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Photoisomerization of Oxime Ethers and Efficiency of Triplet Formation via Exciplexes

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9,10-Dicyanoanthracene(DCA)-sensitized isomerization of (*E*)- and (*Z*)-isomers of an oxime ether of 2-acetylnaphthalene (*E*-**1** and *Z*-**1**, respectively) was investigated in benzene by means of steady irradiation and laser flash photolysis. The excited singlet DCA was effectively quenched by *E*-**1** and *Z*-**1** to afford exciplexes, decay of which gave DCA triplets or **1** triplets. The triplet state of **1** was proposed as the isomerization intermediate and the formation efficiency of **1** triplets was estimated from isomerization quantum yields.

Although photochemical geometrical isomerization of the ethylenic[1] and azo linkage[2] has been well-investigated, little work has been done on photoisomerization of the imine linkage.[3] For many imines, only one geometrical isomer, usually (*E*)-isomer, is stable and the other, usually (*Z*)-isomer, is unstable at room temperature.[4] The (*Z*)-isomers, when formed from irradiation of the (*E*)-isomers, revert quickly to the (*E*)-isomers. This situation made it difficult to work with the imines by the conventional procedures. However, introduction of a methoxyl group on the nitrogen atom of N=C bonds stabilizes effectively configurations of both isomers, enabling one to investigate photochemical geometrical isomerization of oxime ethers, particularly on triplet sensitization.[5]

Recently much effort has been done to investigate photochemical reactions proceeding through electron transfer.[6] During the course of our investigation on photochemical behavior of imines[7] as well as olefins[1c,8] on triplet and electron-transfer sensitization, we found that 9,10-dicyanoanthracene (DCA) sensitizes the isomerization of a pair of oxime ethers of 2-acetylnaphthalene, (*E*)- and (*Z*)-*N*-methoxy-1-(2-naphthyl)ethanimine (*E*-**1** and *Z*-**1**, respectively). In this paper we report in detail isomerization behavior of **1** via exciplexes with DCA.

Experimental

(*E*)- and (*Z*)-*N*-Methoxy-1-(2-naphthyl)ethanimine (*E*-**1** and *Z*-**1**, respectively).[5c] A mixture of 2-acetylnaphthalene (17 g, 0.10 mol) and *O*-methylhydroxyamine hydrochloride (9.3 g, 0.11 mol) was refluxed in ethanol (95%, 210 ml) containing sodium acetate (151 g, 1.85 mol) for 12 h. Usual work-up gave 15 g of a mixture of oxime ethers *E*-**1** and *Z*-**1** (*E*/*Z*=90:10 by GLPC); yield 75%. Crystallization from ethanol afforded pure *E*-**1**; mp 89—90 °C (lit, 89.5—90 °C).[5c]

The mixture of *E*-**1** and *Z*-**1** was dissolved in benzene (1 dm^3), and irradiated under nitrogen with a 400-W high-pressure mercury lamp (>300 nm) for several hours. Evaporation of the solvent left a solid (*E*/*Z*=44:56), which was crystallized from ethanol to give a *Z*-**1** rich filtrate (*E*/*Z*=25:75). This mixture was separated by column chromatography (silica gel, benzene) to afford an oily material, which was distilled twice under vacuum to give pure *Z*-**1**; mp 24.5—26 °C (lit, 25—26 °C).[5c]

DCA was purified by crystallization from ethanol followed by sublimation under vacuum. Benzene was distilled over calcium hydride and acetonitrile was distilled twice over phosphorus pentoxide and then over potassium carbonate.

Fluorescence spectra were obtained on a Hitachi MPF-2A or a Hitachi F-4000 fluorescence spectrophotometer. Fluorescence lifetimes were measured using a single photon counting apparatus, Applied Photophysics Model SP-3X or Horiba NAES 1100.

Laser flash photolyses were performed with 406-nm laser pulses (DPS, 10-nm fwhm) from a XeCl (308 nm) excimer laser (Lambda Physik EMG-101)-pumped dye laser (Lambda Physik FL-3002) and with a pulsed xenon arc (Wacom KXL-151, 150 W) as a monitoring light source. The monitoring light coming from a monochromator (JASCO CT-25C) was amplified by a photomultiplier (Hamamatsu Photonics R928) and stored in a storage scope (Iwatsu TS-8123), and the signals were transferred to a personal computer (NEC PC-9801E) and accumulated for 3—5 times to be averaged. The system was computer-controlled and the decay curves were analyzed by this computer system. Sample solutions containing DCA (1.2×10^{-4} M, M=mol dm^{-3}) and oxime ether *Z*-**1** (0.13 M) were deaerated by bubbling nitrogen for 30 min.

Near-infrared emission from singlet oxygen was observed by a germanium p–n junction detector (Hamamatsu Photonics B2144) with a silicon window. The element was reverse-biased (9 V) and placed in series with a load resistor (1 kΩ). The response time of this system is less than 3 μs.

Redox potentials were measured by cyclic voltammetry with a Hokuto Potentiostat-Galvanostat HA-201 and a Hokuto Function Generator HB-104. The measurements were carried out using a three-electrode cyclic voltammetric cell. The working electrode was a platinum wire and the reference electrode was SCE. Tetraethylammonium perchlorate (0.1 M) was used as a supporting electrolyte. Sample concentrations were ca. 5×10^{-3} M in acetonitrile.

For quantum yield measurements nitrogen-purged solutions of DCA and *E*-**1** or *Z*-**1** were irradiated on a merry-go-round type apparatus with 405- and 436-nm light from a 400-W high-pressure mercury lamp through a Toshiba L-39 glass filter. Light intensities were determined by potassium tris(oxalato)ferrate(III) actinometry. The solutions were analyzed at low conversion (<10%) of the substrate on a Shimadzu GC-4CM-PF gas chromatograph.

Photostationary isomer ratios were measured by irradiating benzene solutions of *Z*-**1** and *E*-**1** in the presence of optically matched concentrations of sensitizers (OD's at irradiation wavelength=ca. 2).

Results

Quenching of DCA Fluorescene by *E*-1 and *Z*-1. The fluorescence intensity and lifetime of DCA (3×10^{-5} M) were effectively quenched by both *E*-**1** (0—0.025 M) and *Z*-**1** (0—0.046 M) in deaerated benzene and acetonitrile (Fig. 1 for *Z*-**1** in benzene). Stern–Volmer plots are linear over the concentration range investigated. Table 1 lists the quenching rate constants (k_q) calculated from the Stern–Volmer constants ($K_{SV}=k_q\tau_S$) of intensity quenching and fluorescence lifetimes (τ_S), 12.4 ns in benzene and 14.9 ns in acetonitrile, determined by single photon counting. The k_q values are close to the diffusion-controlled rate constant in each solvent.[9]

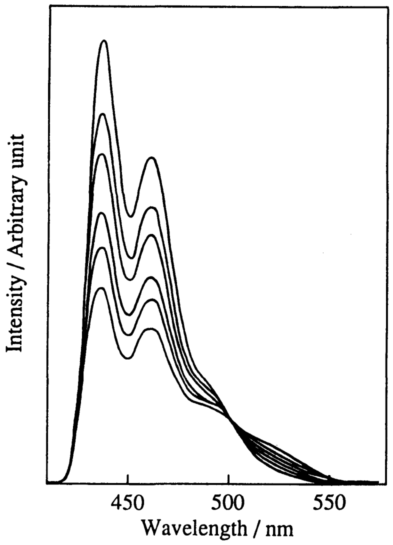


Fig. 1. Quenching of DCA fluorescence by *Z*-1 and exciplex emission in benzene.

On quenching of DCA fluorescence by *E*-**1** and *Z*-**1** in benzene, new weak emissions appeared at the longer wavelength region with their maxima around 520 nm for *E*-**1** and 505 nm for *Z*-**1**. These emissions are reasonably assigned to the exciplexes formed from the excited singlet DCA and the ground-state oximes. Figure 1 indicates the profile of the exciplex emission of *Z*-**1**. The exciplexes decayed with lifetimes of 22.8 and 28.7 ns for *E*-**1** and *Z*-**1**, respectively, as measured by single photon counting. In acetonitrile no exciplex emission was observed for *E*-**1** or *Z*-**1**.

Photostationary State Isomer Ratio. Oxime ethers *E*-**1** and *Z*-**1** (5×10^{-3} M) were irradiated in deaerated benzene or acetonitrile solutions containing DCA (1×10^{-3} M) with 405- and 436-nm light. The irradiation resulted in nearly the same photostationary state isomer ratios ($([E]/[Z])_{pss}$) around 40/60 starting with either isomer in both solvents. When typical triplet sensitizers like acetophenone and benzophenone (1×10^{-2} M) were used in benzene, similar ($([E]/[Z])_{pss}$) values (44/56) were obtained. Direct irradiation of **1** with 313-nm light gave an ($([E]/[Z])_{pss}$) value around 60/40. The results are listed in Table 2.

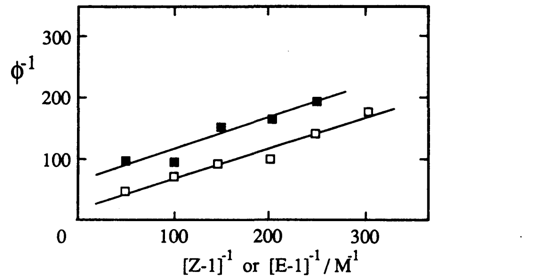


Fig. 2. Stern-Volmer plots of DCA-sensitized isomerization of *E*-1 (■) and *Z*-1 (□) in benzene.

Table 1. Rate Constants for Fluorescence Quenching of DCA by Oxime Ethers in Benzene and Acetonitrile

Oxime ether	In benzene		In acetonitrile	
	$k_q\tau_S/M^{-1}$	$k_q/M^{-1}\,s^{-1}$	$k_q\tau_S/M^{-1}$	$k_q/M^{-1}\,s^{-1}$
E-1	94	7.8×10^{9}	270	1.8×10^{10}
Z-1	27	2.2×10^{9}	420	2.8×10^{10}

Table 2. Photostationary State Isomer Ratios of Oxime Ether 1 on Direct and Sensitized Irradiation in Benzene and Acetonitrile

Sensitizer	Wavelength/nm	Solvent	Isomer ratio	
			Z	*E*
—	313	Benzene	58	42
DCA	405, 436	Benzene	41	59
Benzophenone	366	Benzene	44	56
Acetophenone	313	Benzene	44	56
—	313	MeCN	62	38
DCA	405, 436	MeCN	38	62
Benzophenone	366	MeCN	44	56

Quantum Yields for Isomerization. The quantum yields for DCA(10^{-3} M)-sensitized $E\rightarrow Z$ and $Z\rightarrow E$ isomerization ($\phi_{E\rightarrow Z}$ and $\phi_{Z\rightarrow E}$, respectively) were determined in benzene with varying concentrations (3.3×10^{-3}—2.0×10^{-2} M) of *E*-**1** and *Z*-**1** at their low conversion (<10%). Figure 2 shows Stern-Volmer plots for $E\rightarrow Z$ and $Z\rightarrow E$ isomerization. The reciprocal of the intercept and the ratio of intercept/slope in the plot for $Z\rightarrow E$ isomerization give, respectively, 0.062 as a limiting quantum yield ($\phi_{Z\rightarrow E}{}^{\text{lim}}$) at infinite *Z*-**1** concentration and 32 M^{-1} as a Stern-Volmer constant (K_{SV}). The latter value is in satisfactory agreement with that obtained from the fluorescence quenching, 27 M^{-1}. Similarly the $E\rightarrow Z$ isomerization gives 0.015 as $\phi_{E\rightarrow Z}{}^{\text{lim}}$ and 122 M^{-1} as K_{SV}. This value agrees fairly well with K_{SV} from the fluorescence quenching, 94 M^{-1}. In acetonitrile the isomerization proceeded with much lower efficiencies as estimated from irradiation times needed for accomplishment of the photostationary state.

Triplet Energies of Oxime Ethers. An attempt was done to determine the triplet energies of *E*-**1** and *Z*-**1** by the procedure of Hammond and Saltiel,[10)] since *E*-**1** and *Z*-**1** did not emit phosphorescence in rigid glasses. Thus, the photostationary state isomer ratios of **1** were measured in the presence of various sensitizers with triplet energies covering 42—74 kcal mol^{-1} in benzene (Table 3). Figure 3 plots the ratio against the triplet energy of the sensitizer. This plot allows us to estimate the triplet energies of *E*-**1** and *Z*-**1** as ca. 52 and ca. 60 kcal mol^{-1}, respectively.[10)]

Laser Flash Photolysis. On laser flash photolysis (LFP) of DCA (1×10^{-4} M) with 406-nm laser pulses from excimer laser (XeCl, 308 nm)-pumped dye laser (DPS) in deaerated benzene in the presence of *Z*-**1** (0.1 M) a transient absorption spectrum was observed in the 400—600 nm region (λ_{max} 442 nm), the lifetime being 9.5 μs as observed at 455 nm (Fig. 4). This spectrum can be attributed to DCA triplets.[11)] In the absence of *Z*-**1** the intensity of the absorption was

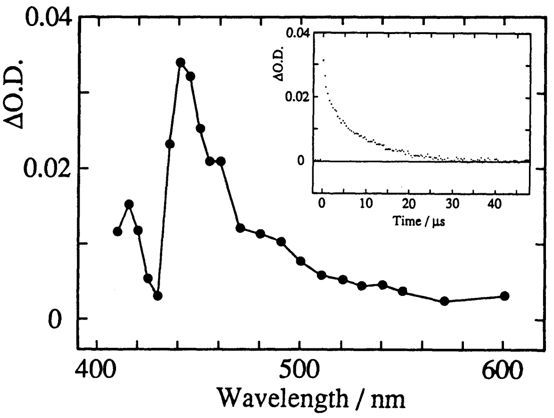


Fig. 4. Transient absorption spectrum in benzene with a decay curve.

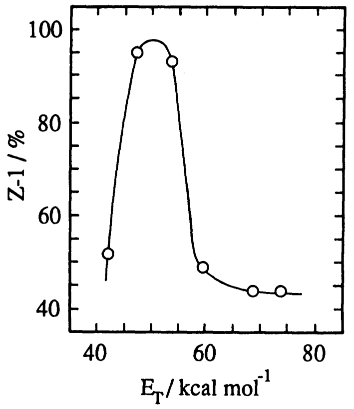


Fig. 3. Hammond-Saltiel plot of triplet sensitized isomerization of **1**.

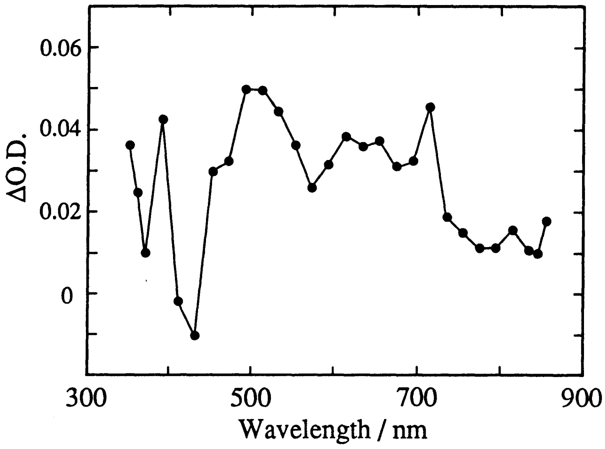


Fig. 5. Transient absorption spectrum in acetonitrile.

Table 3. Photostationary State Isomer Ratios in Triplet Sensitized Irradiation of Oxime Ether **1**

Sensitizer	Triplet energy[a)]/kcal mol^{-1}	Isomer ratio	
		Z	*E*
Anthracene	42.0	52	48
Benz[*a*]anthracene	47.2	95	5
Benzil	53.4	93	7
2-Acetylnaphthalene	59.4	49	51
Benzophenone	68.6	44	56
Acetophenone	73.7	44	56

a) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York (1973), pp. 3—11.

several times weaker than that observed in its presence.

LEP of DCA with *Z*-**1** in acetonitrile gave a transient absorption spectrum different from that in benzene (Fig. 5). The absorption bands in the 440—750 nm region can be mainly attributed to DCA anion radicals,[12] and the bands in longer wavelengths than 750 nm might be attributed to *Z*-**1** cation radicals since γ-radiolysis of *Z*-**1** in Freon matrix gave absorption bands due to *Z*-**1** cation radicals in the 500—1000 nm region with $\lambda_{\max}$'s at 650, 810, and 930 nm.[13]

Singlet oxygen luminescence was monitored at 1.27 μm using a germanium photodiode by exciting benzene solutions of DCA (1×10^{-4} M) with 406-nm laser pulses under air in the absence and presence of *Z*-**1**. In the absence of *Z*-**1** the emission was too weak to determine its lifetime; however, in the presence of *Z*-**1** (0.1 M) was exhibited a strong emission with a lifetime of 30 μs.[14]

Discussion

The quenching interaction of singlet excited DCA and the oxime ethers is considered to be accompanied by exciplex formation in benzene as evidenced by the long wavelength emission, and by electron transfer in acetonitrile as shown by transient absorption ascribed to DCA anion radicals and oxime ether cation radicals in laser plash photolysis. The changes of Gibbs' free energy ($\Delta G°$) associated with electron transfer from the DCA excited singlet to the oxime ethers in acetonitrile were estimated as -3.8 and -5.0 kcal mol^{-1} for *E*-**1** and *Z*-**1**, respectively, by Weller's equation (Eq. 1),[15]

$$\Delta G°/\text{kcal mol}^{-1} = 23.06(E_{\text{ox}} - E_{\text{red}} - e_0{}^2/a\varepsilon - E_{0,0}) \qquad (1)$$

where E_{ox} and E_{red} indicate the oxidation potential of an oxime ether (1.81 V for *E*-**1** and 1.76 V for *Z*-**1** vs. SCE) and the reduction potential of DCA (-0.95 V), respectively, as determined in acetonitrile, $E_{0,0}$ is the singlet excitation energy of DCA (2.87 eV, estimated from its fluorescence spectrum), and $e_0{}^2/a\varepsilon$ is a Coulombic term (0.06 eV). These values show that the electron transfer can take place as an exothermic process in acetonitrile.

The $([E]/[Z])_{\text{pss}}$ ratio in DCA-sensitized irradiation is 1.4 in benzene from Table 1. The ratio is expressed by Eq. 2,

$$([E]/[Z])_{\text{pss}} = (k_q{}^Z/k_q{}^E)(\phi_{Z\to E}{}^{\text{lim}}/\phi_{E\to Z}{}^{\text{lim}}) \qquad (2)$$

where $k_q{}^Z$ and $k_q{}^E$ are the rate constants for quenching of DCA excited singlets by *Z*-**1** and *E*-**1**, respectively, and the limiting quantum yields, $\phi_{Z\to E}{}^{\text{lim}}$ and $\phi_{E\to Z}{}^{\text{lim}}$, mean the quantum efficiencies with which the exciplexes give the isomerized derivatives. Combination of the observed ratios of $k_q{}^Z/k_q{}^E$, 0.28, and $\phi_{Z\to E}{}^{\text{lim}}/\phi_{E\to Z}{}^{\text{lim}}$, 4.2, gives $([E]/[Z])_{\text{pss}}$ as 1.2, which agrees well with the observed value, 1.4. This fact supports the sensitization with DCA of **1** isomerization.

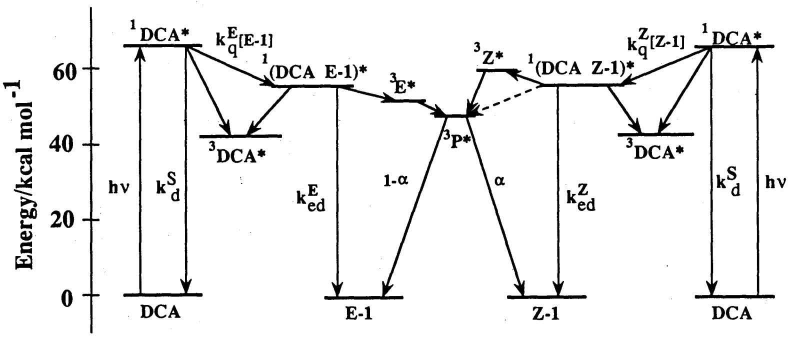
Similarity in the photostationary isomer ratio between DCA and benzophenone sensitization in benzene (Table 2) suggests that the DCA-sensitization generates the triplet state of **1** as the intermediate for isomerization in benzene, as seen in the isomerization of olefins in the presence of electron donors[16] or acceptors[8b,17] in nonpolar solvents where the triplet state of olefins results from the exciplexes.

It is reasonably concluded from energetic considerations and laser flash photolysis study that the triplet state of **1** is the intermediate of isomerization. The Hammond–Saltiel plot (Fig. 3) gave the triplet energies of *E*-**1** and *Z*-**1** as ca. 52 and ca. 60 kcal mol^{-1}, respectively. It is noteworthy that the triplet energy of *Z*-**1** is close to that of naphthalene itself, 61 kcal mol^{-1},[18] indicating that the triplet excitation in *Z*-**1** is nearly localized in the naphthalene moiety which may be twisted around the C–C single bond from the C=N molecular plane. Also, the energies of the exciplexes of DCA with *E*-**1** and *Z*-**1** are estimated around 55 and 56 kcal mol^{-1}, respectively, from their emission maxima.

The energy diagram for DCA-sensitized isomerization of **1** in benzene is depicted in Scheme 1. On excitation of DCA in the presence of *E*-**1**, the resulting singlet excited DCA (66.2 kcal mol^{-1}) interacts with *E*-**1** to give an exciplex, which subsequently either is deactivated to the ground state through nonradiative pathways or exciplex emission, or produces the triplet state of *E*-**1** or DCA (41.5 kcal mol^{-1})[16b] in an exothermic way. In the case of *Z*-**1**, the formation of *Z*-**1** triplets from the exciplex of DCA and *Z*-**1** is nearly 3 kcal mol^{-1} endothermic. However, if the exciplex does not produce directly *Z*-**1** triplets (^{3}Z*) but produces the perpendicular triplet of **1** (^{3}P*) through a nonvertical pathway, it is certainly at least 5 kcal mol^{-1} exothermic, since in the triplet state of stilbene ^{3}P* is nearly the same as, or slightly lower than, ^{3}E* in energy.[1] In any case, ^{3}P* produced either from ^{3}E*, ^{3}Z*, or directly from the exciplexes undergoes deactivation to the ground state *E*-**1** and *Z*-**1** with a certain ratio.

Laser excitation of DCA in deaerated benzene exhibited only a weak transient absorption band due to DCA triplets because of low efficiency of intersystem crossing of DCA excited singlets.[19] It is remarkable that in the presence of *Z*-**1**, laser excitation of DCA afforded the absorption bands of the DCA triplets ($\lambda_{\max}$ 442 nm) with several times stronger intensity than in the absence of *Z*-**1**; however, any transient absorption bands assignable to the triplet states of **1** were not detected. This may be owing to their very short lifetimes, since, even on benzophenone-sensitized laser excitation, only the benzophenone triplet was observed with no detection of **1** triplets.

Likewise, laser excitation of DCA in aerated benzene



Scheme 1.

gave only a very low yield of singlet oxygen, as determined by singlet oxygen luminescene technique. This may be also due to the low quantum yield for intersystem crossing of the DCA excited singlets. However, in the presence of *Z*-**1**, a strong emission from singlet oxygen was detected. This is reasonably attributed to a more efficient production of the DCA triplets under these conditions.

The fact that the DCA triplet is produced from the excitation of DCA in the presence of *Z*-**1** but not in the absence of *Z*-**1** clearly shows that the quenching of DCA singlets by *Z*-**1** gives the DCA triplet and probably also the triplet state of **1**. Therefore, it is reasonable to propose such a mechanism for the isomerization as shown in Scheme 1, where *k*'s are the rate constants for the corresponding processes.

According to this mechanism, the quantum yields for the isomerization can be expressed as follows:

$$\phi_{E\to Z} = \frac{k_q{}^E[E\text{-}\mathbf{1}]}{\tau_s{}^{-1} + k_q{}^E[E\text{-}\mathbf{1}]} \cdot \phi_T{}^E \cdot (1-\alpha) \qquad (3)$$

$$\phi_{Z\to E} = \frac{k_q{}^Z[Z\text{-}\mathbf{1}]}{\tau_s{}^{-1} + k_q{}^Z[Z\text{-}\mathbf{1}]} \cdot \phi_T{}^Z \cdot \alpha \qquad (4)$$

where $\phi_T{}^E$ and $\phi_T{}^Z$ denote the efficiencies for the production of the triplet state of **1** from the exciplexes. Therefore, the Stern–Volmer equation can be reduced as follows:

$$\frac{1}{\phi_{E\to Z}} = \frac{1}{(1-\alpha)\phi_T{}^E}\left(1 + \frac{1}{k_q{}^E\tau_S[E\text{-}\mathbf{1}]}\right) \qquad (5)$$

$$\frac{1}{\phi_{Z\to E}} = \frac{1}{\alpha\phi_T{}^Z}\left(1 + \frac{1}{k_q{}^Z\tau_S[Z\text{-}\mathbf{1}]}\right) \qquad (6)$$

The limiting quantum yields at the infinite concentration of *E*-**1** and *Z*-**1**, $\phi_{E\to Z}{}^{\text{lim}}$ and $\phi_{Z\to E}{}^{\text{lim}}$, are written as follows:

$$\phi_{E\to Z}{}^{\text{lim}} = (1-\alpha)\phi_T{}^E \qquad (7)$$

$$\phi_{Z\to E}{}^{\text{lim}} = \alpha\phi_T{}^Z \qquad (8)$$

The values for α and $1-\alpha$, the ratios of giving *E* and *Z* from the common twisted triplet state of **1**, ^{3}P*, are seen as 0.56 and 0.44, respectively, from the photostationary state isomer ratio arising from sensitizers with sufficiently high triplet energies like acetophenone and benzophenone (Table 1). Substitution of the observed $\phi_{E\to Z}{}^{\text{lim}}$ and $\phi_{Z\to E}{}^{\text{lim}}$ values in Eqs. 7 and 8 affords $\phi_T{}^Z$ and $\phi_T{}^E$ as 0.14 and 0.027, respectively.

The above values ϕ_T's are nearly comparable or lower than the values for the triplet olefin production from the quenching of the singlet excited state of 2-NaphthylCH=CHBu^t with 1,4-dicyanobenzene in benzene, 0.26[8b)] and for the quenching of the singlet excited stilbene with various amines in benzene, 0.09—0.51.[16a)] The lower efficiency for the production of triplet **1** in the present reaction can be attributed to the dual courses which the exciplex can take, that is, giving either triplet **1** or triplet DCA; the latter is energetically preferable. Also, the present exciplexes might have higher probability to undergo deactivation than those between the olefins and electron donors or acceptors.

The isomerization efficiency was lower in acetonitrile than in benzene, indicating that the isomerization does not proceed efficiently through cation radicals of **1**. On LFP of DCA with *Z*-**1** in acetonitrile only the ionic species were observed but no triplets were detected. However, the photostationary state isomer ratio of DCA-sensitized isomerization was close to that of benzophenone sensitization in the same solvent (Table 1).

The ion radical pairs E-$\mathbf{1}^{\ddagger}$/DCA$^{\overline{\cdot}}$ and Z-$\mathbf{1}^{\ddagger}$/DCA$^{\overline{\cdot}}$ are estimated to be 63.5 and 62.4 kcal mol^{-1}, respectively, higher in energy than the neutral species in the ground state from their electrochemical potentials. Back electron transfer in the radical ion pairs can generate the triplet states of DCA and **1**; however, the major role in isomerization of **1** may be played by the **1** triplet thus formed.

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