3542 © *1989 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* ***62,*** *3542—3548 (1989)* [Vol. 62, No. 11

Photochemical Hydrogen Abstraction Reactions of 9,10-Dihydro-9,10-*o*-benzenoanthracene-1,4-dione Derivatives with Xanthene: Intramolecular Charge Transfer Quenching

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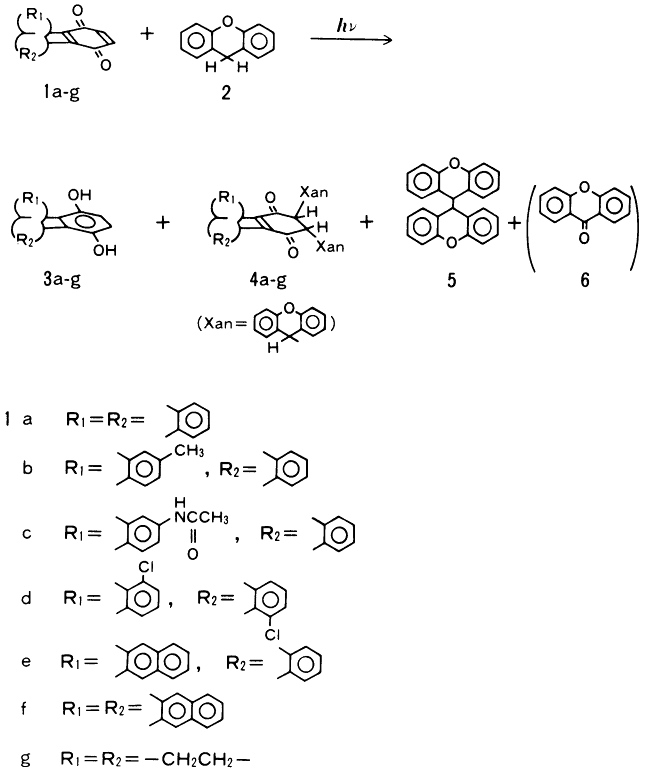
(Received April 19, 1989)

Intramolecular charge transfer interaction in triptycene system was investigated. 9,10-Dihydro-9,10-*o*-benzenoanthracene-1,4-dione (triptycenequinone) and its analogs were readily photoreduced with xanthene to give the corresponding hydroquinones and the adducts with two xanthenyl radicals. The chemically induced dynamic nuclear polarization examination and the corresponding thermal reaction proved the adducts to be originated from free radical coupling of xanthenyl radicals and quinones. The quantum yield for disappearance of the quinones depended upon both the substituents and solvents. Kinetic analysis by applying Stern–Volmer plot, using anthracene as a quencher, revealed that the quantum yield of intersystem crossing and the lifetime of the triplet state decreased with increasing electron-donating power of the aromatic rings in triptycenequinones. These solvent and substituent effects suggest that intramolecular charge transfer quenching of both the singlet and the triplet excited states of quinones by neighboring aromatic rings occurs in the triptycenequinone system. Such intramolecular charge transfer interaction would lower the rate constants of hydrogen abstraction reaction from xanthene via the triplet states of triptycenequinone derivatives.

Transannular π-π interaction among neighboring benzene rings in triptycene system is one of the problems of increasing interest in organic chemistry.[1–8] It will be fascinating to investigate a change of such intramolecular interaction caused by introducing benzoquinone moiety into the triptycene system. 9,10-Dihydro-9,10-*o*-benzenoanthracene-1,4-dinoe (triptycenequinone) (**1a**) has one benzoquinone moiety and two benzene rings. Murata has observed the charge transfer (CT) transition for symmetry-forbidden CT interaction in unsubstituted and methyl- or methoxy-substituted triptycenequinones.[6,7] The present author has reported the substituent and solvent effects on the electronic spectra of triptycenequinones **1a**—**f**.[8] Triptycenequinones show characteristic absorption maxima as a result of intramolecular charge transfer. The substituents on the benzene rings strongly affect the CT bands. Strong electron-donating substituents induce shifts of the absorption maxima to long wavelengths. Calculations by the extended Hückel theory reveal that the charge of aromatic ring is somewhat delocalized to the benzoquinone moiety in the course of HOMO–LUMO excitation.[8] These findings clearly show that intramolecular CT interaction does exist in the singlet excited state of the triptycenequinone system.

On the other hand, benzoquinone derivatives are easily photoreduced with hydrogen donors such as xanthene (**2**) to the corresponding hydroquinones by hydrogen abstraction reactions.[9–14] Some quinones gave 2,3-di(9-xanthenyl)-2,3-dihydro-1,4-naphthoquinone derivatives.[11]

In this paper, the effect of the substituents on the hydrogen abstraction reaction of triptycenequinones with xanthene will be reported to reveal the efficiency of the intramolecular CT quenching of the singlet and triplet excited states of triptycenequinones.



Results and Discussion

Product Analysis. In the photoreactions of tripty-

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Table 1. Product Yields[a)] in Photoinduced Reductions of Triptycenequinones with Xanthene (**2**)

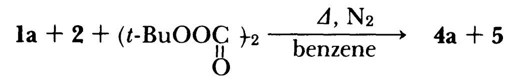
Solvent	Quinone	Hydroquinone **3**	Adduct **4**
		Yield/%	Yield/%
C_6H_6	**1a**	78	17
	1d	75	Trace
	1e	69	23
	1f	93	n.d.[b)]
	1g	83	Trace
CH_3CN	**1a**	66	10
	1e	77	n.d.[b)]
$(CH_3)_2CO$	**1a**	86	n.d.[b)]

a) Yields of isolated products based on the consumed quinones. b) Not detected.

cenequinones **1a**—**f** and 5,6,7,8-tetrahydro-5,8-ethano-1,4-naphthoquinone (**1g**) with xanthene (**2**), all quinones were reduced to the corresponding hydroquinones in high yields. A degassed C_6H_6 solution of **1a** and **2** (molar ratio was 1:2) was irradiated to give the hydroquinone **3a**, the adduct **4a** and 9,9′-bixanthenyl (**5**). The results of various quinones in three solvents are summarized in Table 1. When acetone was used as a solvent, the solution was irradiated at longer wavelengths than 340 nm. In acetonitrile, xanthone (**6**) was also isolated. Triptycensquinones other than those summarized in Table 1 were similarly photoreduced to give only the corresponding hydroquinones.

The structures of the adducts **4** were determined by mass, ^{1}H NMR, UV, and IR spectra. Further, 7.4×10^{-5} mol of the adduct **4a** was oxidized with $KBrO_3$ in acetic acid to give triptycenequinone (**1a**) (6.1×10^{-5} mol) and xanthone (**6**) (1.0×10^{-4} mol). This result confirms that **4a** consists of **1a** and xanthenyl moieties in the ratio of 1:2. Since the ^{1}H NMR spectrum of **4e** shows multiplet-like two doublets at δ=4.16, two xanthenyl groups may be in trans.

Formation of **4a** can be explained in terms of attack of two 9-xanthenyl radicals on **1a** in the ground state. In a thermal coupling experiment, **1a** and 9-xanthenyl radical generated by thermal reaction of **2** and di-*t*-butyl peroxyoxalate gave the adduct **4a** and bixanthenyl (**5**).



$$\mathbf{1a} + \mathbf{2} + (t\text{-BuOO}\underset{\underset{\displaystyle O}{\|}}{C})_2 \xrightarrow[\text{benzene}]{\Delta,\ N_2} \mathbf{4a} + \mathbf{5}$$

On the contrary, the irradiation of **1a** and **5** in benzene gave no adduct **4a** but gave xanthone (**6**) and hydroquinone **3a**.

Chemically Induced Dynamic Nuclear Polarization (CIDNP) Examination of Photoinduced Hydrogen Abstraction Reaction of 1a with 2. In the photoreaction of **1a** with **2**, enhanced ^{1}H NMR signals were observed, although the signals were not so intense compared with those of 1,4-benzoquinone[10,12)] or 1,4-naphthoquinone.[10,11)] Figures 1 and 2 show the ^{1}H NMR signals observed in the reactions of **1a** with **2** and of **1g** with **2** for comparison. Signal No. 1 was due to the methylene protons of **2**, signals Nos. 2 and 3 due to **1a**, signals Nos. 4 and 10 due to **5**, and signals Nos. 8 and 9 due to the hydroquinone **3a**. By comparison of the spectra given in Fig. 1 A—D, signals Nos. 5, 7, and 11 can be assigned to the methylene protons of xanthenyl groups and signal No. 6 to the bridgehead protons of a triptycenequinone moiety. Signal No. 12 may be due to an unstable intermediate in the reaction of **1a** and the corresponding hydroquinone **3a**, because the similar absorption signal was observed during irradiation of a solution of these two compounds.

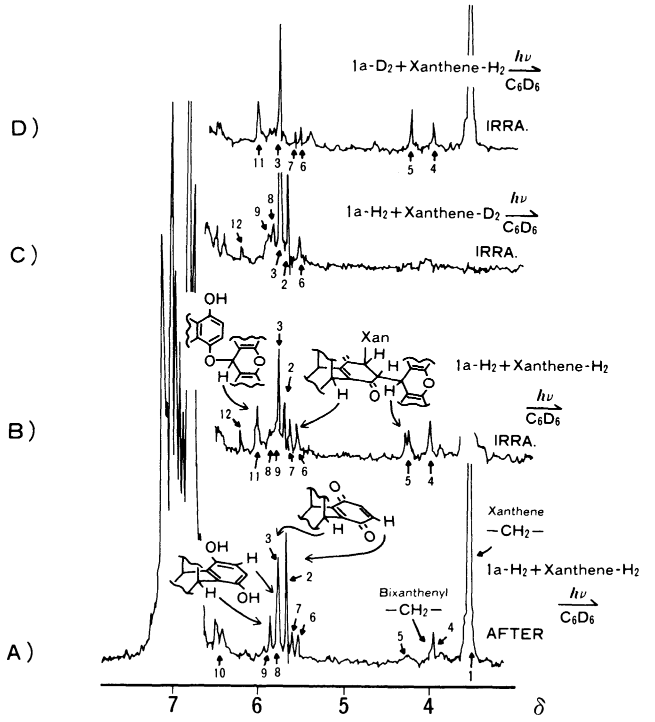


Fig. 1. ^{1}H NMR spectra observed in the photochemical reaction of **1a** with **2** at room temperature (solvent; C_6D_6). A) After irradiation. B) During irradiation. C) During irradiation with xanthene-9,9-d_2 instead of **2**. D) During irradiation with triptycenequinone-2,3-d_2 instead of **1a**.

The chemical shifts of signals Nos. 5 and 6 were compatible with those of the adduct **4a**. Since these enhanced signals Nos. 5. and 6 were hardly observed at 6 °C and clearly observed at 78 °C (Fig. 2), they may be due to escape products from the solvent-caged initial radical pair. Application of "Kaptein's simple rule",[15)] as well as the results of the thermal coupling reaction described in the previous section, also confirms that the precursor of **4a** is a free radical pair (Scheme 1).

In the photoreduction of naphthoquinone derivatives with **2**,[11)] the CIDNP examination and the analysis of the structures of isolated products reveal that the quinones give 1:1 adducts, 2-(9-xanthenyl)-

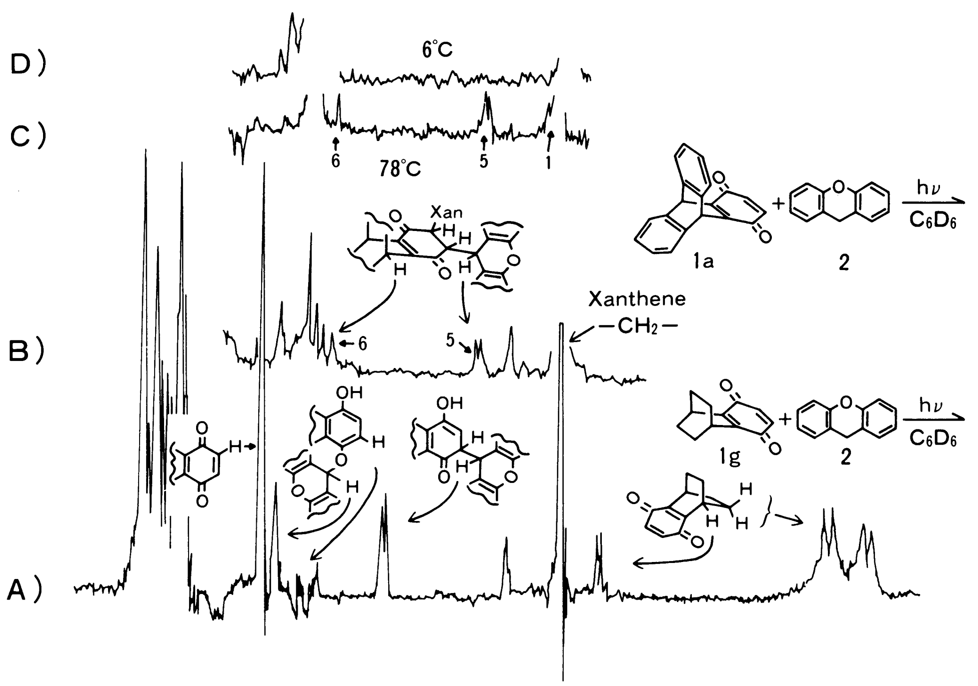
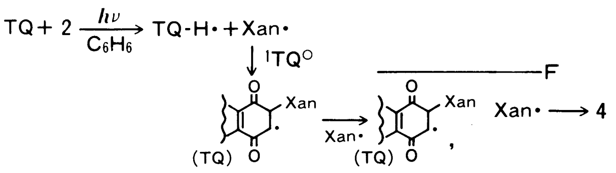


Fig. 2. ^{1}H NMR spectra observed in the photochemical reaction of quinones **1g** or **1a** with **2** during irradiation (solvent; C_6D_6). A) Non-aromatic quinone **1g** was irradiated at room temperature. B—D) Triptycenequinone **1a** was irradiated: B) at room temperature, C) at 78 °C, D) at 6 °C.



TQ : triptycenequinone
TQ-H• : semiquinone radical

Scheme 1.

Table 2. Quantum Yields for Disappearance of Quinones in the Photoreductions with Xanthene (**2**)[a]

Solvent	Quinone[b]	$\Phi_{\text{disap.}}$[c]
C_6H_6	**1d**	0.65
	1a	0.35
	1b	0.25
	1c	0.002
	1e	0.50
	1f	0.45
	1g	0.4
CH_3CN	**1d**	0.67
	1a	0.46
	1b	0.12
	1c	0.008
	1e	0.07
	1f	0.04
	1g	0.5
$(CH_3)_2CO$	**1a**	0.21
	1e	0.07
	1f	0.04

a) [**2**]=2.0×10^{-2} mol dm^{-3}. b) [Quinone]=$2—5\times10^{-3}$ mol dm^{-3}. c) Measured by means of iron(III) oxalate actinometry.

2,3-dihydro-1,4-naphthoquinones, as well as 1:2 adducts. In the present study, the non-aromatic derivative **1g** gave CIDNP signals of 1:1 coupling products as shown in Fig. 2. Although triptycenequinone (**1a**) also gave a CIDNP signal which may be assigned to a proton of a 1:1 adduct (Fig. 1B), such 1:1 adduct was not isolated in any photoreactions of triptycenequinone derivatives. Phenoxy type 1:1 adducts may be unstable because of susceptibility to oxidation and steric hindrance between a xanthenyl group and benzene rings of triptycenequinones.

Quantum Yields for Disappearance of Triptycenequinones ($\Phi_{\text{disap.}}$). The data of $\Phi_{\text{disap.}}$ in the reactions with **2** are summarized in Table 2. The details of the measurement method are described in the experimental section. Electron-donating substituents on benzene ring clearly suppressed the $\Phi_{\text{disap.}}$ values in each solvent (**1d**>**1a**>**1b**). Further, the $\Phi_{\text{disap.}}$ values of triptycenequinones having electron-donating groups, **1b**, **e**, and **f**, were much smaller in the reactions in polar solvents (acetonitrile and acetone) than in a nonpolar solvent (benzene). As previously reported,[8] change of the reduced charge (population change) in the course of HOMO–LUMO excitation, calculated by the extended Hückel theory, can be adopted as a parameter of electron-donating ability. The $\Phi_{\text{disap.}}$ values are plotted against the population change of

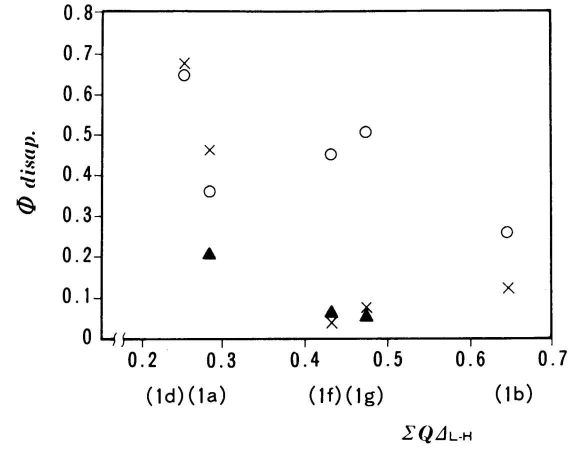


Fig. 3. A plot of $\Phi_{\text{disap.}}$ against population change of benzoquinone moiety ($\sum Q\Delta_{\text{L-H}}$).[8] Open circle, in benzene; cross, in acetonitrile; closed triangle, in acetone.

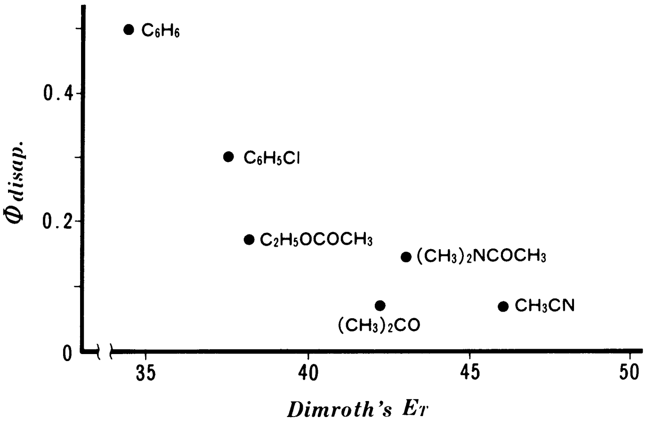


Fig. 4. Effect of solvent polarity on $\Phi_{\text{disap.}}$ of **1e**. [**2**]=2.0×10^{-2} mol dm^{-3}. Dimroth's E_T value of DMF was estimated from its Z value.[8]

benzoquinone moiety ($\sum Q\Delta_{\text{L-H}}$) in Fig. 3. The $\Phi_{\text{disap.}}$ values obtained in benzene gently decrease with increasing population change $\sum Q\Delta_{\text{L-H}}$, while those in more polar solvents, acetonitrile and acetone, steeply decrease to go down to about 0.1 at $\sum Q\Delta_{\text{L-H}}$ value of 0.4—0.5. This population-change dependency of $\Phi_{\text{disap.}}$ values suggests that CT quenching occurs in the triplet excited state of triptycenequinones.

The $\Phi_{\text{disap.}}$ values of **1e** in various solvents clearly showed a decisive effect of solvent polarity. Figure 4 shows that the $\Phi_{\text{disap.}}$ values decrease with increasing solvent polarity; Dimroth's E_T values.[16,17] The reason why Kosower's Z-values were not adopted was described previously.[8]

These substituent and solvent effects on the $\Phi_{\text{disap.}}$ values suggest that the lowest excited states of triptycenequinones, especially the quinones having electron-donating substituents, may have a strong CT character in polar solvents.

Exceptionally, the $\Phi_{\text{disap.}}$ values of **1c** were exceedingly low compared with others (Table 2). Although the Hammett σ^+ constant of acetylamino group (−0.25) is almost identical with that of methyl group (−0.26),[21] the $\Phi_{\text{disap.}}$ values of **1c** in both benzene and acetonitrile were less than one-tenth of those of **1b**. This can be explained in terms of quenching of the excited state of quinones by intra- and/or intermolecular electron transfer from lone pair electrons of the nitrogen atom of amino group to carbonyl groups.[18—20] This conception was confirmed by the intermolecular quenching experiment of the photoreduction of **1a** with **2** using acetanilide or acetotoluidide as a quencher. Acetanilide and acetotoluidide strongly decreased the $\Phi_{\text{disap.}}$ value of **1a** as shown in Table 3. More effective intramolecular quenching by 3,4-dimethylaniline moiety could suppress the $\Phi_{\text{disap.}}$ value of **1c** to about one-tenth of that of intermolecularly-quenched **1a**. A similar substituent effect is observed in the photoreduction of substituted fluorenone.[20] In that case, acetylamino group gives much higher quenching efficiency than ethoxy group (σ^+=−0.78).

Table 3. Quenching of Triplet Excited Triptycenequinone (**1a**) by Anilides in C_6H_6[a)]

Quencher	[Quencher] / mol dm^{-3}	$\Phi_{\text{disap.}}$
None[b)]	—	0.35
Acetanilide[c)]	5.4×10^{-3}	0.052
	5.0×10^{-2}	0.022
p-Acetotoluidide[d)]	5.0×10^{-3}	0.040
	2.5×10^{-2}	0.015

a) Hydrogen donor was **2**; [**2**]=2.0×10^{-2} mol dm^{-3}. b) [**1a**]=4.0×10^{-3} mol dm^{-3}. c) [**1a**]=4.9×10^{-3} mol dm^{-3}. d) [**1a**]=4.7×10^{-3} mol dm^{-3}.

Quenching of the Photoreductions of Triptycenequinones. Photoreductions of triptycenequinones with **2** were quenched by anthracene (the energy of the excited singlet state E_S=319.7 kJ mol^{-1}, the energy of the excited triplet state E_T=176.0 in a non-polar solvent), *trans*-stilbene (E_S=394.7, E_T=209.5 in a non-polar solvent), pyrene (E_S=322.2 in a non-polar solvent, E_T=201.5 in a polar solvent)[21], and oxygen. Because quinones were excited with the 450 nm monochromatic light (265.6 kJ mol^{-1}) in the present experiments of quantum yield determination, the quenchers described above could quench the triplet, not singlet, excited states of the quinones. Further, in general, hydrogen abstraction reactions have been considered to occur via the n-π^* triplet excited states.[22] Therefore, the present photoreduction reactions also can be considered to proceed through the n-π^* triplet excited states.

The triplet energy of triptycenequinone was assumed to be similar to the value of 2,3-dimethyl-1,4-benzoquinone (216.2 kJ mol^{-1}).[23] In the following experiments on kinetics, anthracene was used as a suitable quencher because of its E_S and E_T values. Pyrene and *trans*-stilbene were not suitable because pyrene formed a CT complex with **1a** in the ground state, and the quenching efficiency of *trans*-stilbene was fairly small.

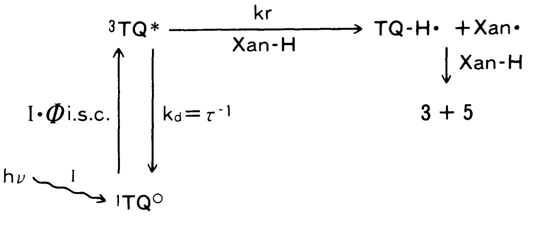
The reaction scheme for the hydrogen abstraction reactions of triptycenquinones can be drawn as described in Scheme 2.

From the thermal coupling experiment and the CIDNP examination described in the previous sections, the excited states of quinones might not directly participate in the formation of the adducts **4**, and the amount of **4** may be negligibly small in the initial step of the reaction. Therefore, formation of the adducts can be excluded from the following kinetic analysis. Based on Scheme 2, a straight line is expected in the Stern–Volmer plot of $\Phi_{\text{disap.}}^{-1}$ vs. $[\mathbf{2}]^{-1}$ from the following equation:

$$\Phi_{\text{disap.}}^{-1} = \Phi_{\text{i.s.c.}}^{-1} + k_{\text{d}} \times \Phi_{\text{i.s.c.}}^{-1} \times k_{\text{r}}^{-1} \times [\mathbf{2}]^{-1} \qquad (1)$$

where $\Phi_{\text{i.s.c.}}$ is the quantum yield of intersystem crossing, k_{r} is the rate constant of the reaction between the triplet excited triptycenequinones (^{3}TQ*) and **2**, and k_{d} is the decay rate constant of ^{3}TQ*, that is, the reciprocal of the lifetime τ of ^{3}TQ*.

As another pathway to the hydroquinones **3**, the disproportionation of the semiquinone radicals (TQ–H·) could also be included in the reaction scheme. Based on the scheme containing disproportionation pathway, the intercept in the plot of $\Phi_{\text{disap.}}^{-1}$ vs. $[\mathbf{2}]^{-1}$ ($2/\Phi_{\text{i.s.c.}}$) cannot be less than two. However, the intercept was found to be less than two in many cases in the present study, suggesting that the contribution of the disproportionation of TQ–H· can be estimated to be small. In such cases, the hydroquinones **3** may be produced mainly by hydrogen abstraction reaction of TQ–H· from **2**.



Scheme 2.

In the presence of a quencher (Q) of ^{3}TQ*, Eq. 1 is modified as follows:

$$\Phi_{\text{disap.}}^{-1} = \Phi_{\text{i.s.c.}}^{-1} + k_{\text{d}} \times \Phi_{\text{i.s.c.}}^{-1} \times k_{\text{r}}^{-1} \times [\mathbf{2}]^{-1} + k_{\text{q}} \times \Phi_{\text{i.s.c.}}^{-1} \times k_{\text{r}}^{-1} \times [\mathbf{2}]^{-1} \times [\text{Q}] \qquad (2)$$

where k_{q} is the quenching rate constant and [Q] is the concentration of the quencher. Based on Eq. 2, a straight line is expected in the Stern–Volmer plot of $\Phi_{\text{disap.}}^{-1}$ vs. [Q] at a constant concentration of [**2**].

Stern–Volmer Plots. Benzene (Dimroth's E_{T} value is 34.5) and acetonitrile (46.0) were adopted as a nonpolar and a polar solvent, respectively. Since the quenching reactions proceed nearly in the diffusion-control, the following rate constants of the quenching reactions were adopted, $k_{\text{q}}=5.0\times10^9$ dm^3 mol^{-1} s^{-1} in benzene and 1.0×10^{10} dm^3 mol^{-1} s^{-1} in acetonitrile.[19,24] All quinones investigated (**1a**, **b**, **d**, **e**, and **g**) gave straight lines in the plots of $\Phi_{\text{disap.}}^{-1}$ vs. $[\mathbf{2}]^{-1}$ in both solvents. Since the $\Phi_{\text{disap.}}$ values did not depend on the concentration of triptycenequinones (data not shown), intermolecular interaction of triptycenequinones can be neglected at least in the concentrations adopted in these experiments.

The kinetic parameters obtained by Stern–Volmer plots are summarized in Table 4. The $\Phi_{\text{i.s.c.}}$ values of the investigated quinones were mostly similar to each other in benzene, but they greatly changed in acetonitrile. The $\Phi_{\text{i.s.c.}}$ and τ values obtained in acetonitrile decreased in the order of electron-donating power of the aromatic rings except for the τ value of **1g**. The k_{r} values of substituted triptycenequinones **1a**, **b**, and **d** in both solvents decreased in the same order as the $\Phi_{\text{i.s.c.}}$ and τ values in acetonitrile. These results can be explained by intramolecular CT quenching, that is, by increase of the CT characters of the lowest excited

Table 4. Kinetic Parameters of the Triplet State of Triptycenequinones in the Reactions with Xanthene (**2**)

Solvent	Quinone	$\Phi_{\text{i.s.c.}}$	τ	k_{r}
			10^{-7} s	10^8 mol^{-1} dm^3 s^{-1}
C_6H_6	**1d**	0.72	5.4	8.0
	1a	0.70	4.2	1.1
	1b	0.74	4.8	0.48
	1e	0.58	11	2.1
	1g[a)]	0.83	0.4	4.8
CH_3CN	**1d**	0.67	>20	33
	1a	0.49	16	6.9
	1b	0.16	3.6	5.7
	1e	0.09	1.1	26
	1g	0.7	0.8	17

a) Because **1g** formed CT complex with C_6H_6, **2**, and **5**, the kinetic parameters of **1g** were not so accurate as those of other quinones.

singlet (^{S_1}TQ) and triplet (^{T_1}TQ) states of the quinones.

As previously reported,[8] increase of electron-donating power of the neighboring aromatic rings enlarges the CT character of ^{S_1}TQ, especially in polar solvents. This substituent effect on the $\Phi_{\text{i.s.c.}}$ values in acetonitrile (Table 4) can be explained by increase of the CT character, therefore, decrease of the n–π^* character, of ^{S_1}TQ. Similarly to the singlet state, the CT character of ^{T_1}TQ may increase in the order of electron-donating power of the substituents in **1a**, **b**, and **d**, resulting in decrease of the n–π^* character of ^{T_1}TQ to give the low k_r values. Further, the k_r values of the respective quinones were larger in acetonitrile than in benzene. This solvent dependency of the k_r values suggests great contribution of a polar transition state in the reaction with **2**, that is, the exciplex of the triplet excited quinone and **2**. The electron-donating substituents could enlarge electron density in the benzoquinone moiety, resulting in suppression of the formation of the exciplex with the electron-rich hydrogen donor **2**. The large k_r values of **1e** suggest that a naphthalene ring may accelerate such exciplex formation.

The small τ values of the lowest excited triplet state of the quinones having electron-donating substituents, determined by Stern–Volmer plot analysis, can be explained by assuming that the lifetimes of the CT triplet states of triptycenequinones are shorter than those of the n–π^* triplet states, whereas the lifetimes of the CT triplet states of substituted benzophenones, determined by phosphorescence measurement, are longer than those of the n–π^* triplet states.[25]

In benzene, the $\Phi_{\text{i.s.c.}}$ and τ values of substituted triptycenequinones (**1a**, **b**, and **d**) were almost identical (Table 4). Since CT levels are higher and n–π^* excited levels are lower in non-polar solvents than in polar solvents, the CT characters of ^{S_1}TQ and ^{T_1}TQ may decrease in benzene. As a result, the $\Phi_{\text{i.s.c.}}$ and τ values would not be affected by the electron-donating power of aromatic rings. The τ value of **1e** with a naphthalene ring, was about twice and that of **1g**, without an aromatic ring, was about one-tenth of those of other triptycenequinones in benzene (Table 4). Therefore, the τ values in benzene seem to depend on somewhat the number of neighboring π electrons (**1e**>**1a**=**1b**=**1d**>**1g**). This can be explained in terms of increasing π–π^* character of ^{T_1}TQ. That is, since increase of neighboring π electrons may cause increase of the π–π^* character of ^{T_1}TQ and the lifetime of the π–π^* triplet state is reported to be much longer than that of the n–π^* triplet state,[26,27] the τ values of **1e** would be larger and that of **1g** would be smaller than others.

In the case of non-aromatic derivative **1g**, since the lowest excited singlet and triplet states may be n–π^* both in benzene and in acetonitrile, the $\Phi_{\text{i.s.c.}}$ and τ values of **1g** showed weaker solvent dependency than those of other quinones.

The CT quenching described above is hard to explain in terms of the energy transfer from the neighboring π-electron systems to benzoquinone moiety, because the triplet energy of the neighboring aromatic ring (benzene, E_T=353.2 kJ mol^{-1}; naphthalene, 255.2)[21] may be too high to quench the triplet excited triptycenequinones (E_T of **1a** is assumed to be about 216.2 kJ mol^{-1} as described in the previous section, and was estimated to be about 200 kJ mol^{-1} by the comparison of the quenching rate constant of **1a** with those of E_T-known compounds, using *trans*-stilbene as a quencher, data not shown).

In conclusion, intramolecular CT quenching may occur both in the singlet and triplet excited states of the triptycenequinone system. Such intramolecular CT interaction may also suppress the exciplex formation between triptycenequinones and an electron-rich hydrogen donor **2**.

Experimental

Apparatus for Measurements. Electronic spectra were taken with a Shimadzu UV-200 spectrometer. ^{1}H NMR and CIDNP spectra were taken with a JEOL PS-100 MHz spectrometer in suitable solvents using TMS as an internal standard. IR spectra were recorded on a JASCO IR-G spectrometer using a KBr disc.

Quinones. **1a**—**g** were synthesized according to the previous report.[8] **Deuterated Compounds.** 2,3-d_2-Derivative of **1a** was synthesized by Diels–Alder reaction of 1,4-benzoquinone-2,3,5,6-d_4 with anthracene and subsequent oxidation in the same manner as described previously.[8] Xanthene-9,9-d_2 was obtained by the reduction of xanthone (**6**) with $LiAlD_4$.

Photoreductions of the Quinones with 2 on a Large Scale. Deaeration of a reaction solution was undertaken by means of pump-freeze-thaw cycles using a vacuum line covered with black sheets. A degassed solution in a usual glass tube was irradiated with a 300 W high pressure Hg-arc lamp through a water layer 5 cm thick at room temperature, with or without suitable filters. The products, except precipitated hydroquinones, were isolated by column chromatography or by preparative thin-layer chromatography on silica gel. The structure of the hydroquinones were identified after acetylation by comparison of their spectra and melting points with the authentic diacetates. The structure of 9,9'-bixanthenyl was determined by comparison of its spectra and melting point with the authentic sample. Physical properties of the adduct **4a** were as follows. ^{1}H NMR ($CDCl_3$): δ=3.06 (d, J=4 Hz, 2H), 4,21 (d, J=4 Hz, 2H), 5.46 (brs and m like d, 4H), 5.82 (m like d, 2H), 6.5—7.5 (m, 20H). IR (KBr): ν_{CO}=1663 cm^{-1}, $\nu_{\mathrm{C=C\text{-}O\text{-}C}}$=1607, 1578, 1480, 1460, 1240. UV(ethyl acetate): $\lambda_{\max}$=437 nm (sh, ε=300), 408 (sh, 660), 389 (sh, 920), 341 (1670), 274 (sh, 6800), 265 (sh, 7100). MS m/z=647 (M$^+$), 646, 466 (M−Xan), 465, 464, 463, 285 (M−2Xan), 284, 182 (Xan+1). Molecular weight measured by vapor pressure method; 638±26 (calcd. 646.8). Found: C, 85.21; H, 4.82%. Calcd for $C_{46}H_{30}O_4$: C, 85.43; H, 4.68%. Physical properties of the adduct **4e** were as follows. Mp >195 °C (decomp), 268 °C (melt). ^{1}H NMR ($CDCl_3$):

δ=3.04 (d, J=4 Hz, 2H), 4.13 (d, J=4 Hz, 1H), 4.17 (d, J=4 Hz, 2H), 4.52—4.80 (m, 2H), 5.26—5.50 (m, 2H), 5.45 (s, 2H), 5.65—5.89 (m, 2H), 6.2—7.8 (m, 1H). IR (KBr): ν_{CO}=1660 cm^{-1}, $\nu_{C=C-O-C}$=1605, 1575, 1477, 1458, 1245. MS m/z=515 (M−Xan), 334 (M−2Xan), 181 (Xan). Found: C, 85.91; H, 4.50%. Calcd for $C_{50}H_{32}O_4$: C, 86.19; H, 4.63%.

Quantum Yield Measurement. The $\Phi_{disap.}$ values were measured directly by means of iron(III) oxalate actinometry or indirectly with a merry-go-round as relative quantum yields to a standard solution. A reaction solution in a glass ample was degassed by means of pump-freeze-thaw cycles as described in the previous paragraph and was irradiated at room temperature with the 450 nm monochromatic light (using a 300 W high pressure Hg lamp with one Toshiba KL-45 and two VY-42 filters). A glass ample equipped with a 4 ml cuvette for irradiation and electronic spectra measurements was used in absolute $\Phi_{disap.}$ measurements. The disappearance of quinones was monitored with their visible absorption at more than three points of wavelength. High pressure liquid chromatography (column, μ-porasil Waters; eluent, CH_2Cl_2) was adopted in the case of **1g**.

Stern–Volmer Plot. In the absence of anthracene, the concentration of **2** ([**2**]) was set at several points from 1×10^{-2} to 2×10^{-1} mol dm^{-3} and that of the quinones ([quinone]) were 4×10^{-2} (**1a** in benzene), 3×10^{-3} (**1a** in acetonitrile), 5×10^{-3} (**1b** in both solvents), 3×10^{-3} (**1d** in both solvents), 3×10^{-3} (**1e** in both solvents), 3×10^{-2} mol dm^{-3} (**1g** in both solvents).

In quenching experiments, the concentration of anthracene was set at several suitable points from 0 to 2×10^{-2} mol dm^{-3}. [**2**] was 2×10^{-2} (**1d** in acetonitrile), 5×10^{-2} (**1g** in both solvents), 6.7×10^{-2} mol dm^{-3} (other cases). [Quinone]'s were almost the same as in the anthracene-free experiments.

In all experiments, good straight lines were obtained in the plots of $\Phi_{disap.}$ vs. [**2**]$^{-1}$ or vs. [quencher].

The author wishes to express his grateful thanks to Professor Kazuhiro Maruyama for his guidance and invaluable discussions in this work. The author is grateful to Dr. Yasuo Kubo for his helpful suggestions. Thanks are also due to Dr. Tetsuo Otsuki, Dr. Yoshinori Naruta, and Dr. Tatsuhisa Kato for fruitful discussion.

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