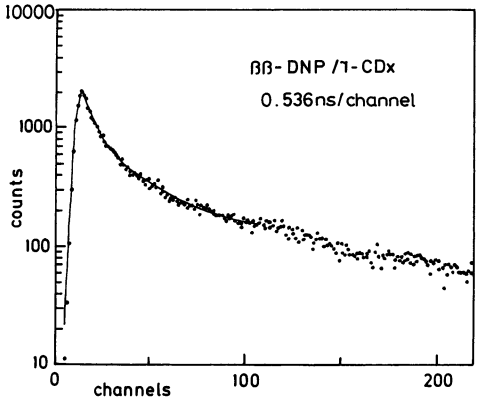

Fig. 5. Fluorescence decay of the long wavelength fluorescence (collected at 370—450 nm) of the γ-CDx solution of $\beta\beta$-DNP. The curve shows the calculated decay based on the data shown in Table 2.

Table 2. Fluorescence lifetimes (collected at 370—450 nm) of DNP in the CDx solutions at room temperature (τ ns)

DNP	CDx	Aerated τ_1	Aerated τ_2	Aerated τ_3	Deaerated τ_1	Deaerated τ_2	Deaerated τ_3
$\beta\beta$-DNP	β	1.5 (80%)	13.0 (18%)	46.2	1.9 (75%)	8.7 (20%)	48.2
	γ	1.4 (71%)	8.0 (22%)	56.3	1.8 (72%)	7.8 (20%)	56.0
$\beta\alpha$-DNP	β	1.8 (55%)	16.1 (6%)	53.6	2.0 (56%)	15.7 (2%)	53.7
	γ	1.6 (50%)	26.4 (18%)	107.3	1.6 (50%)	25.8 (19%)	93.8

$I(t)=A_1\exp(-t/\tau_1)+A_2\exp(-t/\tau_2)+(1-A_1-A_2)\exp(-t/\tau_3)$. Data in bracket are fraction of components. Errors are approximately ±5%.

cence decay curve of the β-CDx solution of $\beta\alpha$-DNP was observed in the excitation at 230 nm, though a small amount of the short decay component due to the naphthyl moiety sounds to be superimposed on the fluorescence rise. Upon excitation at 290 nm, however, no fluorescence rise was observed in this solution. Further, neither fluorescence in the excitation at 290 nm nor at 230 nm was detected in the γ-CDx solution of $\beta\alpha$-DNP. The lack of the fluorescence rise may be attributable to the involvement of the ground state complex fluorescence in the decay curve of the excimer. On the analogy of the ground state complex in $\beta\beta$-DNP, there may be a weak absorption band hidden by the absorption band due to the naphthyl moiety in this 290—330 nm region. The decay curves were analyzed also as a triple exponential decay without rise, as shown in Figs. 7 and 8, whose decay times are summarized in Table 2.

These results in the CDx solutions demonstrate that the intramolecular excimer and the ground state complex formations take place both in the β- and γ-CDx solutions of $\beta\alpha$- and $\beta\beta$-DNP, though the excimer formation is more significant in $\beta\alpha$-DNP than in $\beta\beta$-DNP. If the intramolecular excimer and ground state complex fluorescences can be observed in the almost same wavelength region (≈400 nm) and if the naphthyl moiety fluorescence may be overlapped in this re-

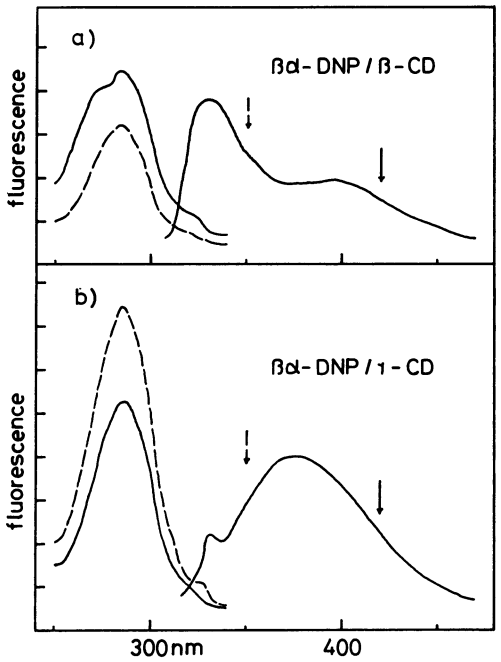

Fig. 6. Fluorescence (uncorrected, excited at 305 nm) and excitation spectra of the β- and γ-CDx (5×10^{-3} mol dm^{-3}) of βα-DNP (3.7×10^{-6} mol dm^{-3}) at room temperature. The excitation spectra were monitored at 420 nm (——) and at 350 nm (------).

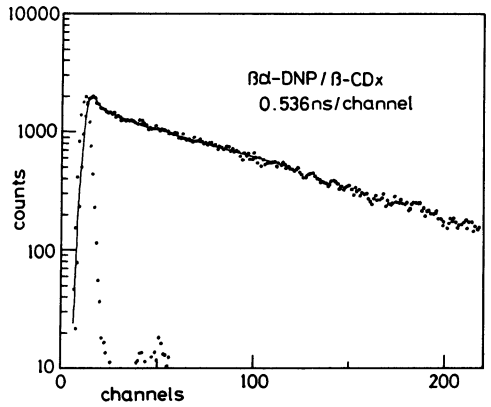

Fig. 7. Fluorescence decay of the long wavelength fluorescence (collected at 370—450 nm) of the β-CDx solution of βα-DNP (3.7×10^{-6} mol dm^{-3}) at room temperature. The decay line is the calculated decay curve based on the data shown in Table 2.

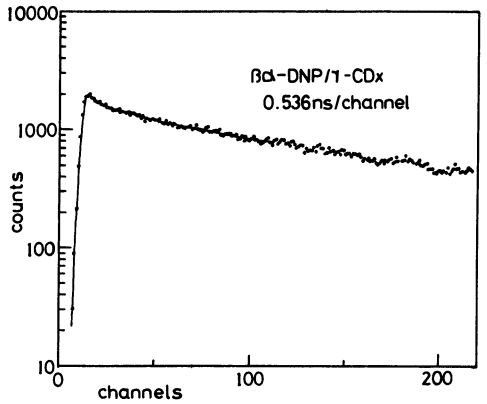

Fig. 8. Fluorescence decay of the long wavelength fluorescence (collected at 370—450 nm) of the γ-CDx solution of βα-DNP (3.7×10^{-6} mol dm^{-3}). The line is the calculated decay curve based on the data shown in Table 2.

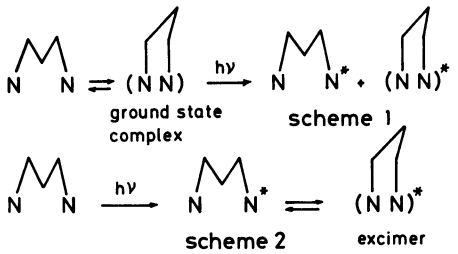

Fig. 9. Schematic reaction diagram of the intramolecular excimer and ground state complex formations (N=naphthyl moiety).

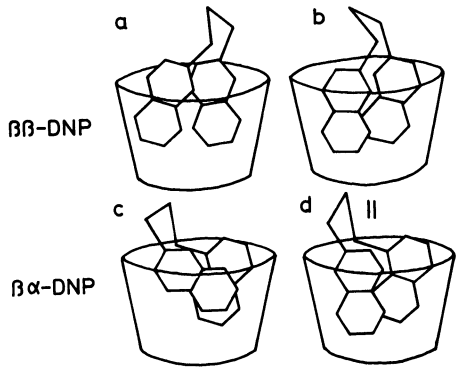

Fig. 10. Illustrated conformations of the ground state complex and/or excimer of βα- and ββ-DNP in the CDx cavity.

gion, four fluorescence decay components should be observed; two long time decay may be ascribed to the excimer and the ground state complex while two short ones to the naphthyl moiety fluorescence. However, the decay curve of the ≈400 nm fluorescence was analyzed approximately as three component decays, as mentioned above. If the excimer and ground state complex fluorescence spectra may show the approximately same fluorescence lifetime each other, the long lifetime decay due to the excimer and the ground state complex and two short lifetimes due to the naphthyl moiety may be observed. According to the well known reaction scheme as shown in Fig. 9, the shortest decay time (1—2 ns) of the naphthyl moiety fluorescence may be ascribed to the naphthyl moiety in the excited state equilibrium forming the excimer, while the decay time of 8—25 ns to that in the equilibrium with the ground state complex formation.

Turro *et al.*[2] reported the intramolecular excimer formation of αα-DNP in aqueous β- and γ-CDx solutions. The favor sturcture was proposed to be eclipsed and buried in the cavity of the CDx, where the long axes of naphthyl moieties are parallel each other. However, it is not obvious whether the structures of the fluorescent state of the ground state complex and the excimer are identical or different from each other. In the intermolecular electron donor acceptor systems, the identical fluorescent state of the exciplex and the ground state complex was evidenced as mentioned above.[7-9] However, no evidence for the identical fluorescent state of the excimer and the ground state complex has been reported, because there is no appro-

priate system exhibiting both excimer and ground state complex fluorescences . According to the geometrical allowance of the bichromophoric propanes in the CDx cavity, two each conformations of both $\beta\alpha$- and $\beta\beta$-DNP concerning with two naphthyl moieties may be considered, as shown in Fig. 10. The two closed conformers cannot be interchangeable in the small CDx cavity. If the excimer and ground state complex fluorescences may emit from an identical fluorescent state, both $\beta\alpha$- and $\beta\beta$-DNP may show similar excimer and ground state complex fluorescences, otherwise may show either the former or the latter fluorescence. However, $\beta\beta$-DNP is more favorable for the ground state complex, while $\beta\alpha$-DNP more favorable for the excimer mentioned above. Therefore, it is likely that the excimer is not identical with the fluorescent state of the ground state complex, though their fluorescence states cannot be assigned to the particular structure shown in Fig. 10.

References

1) A. Ueno, K. Takahashi, and T. Osa, *J. Chem. Soc., Chem. Commun.*, **1980**, 921.
2) N. J. Turro, T. Okubo, and G. C. Weed, *Photochem. Photobiol.*, **35**, 325 (1982).
3) M. Itoh, T. Mimura, H. Usui, and T. Okamoto, *J. Am. Chem. Soc.*, **95**, 4388 (1973).
4) E. A. Chandross and C. J. Dempster, *J. Am. Chem. Soc.*, **92**, 3586 (1970).
5) T. Mimura and M. Itoh, *J. Am. Chem. Soc.*, **98**, 1095 (1976).
6) P. R. Berington, "Data Deduction and Error Analysis of the Physical Sciences" McGraw Hill, New York, 1969.
7) M. Itoh and T. Mimura, *Chem. Phys. Lett.*, **24**, 551 (1974).
8) E. Gaweda and J. Prochorow, *Chem. Phys. Lett.*, **30**, 155 (1975).
9) M. Itoh, Y. Kumano, and T. Okamoto. *Bull. Chem. Soc. Jpn.*, **49**, 42 (1976).