Photochemical Reaction between Intramolecular Separated π-Electronic Systems—Photochemistry of [10](9,10)Anthracenopha-4,6-diyne

Toyoharu Hayashi,[1a] Noboru Mataga,*[1a] Taichi Inoue,[1b] Takahiro Kaneda,[1b] Masahiro Irie,[1b] and Soichi Misumi[1b]

Contribution from the Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka 560, Japan, and the Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565, Japan. *Received June 23, 1976*

Abstract: [10](9,10)Anthracenopha-4,6-diyne (I) gives an interesting photodimerization product (III) without any by-product, and the yield of III is independent of the concentration of I. The photodimerization takes place by a two-step mechanism through an intermediate with highly strained structure (II) which has been detected by means of the low-temperature trapping technique. The existence of this intermediate is of crucial importance for this somewhat novel photochemical reaction.

In the course of the studies upon the intramolecular interactions between π-electronic systems connected by methylene chains and their photochemical primary processes such as the photodimerization reactions of anthracenophanes and related compounds, we have found a very efficient photodimerization reaction of [10](9,10)anthracenopha-4,6-diyne (I) giving a tetramethylenecyclobutane derivative III. This reaction is somewhat peculiar in that the quantum yield of reaction is independent of the concentration of the reactant with no detectable side reaction. These results seem to indicate that the photochemical cycloaddition of I may not proceed through the direct reaction between excited and ground state molecules of I, but through intermediates which can react with each other to form III but cannot react with I in the ground state.

We have confirmed the formation of the intramolecular photoadduct intermediate II from I, by trapping the intermediate at low temperatures. II has a highly strained cyclic butatriene structure. As it will be discussed in the following, the existence of this intermediate plays an essential role in this somewhat novel photochemical reaction.

Experimental Section

Materials. The determination of the structure of the final photoproduct III was reported in the literature.[2] The preparation methods of I and [10](9,10)anthracenophane (abbreviated as [10]AH) will be reported elsewhere.[3] Methyltetrahydrofuran was distilled over metallic sodium wire. The other solvents were spectrograde and used without purification.

Apparatus. A high-pressure mercury lamp or xenon lamp was used for irradiation of solutions. Absorption spectra were measured on a Cary 15 spectrophotometer. Fluorescence spectra were measured on an Aminco-Bowman spectrophotofluorometer which has been calibrated so as to give correct quantum spectra. Fluorescence lifetimes were determined by use of a pulsed nitrogen gas laser as the exciting light source combined with a sampling oscilloscope and an X-Y recorder.

Sample solutions were deaerated by means of freeze–pump–thaw cycles. Preparations and deaerations of sample solutions were conducted in a dark room.

For the measurements of the temperature dependence of the fluorescence lifetime, a cuvette was immersed in isopentane in a quartz Dewar and the temperature of isopentane was controlled by dropping liquid nitrogen. The temperature could be lowered to 120 K by this method.

The quantum yields of photochemical reactions were determined by means of ferrioxalate actinometry.

Results

1. Relation between the Rate of Photodimerization and Light Intensity. The dependence of the formation rate of III, that is, the consumption rate of I in the initial stage of the reaction, upon the irradiating light intensity was examined. The 5×10^{-5} M solution of I in ethanol was irradiated at 405 nm, where the absorbance of the solution is so small (<0.2) that the absorbed light is proportional to the irradiating light intensity. The same initial concentration of I was used for each measurement. The result of measurement is shown in Figure 2, which can be expressed as

$$\log\,(\mathrm{d}[\mathrm{I}]/\mathrm{d}t)_{t\to 0} = \log i_0 + \text{constant} \tag{1}$$

where i_0 is the irradiating light intensity.

2. Relation between the Photodimerization Quantum Yield and the Concentration of I. The consumption yields, Φ, of I were measured for 10^{-4}–10^{-6} M solutions of I in ethanol by means of ferrioxalate actinometry. As indicated in Figure 3, no dependence of Φ on the concentration of I was detected.

3. Effects of Oxygen and/or Radical Scavenger on the Photodimerization. The effect of oxygen on the consumption rate of I was examined by irradiating at 405 nm the 5.7×10^{-5} M solution of I in ethanol saturated with oxygen. The reaction rate was not affected by the presence of oxygen. Furthermore, the effect of a radical scavenger such as hydroquinone upon the reaction was examined. To the 1.3×10^{-4} M solution of I in ethanol, 5.2×10^{-2} M hydroquinone was added, and the solution was irradiated with the high-pressure mercury lamp. It was confirmed that, just as in the absence of the radical scavenger, the photodimerization yield was 100%.

4. Trapping of the Intermediate. The presence of the intermediate could not be detected by means of the conventional absorption spectral measurement owing to the rapidity of the reaction at room temperature. It seems also difficult to detect the intermediate by means of the laser photolysis method, because the predicted absorption coefficient of the intermediate might be much smaller compared with those of I and III.

It might be possible to trap the intermediate in a rigid solution at low temperature. However, the absorption spectrum of I in rigid solution of methyltetrahydrofuran and/or the 1:1 mixture of glycerol and ethanol at 77 K did not change on irradiation for several hours with a high-pressure 500-W mercury lamp. The experimental conditions for capturing the intermediate were as follows. For a sample solution were repeated very carefully the freezing–softening–UV irradiation cycles in a quartz Dewar containing liquid nitrogen. Irradiation was conducted by using a 500-W high-pressure mercury lamp, with Toshiba UV35 filter and $CuSO_4$ solution filter. A thin quartz cell with the path length of 1 mm was used in order to ascertain the homogeneity of temperature over the sample solution.

The absorption spectrum of the intermediate was observed at 77 K in a solution of a 1:1 mixture of glycerol and ethanol,

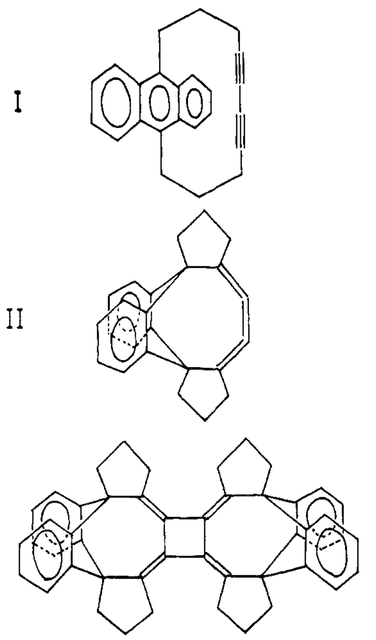

Figure 1.

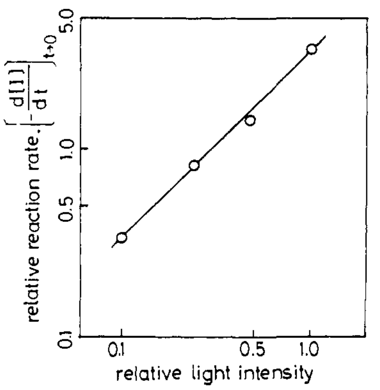

Figure 2. The relation between the rate of the consumption of I and the irradiation intensity.

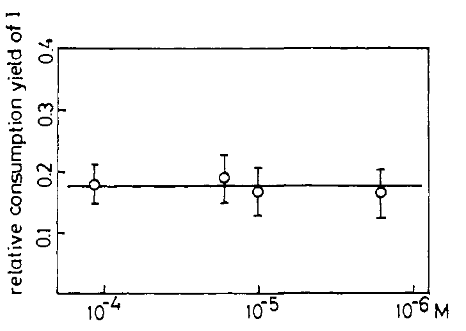

Figure 3. The relation between the consumption yield and the concentration of I.

which was the most adequate solvent system for our purpose. The reproducibility of the measurement was confirmed. The variation of absorption spectrum on irradiation is shown in Figure 4. When the intermediate was irradiated in a rigid solution at 77 K at shorter wavelength, it was converted to I quantitatively. Without irradiation, the intermediate remains unchanged in rigid solution at 77 K, but it is converted quite easily to III by raising the temperature.

5. Fluorescence Spectra and Lifetimes. The fluorescence spectra of [10]AH and I are much the same except for a small shift as shown in Figure 5. The results of measurements of the fluorescence lifetimes are shown in Table I. Fluorescence quantum yields of [10]AH and I at room temperature were 1.0 and 0.02, respectively. Therefore, the fluorescent state of I at room temperature undergoes a very rapid deactivation, compared with [10]AH. However, the fluorescence lifetime of I becomes longer up to the value of [10]AH with decrease of the temperature from 300 to 77 K, as indicated in Figure 6. In order to examine the possibility of the rapid deactivation from the excited Franck–Condon state, the dependence of the fluorescence quantum yield upon the excitation wavelength was measured. As shown in Figure 7, no such effect was observed, so that the reaction proceeds from the equilibrium fluorescent state.

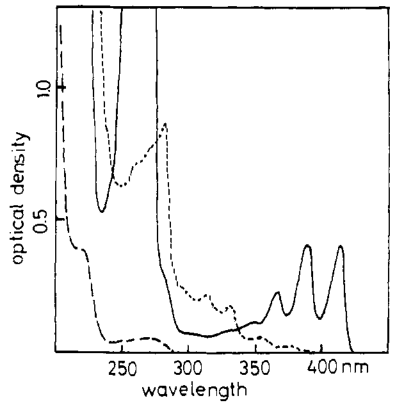

Figure 4. Absorption spectra of I, II, and III: —, I; – –, II; - - -, III.

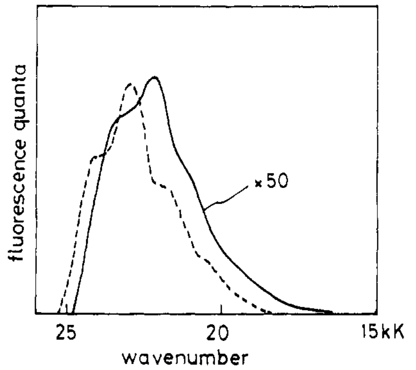

Figure 5. Fluorescence spectra of I and [10]AH in ethanol at room temperature: —, I; - - -, [10]AH.

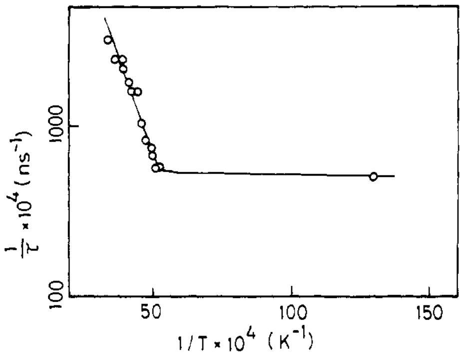

Figure 6. The dependence of the fluorescence lifetime of I (τ) in methyltetrahydrofuran on the temperature.

Discussion

1. The Initial Process of I → II. Experimental results suggest that the photochemical processes of I originate from the relaxed state of the excited singlet. The following scheme for the

Table I. Fluorescence Lifetimes of I and [10]AH in Ethanol (ns)[a]

	Room temp	77 K
I	<3.0	20
[10]AH	20	20

[a] Decay time of exciting pulse was 2.5 ns.

deactivation process of the fluorescent state can be assumed.

$$\mathrm{I}^* \xrightarrow{k_M} \mathrm{I},\ \mathrm{I}^* \xrightarrow{k_R} \mathrm{II} \qquad (2)$$

The reciprocal of the lifetime, $1/\tau = (k_M + k_R)$, may be written as follows.

$$1/\tau = 1/\tau_0 + A\exp(-\Delta E/RT) \qquad (3)$$

From the plot of $1/\tau$ vs. $1/T$ in Figure 6, the value of the activation energy ΔE was estimated to be 8.8 kJ/mol. This activation energy may be ascribed mainly to the process k_R, if we assume that the process k_M of I is rather similar to the deactivation process of [10]AH. This assumption seems to be reasonable since the fluorescence lifetime of I at 77 K is the same as that of [10]AH.

Considering that the fluorescence lifetime of I is 20 ns in a rigid solution at 77 K, the lifetime at room temperature can be estimated to be about 0.4 ns, which does not contradict the direct observation ($\tau < 3$ ns). Therefore, the rate of the reaction from the fluorescent state of I can be estimated to be 2.5×10^9 s^{-1}. This reaction rate is considerably smaller than the common vibrational relaxation rate of 10^{12}–10^{14} s^{-1}, which is in agreement with the experimental result that no effect of the excitation wavelength on the fluorescence yield was observed.

The reaction rate, $2.5 \times 10^9\ s^{-1}$, is much larger than the rate of bimolecular encounter, ca. $10^6\ s^{-1}$, estimated for $k_{diff} \sim 10^{10}$ $M^{-1}\ s^{-1}$ and 10^{-4} M concentration of I. Thus, the intermolecular process is not favored for the interpretation of the deactivation process. However, the intramolecular process does not mean the formation of triplet state or some radical, since it has been confirmed that oxygen as well as radical scavenger has no effect on the reaction of I.

In view of the above facts, the process including the formation of the intramolecular adduct which is not in the triplet state and is not a radical is favored for explaining the feature of this reaction.

2. Assignment of the Intermediate. The molecular structure of II indicated in Figure 1 could be thought of as the most reasonable intramolecular reaction intermediate. The intermediate II is composed of two benzene rings and an extremely strained butatriene skeleton. It has been reported[4] that tetra-*tert*-butylbutatriene shows absorption maxima at 300, 264, and 228 nm with extinction coefficients ϵ of 3150, 32 400, and 9050, respectively. Wavelengths of the absorption bands of II and tetra-*tert*-butylbutatriene are approximately coincident, but their extinction coefficients are not. The reason for this discrepancy might be due to the strain in II, but is not very clear at the present stage of the investigation.

3. Formation Scheme of III from the Intermediate. Two possible mechanisms could be considered for the formation of III.

$$\mathrm{II} + \mathrm{II} \rightarrow \mathrm{III} \qquad (4)$$

$$\mathrm{II} + \mathrm{I} \rightarrow \mathrm{III} \qquad (5)$$

The experimental results show that the mechanism of eq 5 is not acceptable, since the quantum yield of reaction does not depend upon the concentration of I.

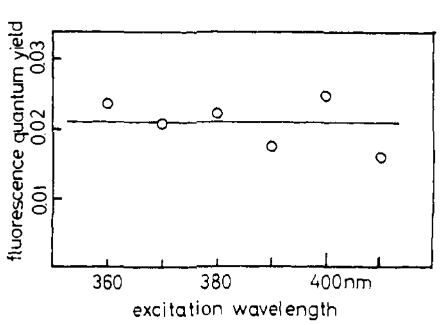

Figure 7. The dependence of the fluorescence quantum yield of I in EPA on the excitation wavelength.

If we assume the mechanism of eq 4, one might argue that the consumption rate of I should be proportional to the square of the irradiating light intensity, which contradicts the observed result in Figure 2. However, we can derive eq 1 by assuming the mechanism of eq 4 as follows.

$$\begin{aligned} &\mathrm{I} \xrightarrow{\alpha i_0} \mathrm{I}^* \\ &\mathrm{I}^* \xrightarrow{k_M} \mathrm{I} \\ &\mathrm{I}^* \xrightarrow{k_R} \mathrm{II} \\ &\mathrm{II} \xrightarrow{k_1} \mathrm{I} \\ &\mathrm{II} + \mathrm{II} \xrightarrow{k_2} \mathrm{III} \end{aligned} \qquad (6)$$

Under stationary condition,

$$[\mathrm{I}^*] = \left(\frac{\alpha i_0}{k_M + k_R}\right)[\mathrm{I}] = \beta i_0[\mathrm{I}] \qquad (7)$$

Therefore,

$$\begin{aligned} \mathrm{d[II]/d}t &= k_R[\mathrm{I}^*] - k_1[\mathrm{II}] - k_2[\mathrm{II}]^2 \\ &= k_R\beta i_0[\mathrm{I}] - k_1[\mathrm{II}] - k_2[\mathrm{II}]^2 = 0 \end{aligned} \qquad (8)$$

Assuming that $k_2[\mathrm{II}] \gg \mathrm{k}_1$,

$$[\mathrm{II}]^2 = \beta(k_R/k_2)i_0[\mathrm{I}]$$

Thus,

$$-\mathrm{d[I]/d}t = 2k_2[\mathrm{II}]^2 = 2\beta k_R i_0[\mathrm{I}]$$

$$\log(-\mathrm{d[I]/d}t)_{t\rightarrow 0} = \log i_0 + \log(2\beta k_R[\mathrm{I}]_0) \qquad (9)$$

where $[\mathrm{I}]_0$ is the initial concentration of I. The relation in eq 9 between the consumption rate of I and light intensity i_0 is coincident with the experimental result of eq 1.

The assumption that $k_2[\mathrm{II}] \gg k_1$ seems to be reasonable, since the intrinsic lifetime of the intermediates appears very long, practically infinity, in view of the fact that they remain unchanged in the rigid solvent where they cannot move to form III by encounter collision.

4. Role of Rigid Matrix in the Trapping of the Intermediates. The present intramolecular photochemical addition reaction was very sensitive to surroundings or the rigidity of solvents. It is necessary for the formation of the intermediate to occur that the solvent cage is sufficiently "soft". The result in Figure 6 suggests that the reaction in methyltetrahydrofuran can take place in the range of viscosity considerably lower than that at the melting point. By lowering the temperature in methyltetrahydrofuran solution, the reaction can be stopped easily, probably due to the rigidity of the solvent. On the contrary, the reverse photochemical reaction induced by irradiation of II, that is, II* → I, occurs very effectively even in a rigid solution at 77 K.

The above results may be explained as follows. (a) It might be necessary for the intramolecular adduct formation of I that some solvent molecules are pushed out, and not for the reverse reaction, or (b) the excess energy corresponding to the difference between the S_1 states of II and I might be partly used for softening the surroundings.

References and Notes

(1) (a) Department of Chemistry, Faculty of Engineering Science; (b) Institute of Scientific and Industrial Research.

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Deactivation of Benzophenone Triplets via Exciplex Formation. Evidence for Dual Reaction Pathways

Monte W. Wolf, Ronald E. Brown, and Lawrence A. Singer*

Contribution from the Department of Chemistry, University of Southern California, Los Angeles, California 90007.

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Abstract: Self-quenching ($^3B^* + B \rightarrow 2B$, k_{SQ}) data in benzene and carbon tetrachloride are presented for a series of para,-para′-disubstituted benzophenones: X = $(CH_3)_2N$, CH_3O, CH_3, F, Cl, H, $COOCH_3$, CF_3, and CN. The k_{SQ}'s correlate with $\sigma_p{}^+$'s but in a discontinuous manner resulting in a minimum for the cases of X = F, Cl, H. Thus, the correlation for the electron-donating X's gives a negative slope while the correlation for the electron-withdrawing X's gives a positive slope. Similar behavior is noted for phosphorescence quenching by a series of substituted benzenes of 4,4′-dimethoxybenzophenone, benzophenone, and 4,4′-bis(trifluoromethyl)benzophenone in 1,1,2-trichlorotrifluoroethane. These profiles are interpreted in terms of competing deactivation pathways via "n-type" and "π-type" exciplexes. The variation of the k_Q's with solvent for the benzophenone-anisole system indicates no dependence on solvent viscosity and only a modest (factor of ~6) variation between freon solvents and acetonitrile. A general kinetic scheme for reversible exciplex formation is presented and developed in terms of the present systems. The low temperature emission observed from the benzophenone-*N,N*-dimethylaniline system is reinvestigated and attributed as before to excitation of a ground state complex.

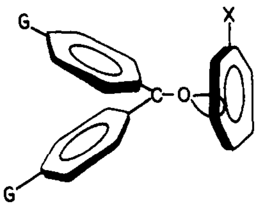
The deactivation scheme of aromatic aldehyde and ketone triplets in fluid aromatic media at room temperature is dominated by the nonradiative decay pathways (Scheme I) as evidenced by very low phosphorescence quantum yields ($\Phi_p \lesssim 10^{-3}$).[1] In the past few years, very significant photokinetic work in several laboratories has shown that the nonradiative decay path in aromatic solvents, in fact, is dominated by a bimolecular quenching process, step 5, that proceeds via a short-lived complex having some charge transfer character.[2]

Scheme I

(1) $S_0 \xrightarrow{h\nu} S_1$	excitation
(2) $S_1 \xrightarrow{k_{isc}} T_1$	intersystem crossing ($\Phi_{isc} \approx 1$)
(3) $T_1 \xrightarrow{-h\nu'} S_0$	phosphorescence
(4) $T_1 \xrightarrow{k_d} S_0$	nonradiative decay
(5) $T_1 + Q \xrightarrow{k_Q} S_0$	quenching
(6) $T_1 + S_0 \xrightarrow{k_{SQ}} 2S_0$	self-quenching

In addition to the above observations, a number of reports appeared in recent years of the self-quenching of aromatic aldehydes and ketones, step 6.[3] In the course of investigating a series of para,para′-disubstituted benzophenones, we noted an apparent linear correlation between log k_{SQ} and $\sigma_p{}^+$ ($\rho = -1.7$) for benzophenone and substituted benzophenones having *p*-Cl, F, CH_3, CH_3O, and $(CH_3)_2N$.[1] Previously, Cohen and Guttenplan[2a] reported that the quenching rates of benzophenone triplet by substituted benzenes increased with decreasing ionization potential of the latter. We found that a Hammett plot of their data also correlated well with $\sigma_p{}^+$ giving a negative ρ. We concluded that for benzophenone triplets both self-quenching and quenching by aromatic solvents proceed via exciplex **1** (hereafter called n-type exciplex) where there is some charge transfer character. In the n-type exciplex, the resulting charge polarization gives the triplet an acceptor role.

In contrast to the above results, Schuster, Weil, and Halpern[2b] found that electron-deficient benzenes quench benzophenone triplet *faster* than benzene. Accordingly, we found that a Hammett plot of their data tended towards a positive ρ. The apparent reversal of donor-acceptor roles is understandable if a different exciplex (**2**) (hereafter called π-type exciplex) were involved in these cases. Note that in the n-type exciplex electron transfer is facilitated between the π system of the aromatic ring and the half-filled n orbital of T_1 while in the π-type exciplex, electron transfer is facilitated between the half-filled π^* of T_1 and the unfilled π^* of Q.



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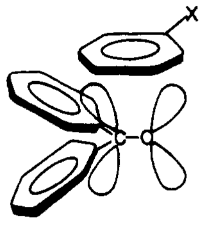

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If self-quenching and quenching by aromatic solvents are mechanistically similar, then we would also expect to find a changeover from the n- to the π-type exciplex at some point in the self-quenching mechanism for benzophenones having electron-withdrawing substituents. Further, the tendency of