cloudy white precipitate formed which was collected by filtration, washed with H_2O, MeOH, and ether, and dried. A total of 14 mg (43%) of the hexafluoroantimonate 17 was obtained: mp >360 °C; IR (KBr) 3138 (m), 1644 (s), 1462 (m), 1276 (m), 662 (s) cm^{-1}; ^1H NMR (CD_3CN) δ 8.35 (d, J = 6.5 Hz, 2 H), 7.75 (d, J = 6.5 Hz, 2 H), 4.10 (s, 3 H). Anal. (PE) Calcd for $C_{42}H_{42}F_{36}N_6Sb_6$: C, 24.66; H, 2.25; N, 4.11. Found: C, 24.30; H, 2.07; N, 4.11.

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Photochemistry of 9,10-Dicyanoanthracene–1,2-Diarylcyclopropane Systems. Photocycloaddition and Photoisomerization

Kazuhiko Mizuno,* Nobuyuki Ichinose,[†] and Yoshio Otsuji*

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591, Japan

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The photochemical reactions of 9,10-dicyanoanthracene (DCA)–1,2-diarylcyclopropane (CP) systems have been investigated. In degassed acetonitrile solution, ($4\pi + 2\sigma$) photocycloaddition between DCA and CP occurred to give *cis*- and *trans*-2,4-diaryl-1,5-dicyano-6,7:8,9-dibenzobicyclo[3.2.2]nona-6,8-dienes in a 3:1 ratio in good chemical yields although the quantum yields were not high (Φ = 0.002–0.04). This photocycloaddition did not occur in benzene. The DCA-sensitized photoisomerization of *trans*- and *cis*-1,2-bis(4-methoxyphenyl)cyclopropanes (**1a** and **2a**) in acetonitrile efficiently occurred to afford a photostationary mixture containing **1a** and **2a** in a 95:5 ratio. The photoisomerization was remarkably accelerated by bubbling air, by adding metal salts such as $Mg(ClO_4)_2$ and $LiBF_4$, and also by aromatic hydrocarbons such as phenanthrene and biphenyl. The quantum yield for the photoisomerization of **2a** to **1a** exceeded unity, indicating that this photoisomerization involved a chain process. The DCA-sensitized photoisomerization of optically resolved (−)-**1a** afforded a racemic mixture of (+)-**1a** and (−)-**1a**. These photoreactions are initiated by a one-electron transfer from CP to the excited singlet of DCA. The photocycloaddition proceeds via radical ion pairs in solvent cage and the photoisomerization proceeds via solvent-separated radical cations of CP.

Introduction

Photoinduced electron transfer reactions from electron donors (D) to electron acceptors (A) in polar media have been a subject of considerable interest in recent years.[1] In these photoreactions, the separation of an initially produced radical ion pair [$D^{+\bullet}\cdots A^{-\bullet}$] to dissociated radical ions $D^{+\bullet}$ and $A^{-\bullet}$ is crucial in determining the efficiency and selectivity of the photoreactions. Recently, Farid et al. have reported that the photodimerization of 1,1-diphenylethene in the presence of DCA proceeds via geminate radical ion pair and also via the free radical cation of 1,1-diphenylethene, and the extent of participation of these reactive species in the photoreaction can be determined by means of kinetic analysis.[2] However, ambiguity still exists about the distinction of these reactive species and their reactivity features. Previously, we proposed that the separation of a radical ion pair to dissociated free radical ions may be facilitated by the addition of certain additives such as aromatic hydrocarbons and metal salts into the reaction system (Scheme I).[3] On the basis of this view, we have studied the effects of metal salts and other additives on photoinduced electron-transfer reactions with the intention of developing highly efficient and selective photoreactions.

This paper deals with the ($4\pi + 2\sigma$) photocycloaddition between 9,10-dicyanoanthracene (DCA) and 1,2-diarylcyclopropanes and the DCA-sensitized photoisomerization of 1,2-diarylcyclopropanes.[3,4] The effects of additives and solvents on these photoreactions have been studied and their mechanistic features are discussed.

Scheme I[a]

$$\mathrm{A} + \mathrm{D} \xrightarrow{h\nu} \underset{\text{Exciplex}}{[\mathrm{A}^{\delta-}\mathrm{D}^{\delta+}]} \longrightarrow \underset{\text{Radical ion pair}}{[\mathrm{A}^{\overset{-}{\cdot}}\ldots\mathrm{D}^{\overset{+}{\cdot}}]}$$

$$[\mathrm{A}^{\overset{-}{\cdot}}\cdots\mathrm{D}^{\overset{+}{\cdot}}] \xrightarrow{\text{Back-electron transfer}} \mathrm{A} + \mathrm{D}$$

$$[\mathrm{A}^{\overset{-}{\cdot}}\cdots\mathrm{D}^{\overset{+}{\cdot}}] \xrightarrow{\text{Dissociation}} \mathrm{A}^{\overset{-}{\cdot}} + \mathrm{D}^{\overset{+}{\cdot}}$$

$$[\mathrm{A}^{\overset{-}{\cdot}}\cdots\mathrm{D}^{\overset{+}{\cdot}}] + \mathrm{X} \longrightarrow [\mathrm{A}\cdots\mathrm{X}]^{\overset{-}{\cdot}} + \mathrm{D}^{\overset{+}{\cdot}}$$

$$[\mathrm{A}^{\overset{-}{\cdot}}\cdots\mathrm{D}^{\overset{+}{\cdot}}] + \mathrm{Y} \longrightarrow \mathrm{A}^{\overset{-}{\cdot}} + [\mathrm{D}\cdots\mathrm{Y}]^{\overset{+}{\cdot}}$$

$$[\mathrm{A}^{\overset{-}{\cdot}}\cdots\mathrm{D}^{\overset{+}{\cdot}}] + \mathrm{M}^+\mathrm{Z}^- \longrightarrow [\mathrm{A}^{\overset{-}{\cdot}}\ldots\mathrm{M}^+] + [\mathrm{D}^{\overset{+}{\cdot}}\ldots\mathrm{Z}^-]$$

[a] A, electron acceptor; D, electron donor; X, Y, M^+Z^-, additives.

Results and Discussion

($4\pi + 2\sigma$) Photocycloaddition between DCA and 1,2-Diarylcyclopropanes. Irradiation of a degassed acetonitrile solution containing DCA and *trans*-1,2-bis(4-methoxyphenyl)cyclopropane (**1a**) with a 500-W high-pressure mercury lamp through an aqueous $CuSO_4$–NH_3 filter solution (≥400 nm) for 50–70 h gave the ($4\pi + 2\sigma$) cycloadducts **3a** and **4a** in 85% yield.[5] The photoreaction

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[†] Present address: Department of Chemical Process Engineering, Faculty of Engineering, Hokkaido University, Sapporo 060, Japan.

(1) For recent reviews, see: (a) Mattes, S. L.; Farid, S. *Organic Photochemistry*; Padwa, A., Ed.; Marcel Decker Inc.: New York, 1983; Vol. 6, p 233. (b) Davidson, R. S. *Advances in Physical Organic Chemistry*; Gold, V., Bethell, D., Eds.; Academic Press: New York, 1983; Vol. 19, p 1. (c) Chanon, M. *Bull. Soc. Chim. Fr.* **1985**, 209. (d) Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401. (e) *Photo-induced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988, Part A–D and references cited therein.

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(3) (a) Mizuno, K.; Ichinose, N.; Otsuji, Y. *Chem. Lett.* **1985**, 455. (b) Mizuno, K.; Kamiyama, N.; Ichinose, N.; Otsuji, Y. *Tetrahedron* **1985**, *41*, 2207. Mizuno, K.; Kamiyama, N.; Otsuji, Y. *Chem. Lett.* **1983**, 477.

(4) Some of these results have been published in preliminary form: (a) Mizuno, K.; Hiromoto, Z.; Ohnishi, K.; Otsuji, Y. *Chem. Lett.* **1983**, 1059. (b) Ichinose, N.; Mizuno, K.; Hiromoto, Z.; Otsuji, Y. *Tetrahedron Lett.* **1986**, *27*, 5619. (c) See also ref 3a.

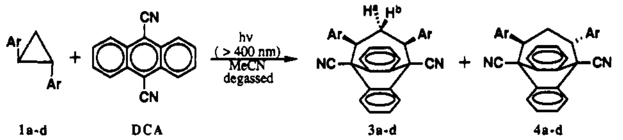
0022-3263/92/1957-1855$03.00/0

Table I. Photocycloaddition between 9,10-Dicyanoanthracene and 1,2-Diarylcyclopropanes in Acetonitrile

compd	total yield, %[a]	3:4[b]	ϕ_{DCA}[c]
1a	85	78:22	0.004
1b	58	*d*	0.002
2b	*d*	79:21	*d*
1c	87	76:24	0.04
2c	*d*	75:25	*d*
1d	90	*d*	0.02

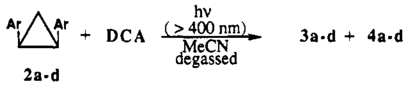
[a] Isolated yields of **3** and **4** obtained by irradiation of mixtures of DCA (0.5 mmol) and **1a–d** (0.5 mmol) with 405-nm light. [b] Determined by 270-MHz ^1H NMR. [c] Quantum yields for the disappearance of DCA determined by measuring the decrease in the absorbance at 420 nm; [DCA] = 2×10^{-4} mol dm^{-3}, [1] = 1×10^{-2} mol dm^{-3}. [d] Not determined.

of DCA with other 1,2-diarylcyclopropanes **1b–d** under similar conditions gave the cycloadducts **3b–d** and **4b–d**.[4b]



a ; Ar = 4-MeOC$_6$H$_4$, b ; Ar = 4-MeC$_6$H$_4$, c ; Ar = 4-ClC$_6$H$_4$, d ; Ar = C$_6$H$_5$

The products were isolated by column chromatography on silica gel, and their structures were established from their spectral properties and elemental analyses. The *cis*-diaryl configuration of **3a–d** was assigned from their ^1H NMR spectra.[6] The cycloadducts **3a–d** have two nonequivalent methylene protons, H_a and H_b, and the signals of H_b appeared at higher fields than those of H_a, whereas the cycloadducts **4a–d** showed triplet signals due to two equivalent methylene protons at δ 1.98 ± 0.01. The photoreaction of DCA with *cis*-1,2-diarylcyclopropanes **2a–d** also afforded **3a–d** and **4a–d**. The ratios of **3** to **4** obtained



from the cis isomers were identical with those obtained from the trans isomers **1a–d** and DCA within the experimental error. During irradiation, the geometrical photoisomerization **1** → **2** was observed. In the cases of **1a** and **2a**, the photoisomerization occurred slowly to give a photostationary mixture containing **1a** and **2a** in a ratio of 95:5. For **1b–d** and **2b–d**, the photoisomerization occurred only to a small extent (≤30%), and the photostationary states were not attained even after prolonged irradiation.[7]

Quantum yields for the formation of **3a–d** and **4a–d** from **1a–d** in degassed acetonitrile solutions were determined by measuring the decrease in absorbance of DCA at 420 nm at appropriate time intervals. The results are summarized in Table I.

This photocycloaddition did not occur in benzene, although the ($4\pi + 2\pi$) photocycloaddition of 1,2-diphenyl-3-(methoxycarbonyl)cyclopropene to DCA has been reported to occur in benzene.[5a] The addition of 1,4-diazabicyclo[2.2.2]octane (DABCO) or triethylamine (TEA) to the DCA–**1a** and DCA–**2a** systems completely quenched the formation of **3a** and **4a**.

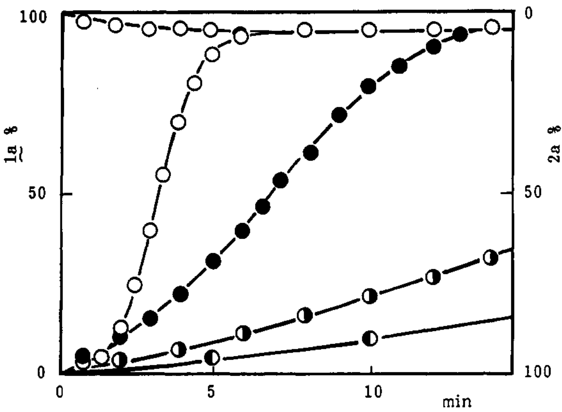


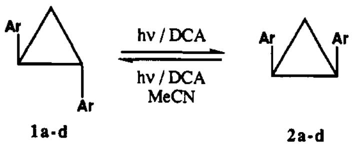
Figure 1. Plots of **1a** and **2a** (%) vs irradiation time. A mixture of DCA and **1a** or **2a** was irradiated in acetonitrile with 405-nm light. [DCA] = 5×10^{-4} mol dm^{-3}, [**1a**] = [**2a**] = 1×10^{-2} mol dm^{-3}. Key: (○) aerated solution, (●) O_2-saturated solution, (◑) N_2-saturated solution, (◐) degassed solution.

Table II. 9,10-Dicyanoanthracene-Sensitized Cis–Trans Isomerization of 1,2-Diarylcyclopropanes in Acetonitrile under Various Conditions

cyclopropane	atmosphere	$\phi_{2\to1}$[a]	$\phi_{1\to2}$[a]
1a–2a	degassed	0.01	
	N_2 saturated	0.03	
	aerated	0.28	0.015
	aerated	1.8[b]	0.1[b]
	O_2 saturated	0.13	
1b–2b	N_2 saturated	0.007	
1c–2c	N_2 saturated	0.001	
1d–2d	N_2 saturated	0.001	

[a] A 405-nm light was irradiated: [DCA] = 5×10^{-4} mol dm^{-3}, [1] = [2] = 1×10^{-2} mol dm^{-3}. [b] Limiting quantum yields obtained from the intercept of linear plots of $1/[\phi]$ vs $1/[1]$ or $1/[2]$.

DCA-Sensitized Cis–Trans Isomerization of 1,2-Diarylcyclopropanes. In contrast to the ($4\pi + 2\sigma$) photocycloaddition under degassed conditions, irradiation of an acetonitrile solution containing **1a** or **2a** and a catalytic amount of DCA under a nitrogen atmosphere afforded a photostationary mixture containing **1a** and **2a**.



This photoisomerization was sensitive to oxygen. In an aerated acetonitrile solution, the photoisomerization occurred more rapidly, giving the same photostationary state (Figure 1). However, under an oxygen atmosphere, the cyclopropanes were gradually consumed to give the oxygenated products, accompanying the rapid isomerization.[3] Under these conditions, no photocycloaddition occurred.

Quantum yields for the photoisomerization were determined under various conditions. The results are given in Table II. In some cases, limiting quantum yields for the reaction of **2a** to **1a** exceeded unity, suggesting that a chain process is involved in this photoisomerization. However, the photoisomerization of **2b–d** to **1b–d** occurred less efficiently under similar conditions (Table II).[7]

The photoisomerization of **1a** and **2a** hardly occurred (Φ < 0.01) in less polar solvents such as dichloromethane,

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(5) (a) Wensley, K. A. B.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1978**, *100*, 4162. (b) Mazzocchi, P. H.; Somich, C.; Edwards, M.; Morgan, T.; Ammon, H. L. *Ibid.* **1986**, *108*, 6828.

(6) The structure of **3d** was confirmed by the X-ray diffraction analysis of its single crystal by Dr. M. Yasuda and Prof. K. Shima at Miyazaki University and will be published in a separate paper. The authors are grateful to Dr. Yasuda and Prof. Shima for this X-ray diffraction study.

(7) Wong, P. C.; Arnold, D. R. *Tetrahedron Lett.* **1979**, 2101. Roth, H. D.; Schilling, M. L. *J. Am. Chem. Soc.* **1980**, *102*, 7958. Roth, H. D.; Schilling, M. L. *Ibid.* **1981**, *103*, 7210.

(8) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259.

Table III. Effect of Metal Salts on the Photoisomerization of 2a to 1a in Aerated Acetonitrile Solutions

additive	mol dm^{-3}	$\phi_{2a\to 1a}$^{a}
none		0.28 (0.01)^b
$KClO_4$	5.0×10^{-3}	2.3
$LiBF_4$	5.0×10^{-3}	2.9
	1.0×10^{-2}	4.7 (4.2)^b
Et_4NClO_4	5.0×10^{-3}	3.3
$NaClO_4$	5.0×10^{-3}	3.8
$LiClO_4$	5.0×10^{-3}	5.4
$Mg(ClO_4)_2$	2.5×10^{-3}	10.9

^{a} A 405-nm light was irradiated: [DCA] = 5×10^{-4} mol dm^{-3}, [**2a**] = 1×10^{-2} mol dm^{-3}. ^{b} Degassed solution.

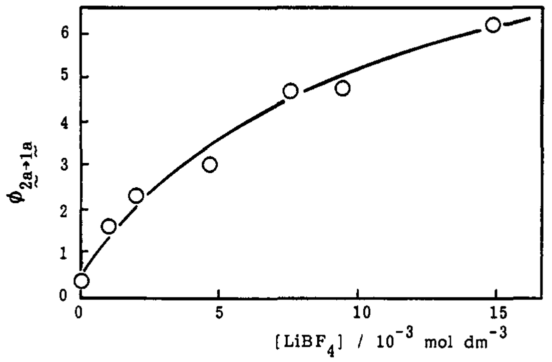
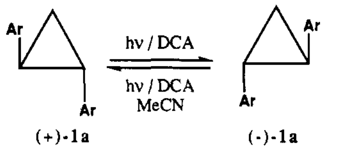


Figure 2. Plot of quantum yield ($\Phi_{2a\to 1a}$) vs the concentration of $LiBF_4$ in aerated acetonitrile solutions. A 405-nm light was irradiated. [DCA] = 5×10^{-4} mol dm^{-3}, [**2a**] = 1×10^{-2} mol dm^{-3}.

ethyl acetate, and benzene. This photoisomerization was completely quenched by the addition of DABCO or TEA.

The DCA-sensitized photoreaction of the optically resolved (−)-**1a** afforded a racemic mixture of (+)-**1a** and (−)-**1a** under similar reaction conditions with a quantum yield of $\Phi_{(-)\text{-}1a\to(+)\text{-}1a} = 0.006$. Similarly, the photoreaction of the optical isomer (+)-**1a** also gave the same racemic mixture.



Effect of Metal Salts. The addition of $LiBF_4$ into a degassed acetonitrile solution containing DCA and **2a** completely suppressed the ($4\pi + 2\sigma$) photocycloaddition between DCA and **2a** and instead caused the efficient cis–trans photoisomerization of **2a**, giving a photostationary mixture of **1a** and **2a** in a ratio of 95:5. The quantum yield for this photoisomerization ($\Phi_{2a\to 1a}$) became more than 10^2 times higher than that in the degassed solution in the absence of $LiBF_4$ (Table III). In the absence of $LiBF_4$, the quantum yield for the photoisomerization was strongly affected by oxygen. However, in the presence of $LiBF_4$, $\Phi_{2a\to 1a}$ was almost the same in degassed and aerated solutions, and it rather depended on the concentration of the added salts (Figure 2). The quantum yield for the photoisomerization was also enhanced by the addition of other metal salts such as $LiClO_4$ or $Mg(ClO_4)_2$ (Table III, Figure 3). In every case, the same photostationary state was obtained. However, the addition of LiCl and LiBr into the reaction system completely quenched the photoisomerization. The photoisomerization of (−)-**1a** to (+)-**1a** was also greatly enhanced by the addition of $Mg(ClO_4)_2$ (0.005 mol dm^{-3}); $\Phi_{(-)\text{-}1a\to(+)\text{-}1a} = 0.72$.

The photoisomerization of **2b,c** to **1b,c** under argon atmosphere was enhanced by a factor of 2–3 by the addition of $Mg(ClO_4)_2$ at the initial stage of the reaction. However, prolonged irradiation gave a complex mixture.

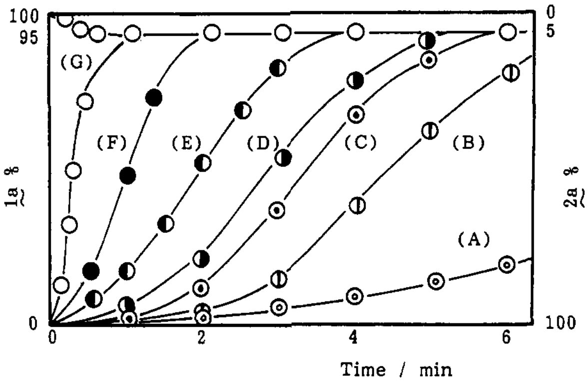


Figure 3. Plots of **1a** and **2a** (%) vs irradiation time in the presence of salts in aerated acetonitrile solutions. [DCA] = 5×10^{-4} mol dm^{-3}, [**1a**] = [**2a**] = 1×10^{-2} mol dm^{-3}, [M^+Z^-] = 5×10^{-3} mol dm^{-3}. Key: (A) (◎) none, (B) (○) $KClO_4$, (C) (⊙) $LiBF_4$, (D) (◑) Et_4NClO_4, (E) (◐) $NaClO_4$, (F) (●) $LiClO_4$, (G) (○) $Mg(ClO_4)_2$.

Table IV. Effect of Additives on the Photoisomerization of 1a and 2a in Acetonitrile[5]

atmosphere	additive	mol dm^{-3}	$\phi_{2a\to 1a}$^{a}	$\phi_{1a\to 2a}$^{a}
aerated	none		0.28 (1.8)^b	0.015 (0.10)^b
	Phen	1×10^{-2}	13.0 (31.3)^b	0.70 (1.10)^b
	Phen	1×10^{-1}		
	Naph	1×10^{-2}	12.5	
	BP	5×10^{-3}	5.6	
	DABCO	1×10^{-3}	0	0
	TEA	1×10^{-3}	0	0
degassed	none		0.01 (0.03)^b	
	Phen	1×10^{-2}	2.8	

^{a} A 405-nm light was irradiated: [DCA] = 5×10^{-4} mol dm^{-3}, [**1a**] = [**2a**] = 1×10^{-2} mol dm^{-3}. ^{b} Limiting quantum yield.

Effect of Aromatic Hydrocarbons.[9] Irradiation of a degassed acetonitrile solution containing DCA, **2a**, and phenanthrene (Phen) did not give the ($4\pi + 2\sigma$) cycloadducts **3a** and **4a**, but gave a photostationary mixture of **1a** and **2a** in a ratio of 95:5. The quantum yield for the photoisomerization in the presence of Phen was more than unity in the degassed solution (Table IV). The enhancement of the efficiency of the photoisomerization was also observed by the addition of naphthalene (Naph) or biphenyl (BP). The results are shown in Table IV. A notable observation in these cases was the effect of oxygen; the quantum yield in the aerated solution was much larger than that in the degassed solution in the presence of Phen.

Fluorescence Quenching and Redox Properties. The fluorescence of DCA was efficiently quenched by the cyclopropanes **1a–d** and **2a–c** in aerated acetonitrile and benzene. The rate constants, k_q, for the fluorescence quenching were calculated from the slope of the Stern–Volmer plots. Table V shows that the fluorescence was quenched at nearly diffusion controlled rates by cyclopropanes. Exciplex emission was not observed in both solvents. The fluorescence of DCA was also quenched by the hydrocarbons and amines, DABCO and TEA, at nearly diffusion controlled rates. However, metal salts did not quench the fluorescence of DCA. The fluorescence quenching rates of DCA by cyclopropanes remained also unchanged by the addition of metal salts.

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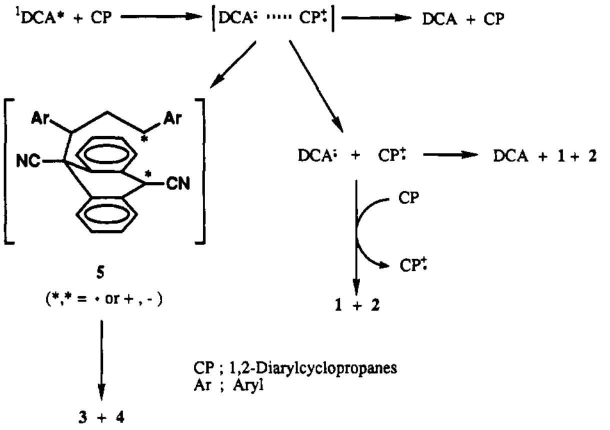
[9] (a) Pac, C. *Pure Appl. Chem.* **1986**, *58*, 1249. Majima, T.; Pac, C.; Sakurai, H. *J. Am. Chem. Soc.* **1980**, *102*, 5265; **1981**, *103*, 4499. (b) Steichen, D. S.; Foote, C. S. *Ibid.* **1981**, *103*, 1855. (c) Schaap, A. P.; Lopez, L.; Gagnon, S. D. *Ibid.* **1983**, *105*, 663. Schaap, A. P.; Siddiqui, S.; Gagnon, D.; Lopez, S. D. *Ibid.* **1983**, *105*, 5149.

Table V. Oxidation Potentials, Calculated ΔG Values for the One-Electron Transfer Process from Electron-Donating Compounds to ^{1}DCA* in Acetonitrile, and Rate Constants for the Fluorescence Quenching of DCA

compd	$E^{ox}_{p/2}$, V^a	ΔG, kJ mol$^{-1\,b}$	k_q, mol^{-1} dm^3 s$^{-1\,c}$
1a	0.55	−103.2	1.8×10^{10}
2a	0.65	−93.6	1.7×10^{10}
1b	0.90	−69.5	1.6×10^{10}
2b			
1c	1.06	−54.0	1.4×10^{10}
2c			
1d	1.14	−46.3	1.4×10^{10}
2d			
Phen	1.17^d	−43.4	1.7×10^{10}
BP	1.45	−34.4	4.6×10^{9}
DABCO	0.31	−126.4	2.8×10^{10}
TEA	0.48	−110.0	2.3×10^{10}

^{a} Oxidation potentials (half-peak potentials) obtained by cyclic voltammetry. ^{b} Calculated free energy changes for the one-electron transfer process from the compounds to ^{1}DCA* in acetonitrile by the application of the Rehm–Weller equation: the excited singlet energy of DCA, 278.86 kJ mol^{-3}; the energy of Coulomb force, 5.79 kJ mol^{-3}, and reduction potential of DCA, −1.33 V.[8,19] ^{c} Rate constant for fluorescence quenching calculated from the Stern–Volmer plots in aerated acetonitrile solutions. τ(DCA, air) = τ(DCA, N_2) × I(DCA, air)/I(DCA, N_2) = 12.8 ns. [τ(DCA, N_2) = 15.3 ns].[19] ^{d} The value from ref 9a.

Scheme II



The free energy changes (ΔG) for a one-electron transfer from electron-donating compounds to the excited singlet DCA (^{1}DCA*) were estimated by the Rehm–Weller equation.[8] The results are shown in Table V. Negative ΔG values were obtained in all cases.

Mechanism

From the results of the fluorescence quenching of ^{1}DCA* by cyclopropanes (CP) and the calculated ΔG values for a one-electron transfer from CP to ^{1}DCA*, it is almost certain that in the DCA–CP systems, the radical ion pairs [$CP^{+\bullet}$···$DCA^{-\bullet}$] are produced upon excitation of DCA in acetonitrile. We now propose the mechanisms shown in Scheme II for the photocycloaddition of CP to DCA and the photoisomerization of CP. An important feature of the present mechanism is that the photocycloaddition proceeds via the radical ion pairs [$CP^{+\bullet}$···$DCA^{-\bullet}$] in solvent cage and the photoisomerization via the solvent-separated radical cations $CP^{+\bullet}$. We will discuss the reactivity features of these reactive species in both photoreactions.

Photocycloaddition. The photocycloaddition of CP to DCA occurred only in degassed acetonitrile solutions in the absence of any additive and did not occur in benzene. In addition, the quantum yields for this photoreaction were generally low (Φ ≤ 0.04). These results can be explained if the reactive species of the photocycloaddition is assumed to be the radical ion pairs in solvent cage and they would decay relatively efficiently to the ground states of their components by a back-electron transfer within the radical ion pairs. This assumption was also supported by the fact that the photocycloaddition was completely quenched by the addition of amines having low oxidation potentials and also by other additives. However, a question arises about the quenching ability of amines toward the photocycloaddition.[10] The photoreaction was completely quenched by a low concentration of amines (10^{-4} mol/dm^3). This indicates that the reactive species should have a long lifetime (≥10^{-6} s). A possible candidate for such long-lived species is 1,7-dipolar or 1,7-biradical species (5 in Scheme II) that are formed by a coupling between $DCA^{-\bullet}$ and $CP^{+\bullet}$, although the possibility of the former is higher than that of the latter; these species might be quenched by air and amines. Another possibility is the formation of ^{3}DCA* via a back-electron transfer from $DCA^{-\bullet}$ to $CP^{+\bullet}$ within the radical ion pairs. However, the possibility that ^{3}DCA* participates as a real reactive species in the photocycloaddition is low, because ^{3}DCA* seems not to have enough reactivity to undergo the cycloaddition with CP.

The coupling of $CP^{+\bullet}$ with $DCA^{-\bullet}$ occurs in a stepwise manner and would give the dipolar ions or biradical intermediates 5 which cyclize to form the stereoisomers 3 and 4.

Effects of Additives on the Fate of the Radical Ion Pairs. The photocycloaddition was completely quenched by the addition of oxygen, aromatic hydrocarbons (ArH) such as Naph and Phen, and some metal salts (M^+X^-), while the DCA-sensitized isomerization of CP was remarkably accelerated by the addition of these additives. This result can be accounted for by assuming that the addition of these additives facilitates the dissociation of the radical ion pairs [$CP^{+\bullet}$···$DCA^{-\bullet}$] to the solvent-separated radical ions $CP^{+\bullet}$ and $DCA^{-\bullet}$ (Scheme I).

A plausible mechanistic explanation of the additive effects is given in Scheme III.

Scheme III^a

$$[CP^{+\bullet}\cdots DCA^{-\bullet}] + O_2 \longrightarrow CP^{+\bullet} + DCA + O_2^{-\bullet} \quad (1)$$

$$[CP^{+\bullet}\cdots DCA^{-\bullet}] + ArH \longrightarrow [CP\cdots ArH]^{+\bullet} + DCA^{-\bullet} \quad (2)$$

$$[CP^{+\bullet}\cdots DCA^{-\bullet}] + M^+Z^- \longrightarrow CP^{+\bullet}Z^- + M^+DCA^{-\bullet} \quad (3)$$

^{a} ArH, aromatic hydrocarbon; M^+Z^-, metal salt.

Foote et al. have shown that the electron-transfer from $DCA^{-\bullet}$ to O_2 is exothermic by 2.9 kJ mol^{-1}.[11] Thus, $DCA^{-\bullet}$ is converted to DCA and $O_2^{-\bullet}$ in the presence of O_2. This interaction would suppress the back-electron transfer within the radical ion pairs and is likely to enhance the generation of the solvent-separated $CP^{+\bullet}$ (eq 1).

The fluorescence quenching rates of ^{1}DCA* by ArH and the negative ΔG values for the electron transfer from ArH to ^{1}DCA* suggest that there are two competing electron-transfer processes that occur in the DCA-sensitized photoreactions of CP in the presence of ArH: (i) CP + ^{1}DCA* → [$CP^{+\bullet}$···$DCA^{-\bullet}$] and (ii) ArH + ^{1}DCA* → [$ArH^{+\bullet}$···$DCA^{-\bullet}$]. The hole-transfer process, $ArH^{+\bullet}$ + CP → ArH + $CP^{+\bullet}$, is also possible, since the oxidation potentials of CP are lower than those of ArH. In addition to this hole-transfer process, the interaction between [$CP^{+\bullet}$···

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[10] The authors are indebted to Dr. S. Fukuzumi (Osaka University), Prof. T. Miyashi, and Dr. Y. Takahashi (Tohoku University) for helpful discussions on this point.

[11] Spada, L. T.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 391. Eriksen, J.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 6083.

$DCA^{-\bullet}$] and ArH may force the separation of [$CP^{+\bullet}\cdots DCA^{-\bullet}$] and enhance the generation of the solvent-separated $CP^{+\bullet}$, probably through a π-interaction between $CP^{+\bullet}$ and ArH in a manner similar to that proposed by Pac et al. (eq 2).[9a]

The effect of added metal salts on the DCA-sensitized photoisomerization was especially remarkable.[3,4,12] The fluorescence of DCA was not quenched by the addition of nonpolarizable, nonnucleophilic metal salts such as $Mg(ClO_4)_2$ and $LiBF_4$, and the rate constants for the fluorescence quenching remained unchanged by the addition of these metal salts. In contrast, the addition of polarizable metal salts such as LiBr not only quenched the fluorescence of DCA but also lowered the efficiency of the photoisomerization of CP. Therefore, the most plausible explanation for the added nonpolarizable metal salts is that the metal salts facilitate the dissociation of the radical ion pairs to the solvent-separated radical ions through a Coulombic interaction between [$CP^{+\bullet}\cdots DCA^{-\bullet}$] and metal salts (eq 3). The polarizable metal salts probably quench $CP^{+\bullet}$ via an electron-transfer process: $CP^{+\bullet} + Br^- \rightarrow CP + Br^\bullet$. Schuster et al. reported that the lifetime of some radical ions were lengthened by the addition of $Mg(ClO_4)_2$.[12a]

Photoisomerization. The DCA-sensitized photoisomerization of CP was completely quenched by the addition of amines such as TEA and DABCO which have low oxidation potentials. However, the striking feature of this photoreaction is that a chain process is involved in the DCA-sensitized photoisomerization of **2a** to **1a**: the quantum yield of this photoreaction largely exceeded unity, especially in the presence of nonpolarizable metal salts and aromatic hydrocarbons. In this case, the chain carrier is the solvent-separated ring-opened $\mathbf{2a}^{+\bullet}$ and the electron transfer from the neutral **2a** to the ring-opened $\mathbf{2a}^{+\bullet}$ occurs exothermically.[9a,13-16] For less-electron-rich cyclopropanes such as *cis*- and *trans*-1,2-diphenylcyclopropanes, the photoisomerization occurs slowly.[7] In these cases, 1,3-biradicals that can be produced by a back-electron transfer from $DCA^{-\bullet}$ to ring-opened $CP^{+\bullet}$ may be involved as reactive intermediates.

Conclusion

In the present work, the photoinduced electron-transfer reactions of 9,10-dicyanoanthracene (DCA) and 1,2-diarylcyclopropane systems have been described. It has been demonstrated that the $(4\pi + 2\sigma)$ photocycloaddition between DCA and the cyclopropanes occurs via the radical ion pairs in solvent cage and the cis–trans photoisomerization of the cyclopropanes occurs via their solvent-separated radical cations. The former reaction was completely quenched by the addition of some additives such as oxygen, metal salts, and aromatic hydrocarbons. On the other hand, the latter reaction was accelerated by the addition of these additives, involving a chain process in some cases.

We have also demonstrated that *the reactivity features of the radical ion pairs in solvent cage and the solvent-separated radical ions can be differentiated by the additives, especially metal salts.*

Experimental Section

General. Melting points were taken on a hot stage and are uncorrected. ^{1}H-NMR spectra were recorded on JEOL JNM-PMX60SI (60 MHz) and JEOL JNM-GX270 (270 MHz) spectrophotometers for solutions in $CDCl_3$ using tetramethylsilane as an internal standard. ^{13}C-NMR spectra were recorded on a JEOL JNM-GX270 (67 MHz) spectrophotometer for solutions in $CDCl_3$ with tetramethylsilane (δ 0.00) and chloroform (δ 77.05) as internal standards. Infrared spectra were obtained on a JASCO FT/IR5000 spectrophotometer, mass spectra on a Shimadzu LKB9000 spectrophotometer, and fluorescence spectra on JASCO FP-770 spectrophotometer. Elemental analyses were carried out on a Yanaco MT-3 elemental analyzer. GLC analyses were performed with Hitachi 163 and 164 instruments, using a 1-m × 3-mm glass column packed with 10% SE-30 on Shimalite W. HPLC analyses were carried out by using a JASCO BIP-1 pump and a JASCO UVIDEC-100-V UV spectrophotometer with a Chromatoscience Nucleosil 5018 column (i.d. 4.6 mm × 150 mm and 4.6 mm × 250 mm) and Daicel Chiralcel OB-L as an optically active column. UV/vis spectra were taken on a Hitachi 124 or a JASCO 660 spectrophotometer. Oxidation and reduction potentials were measured in argon-saturated dry acetonitrile solutions at 20 ± 0.1 °C by cyclic voltammetry, using a NICHIA NP-G 2550 potentiostat and Ag/Ag^+ reference electrode. Tetraethylammonium perchlorate (0.1 mol dm^{-3}) was used as a supporting electrolyte.

Eikosha PIH-300 300 W and PIH-500 500 W high pressure mercury lamps were used as light sources. An aqueous $CuSO_4$ (0.176 mol dm^{-3})–NH_3 (2.7 mol dm^{-3}) filter solution was used to obtain ≥400-nm light.

Quantum yields were determined by the procedure of Murov,[17] using a potassium ferrioxalate actinometer. The light source was a 300-W or a 500-W high-pressure Hg lamp and the 405-nm Hg line was isolated through an aqueous NH_3–$CuSO_4$ filter solution, a Toshiba UV-39 glass filter, and a KL-40 interference filter. The intensity was determined twice before and once after actual photoreactions. No change in light intensity was observed during experiments. For the quantum yield determination, photoreactions were carried out in a quartz cell up to 30–70% conversion of the starting materials. The reaction mixtures were analyzed by ^{1}H NMR, GLC, HPLC, and/or TLC. The quantum yields were estimated from the slope of linear parts of plots in time course conversion.

Materials. Acetonitrile was distilled three times over P_2O_5 and once over anhydrous K_2CO_3 before use. 1,2-Diarylcyclopropane derivatives **1a–d** and **2a–d** were synthesized according

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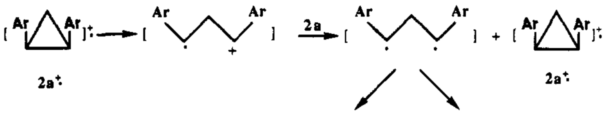
(12) (a) Goodson, B.; Schuster, G. B. *Tetrahedron Lett.* **1986**, *27*, 3123. (b) The enhancement of the efficiency by the addition of salts was reported in the other systems by several groups: Evans, T. R.; Wake, R. W.; Sifan, M. M. *Ibid.* **1973**, 701. Mizuno, K.; Ichinose, N.; Tamai, T.; Otsuji, Y. *Ibid.* **1986**, *26*, 5823. Lewis, F. D.; Petsce, J. R.; Oxman, J. D.; Nepras, M. *J. Am. Chem. Soc.* **1985**, *107*, 203. Saito, I.; Ikehira, H.; Kasatani, R.; Watanabe, M.; Matsuura, T. *Ibid.* **1986**, *108*, 3115. Pac, C.; Fukunaga, T.; Go-an, Y.; Sakae, T.; Yanagida, S. *Photochem. Photobiol.* **1987**, *47*, 37. Mattay, J.; Trampe, G.; Runsink, J. *Chem. Ber.* **1988**, *121*, 1991. Mizuno, K.; Nakanishi, K.; Otsuji, Y. *Chem. Lett.* **1988**, 1833. Shim, S. C.; Lee, H. J. *J. Photochem. Photobiol., A* **1989**, *46*, 59. Tamai, T.; Mizuno, K.; Hashida, I.; Otsuji, Y. *Photochem. Photobiol.* **1991**, *54*, 23. See also reviews: Pac, C.; Ishitani, O. *Ibid.* **1988**, *48*, 767. Santamaria, J., ref 1e, part B, p 483 and references cited therein.

(13) The catalytic chain process for the isomerization of **2a** to **1a** via radical cation was supported by chemical and electrochemical methods. For example, the catalytic isomerization of **2a**, giving a stationary mixture of **1a** and **2a** in a 95:5 ratio, was observed in the presence of $Cu(BF_4)_2$ or $NOBF_4$ in dry acetonitrile. Mizuno, K.; Ichinose, N.; Otsuji, Y. Unpublished results.

(14) Dinnocenzo, J. D.; Schmittel, M. *J. Am. Chem. Soc.* **1987**, *109*, 1561 and references cited therein.

(15) Previously, we have observed that the different radical cation species, the ring-closed and ring-opened radical cation species, are generated from both **1a** and **2a** by their γ-radiolyses at low temperatures and their pulse-radiolyses at room temperature.[16] These species have different reduction potentials and the ring-opened radical cations generated from **2a** serves as a chain carrier in the DCA-sensitized photoisomerization of **2a** via the following pathway:



Ar = 4-MeOC$_6$H$_4$

(16) Toki, S.; Komitsu, S.; Tojo, S.; Takamuku, S.; Ichinose, S.; Mizuno, K.; Otsuji, Y. *Chem. Lett.* **1988**, 433.

(17) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; pp 95 and 119.

to literature methods.[18] Other organic chemicals were purchased and purified by distillation or recrystallization. Inorganic chemicals were also purchased and used without further purification.

Optical active **1a**, (+)-**1a** and (−)-**1a**, were obtained by resolution of racemic **1a** with HPLC using an optically active column (Chiralcel OB, i.d. 250 mm × 4.6 mm). They were purified by repeated recrystallization. (+)-**1a**: mp 92.5–93.5 °C; $[\alpha]_D$ (25 °C, MeOH) 374.4 ± 3.0°. (−)-**1a**: mp 92.0–93.0 °C; $[\alpha]_D$ (25 °C, MeOH) −389.4 ± 2.1°.

Photocycloaddition between 9,10-Dicyanoanthracene (DCA) and 1,2-Diarylcyclopropanes. An acetonitrile solution (8 cm^3) containing **1a** (0.5 mmol) and DCA (0.5 mmol) was degassed by three freeze–pump–thaw cycles (1.3 × 10^{-2} Pa) and sealed in a Pyrex tube (i.d. 10 mm). The sample solution was irradiated with a 500-W high-pressure mercury lamp through an aqueous $CuSO_4$–NH_3 solution filter (≥400 nm) for 60 h. During irradiation, the sample tube was often shaken to dissolve unreacted DCA. After irradiation, unreacted DCA was filtered off and the solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel. From benzene eluent, a mixture of two isomeric photocycloadducts **3a** and **4a** was obtained in 85% yield. Pure **3a** was obtained by repeated recrystallization of the mixture from methanol. The isomer **4a**, which contained a small amount of **3a**, was obtained from the mother liquor as a solid. Similarly, the photocycloadducts **3b–d** and **4b–d** were obtained by the photoreaction of DCA with **1b–d**.

The ratios of **3** to **4** were determined by integration of the characteristic signals (δ 3.18 and 3.54) of **3** and **4** in ^{1}H NMR spectra of the irradiated reaction mixtures.

The quantum yields for the photocycloaddition were determined from the change in absorbance of DCA at 420 nm.

Physical Properties of Photocycloadducts. 6,7:8,9-Dibenzo-1,5-dicyano-*cis*-2,4-bis(4-methoxyphenyl)bicyclo[3.2.2]nona-6,8-diene (3a): mp 239.5–241.0 °C (MeOH); ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.78 (dt, 1 H, *J* = 8.2 and 15.0 Hz), 1.88 (dt, 1 H, *J* = 4.3 and 15.0 Hz), 3.18 (dd, 2 H, *J* = 4.3 and 8.2 Hz), 3.80 (s, 6 H), 6.92 (AB q, 8 H, $\Delta\nu$ = 30.0 Hz, *J* = 8.8 Hz), 7.48 (dd, 2 H, *J* = 3.1 and 5.5 Hz), 7.61 (dd, 2 H, *J* = 3.1 and 5.5 Hz), 7.80 (dd, 2 H, *J* = 3.1 and 5.5 Hz), 7.95 (dd, 2 H, *J* = 3.1 and 5.5 Hz); ^{13}C NMR δ 38.7, 50.6, 54.0, 55.3, 114.2, 118.6, 124.8, 127.2, 128.8, 128.9, 129.1, 132.5, 134.0, 137.3, 159.5; MS (70 eV) *m/z* 482 (M$^+$), 254, 228; IR (KBr) 2248 cm^{-1} (CN). Anal. Calcd for $C_{33}H_{26}O_2N_2\cdot{}^1/_2CH_3OH$: C, 80.70; H, 5.66; N, 5.62. Found: C, 80.26; H, 5.78; N, 5.69.

6,7:8,9-Dibenzo-1,5-dicyano-*trans*-2,4-bis(4-methoxyphenyl)bicyclo[3.2.2]nona-6,8-diene (4a): ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.98 (t, 2 H, *J* = 6.7 Hz), 3.54 (t, 2 H), 3.78 (s, 6 H), 6.81 (AB q, 8 H, $\Delta\nu$ = 19.1 Hz, *J* = 8.9 Hz), 7.39 (m, 4 H), 7.53 (dt, 2 H, *J* = 2.0 and 6.2 Hz), 8.02 (d, 2 H, *J* = 6.9 Hz); ^{13}C NMR δ 36.3, 48.2, 53.7, 55.2, 113.8, 119.1, 125.0, 127.6, 128.8, 129.2, 129.3, 132.4, 132.7, 136.0, 159.3.

6,7:8,9-Dibenzo-1,5-dicyano-*cis*-2,4-bis(4-methylphenyl)bicyclo[3.2.2]nona-6,8-diene (3b): mp 237.5–238.5 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.81 (dt, 1 H, *J* = 11.9 and 14.4 Hz), 1.90 (dt, 1 H, *J* = 4.8 and 14.4 Hz), 2.33 (s, 6 H), 3.18 (dd, 2 H, *J* = 4.8 and 11.9 Hz), 7.04 (AB q, 8 H, $\Delta\nu$ = 49.4 Hz, *J* = 7.9 Hz), 7.48 (dd, 2 H, *J* = 3.2 and 5.6 Hz), 7.61 (dd, 2 H, *J* = 3.6 and 5.6 Hz), 7.80 (dd, 2 H, *J* = 3.6 and 5.6 Hz), 7.95 (dd, 2 H, *J* = 3.2 and 5.6 Hz); ^{13}C NMR δ 21.2, 38.5, 50.9, 53.8, 118.6, 124.9, 127.2, 127.7, 128.9, 129.1, 129.6, 132.6, 137.4, 138.0, 138.9; MS (70 eV) *m/z* 450 (M$^+$), 228, 222; IR (KBr) 2248 cm^{-1} (CN). Anal. Calcd for $C_{33}H_{26}N_2$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.60; H, 5.79; N, 6.23.

6,7:8,9-Dibenzo-1,5-dicyano-*trans*-2,4-bis(4-methylphenyl)bicyclo[3.2.2]nona-6,8-diene (4b): ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.99 (t, 2 H, *J* = 6.7 Hz), 2.31 (s, 6 H), 3.56 (t, 2 H), 6.93 (AB q, 8 H, $\Delta\nu$ = 66.2 Hz, *J* = 8.2 Hz), 7.38 (m, 4 H), 7.52 (dt, 2 H, *J* = 1.8 and 6.4 Hz), 8.02 (d, 2 H, *J* = 7.9 Hz); ^{13}C NMR δ 21.1, 36.1, 48.5, 53.5, 119.1, 125.0, 126.1, 128.3, 129.2, 129.3, 129.8, 132.4, 136.0, 137.6, 137.8.

6,7:8,9-Dibenzo-1,5-dicyano-*cis*-2,4-bis(4-chlorophenyl)bicyclo[3.2.2]nona-6,8-diene (3c): mp 267–269 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.74 (dt, 1 H, *J* = 12.6 and 15.3 Hz), 1.91 (dt, 1 H, *J* = 4.2 and 15.3 Hz), 3.22 (dd, 2 H, *J* = 4.2 and 12.6 Hz), 7.15 (AB q, 8 H, $\Delta\nu$ = 86.0 Hz, *J* = 8.5 Hz), 7.50 (dd, 2 H, *J* = 3.3 and 5.8 Hz), 7.64 (dd, 2 H, *J* = 3.3 and 5.8 Hz), 7.80 (dd, 2 H, *J* = 3.3 and 5.8 Hz), 7.95 (dd, 2 H, *J* = 3.3 and 5.8 Hz); ^{13}C NMR δ 38.3, 50.5, 53.5, 118.2, 124.9, 127.2, 129.1, 129.2, 129.3, 129.4, 132.3, 134.4, 137.0, 140.0; MS (70 eV) *m/z* 492, 490 (M$^+$), 264, 262, 228; IR (KBr) 2248 cm^{-1} (CN). Anal. Calcd for $C_{31}H_{20}N_2Cl_2$: C, 75.76; H, 4.10; N, 5.70. Found: C, 76.26; H, 3.85; N, 5.29.

6,7:8,9-Dibenzo-1,5-dicyano-*trans*-2,4-bis(4-chlorophenyl)bicyclo[3.2.2]nona-6,8-diene (4c): ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.98 (t, 2 H, *J* = 6.7 Hz), 3.56 (t, 2 H), 7.04 (AB q, 8 H, $\Delta\nu$ = 104.3 Hz, *J* = 8.5 Hz), 7.42 (m, 4 H), 7.57 (dt, 2 H, *J* = 1.6 and 3.8 Hz), 8.03 (d, 2 H, *J* = 7.6 Hz); ^{13}C NMR δ 35.7, 48.1, 53.2, 118.7, 125.2, 127.6, 128.7, 129.6, 129.7, 131.9, 134.2, 135.6, 138.7; *m/z* 492, 490 (M$^+$), 264, 262, 228.

6,7:8,9-Dibenzo-1,5-dicyano-*cis*-2,4-diphenylbicyclo[3.2.2]nona-6,8-diene (3d): mp 235–240 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.84 (dt, 1 H, *J* = 9.9 and 15.0 Hz), 1.94 (dt, 1 H, *J* = 4.1 and 15.0 Hz), 3.23 (dd, 2 H, *J* = 4.1 and 9.9 Hz), 7.08 (m, 4 H), 7.33 (m, 6 H), 7.49 (dd, 2 H, *J* = 3.4 and 5.5 Hz), 7.63 (dd, 2 H, *J* = 3.4 and 5.5 Hz), 7.83 (dd, 2 H, *J* = 3.4 and 5.5 Hz), 7.97 (dd, 2 H, *J* = 3.4 and 5.5 Hz); ^{13}C NMR δ 38.5, 51.2, 53.7, 118.4, 124.9, 127.3, 127.8, 128.4, 128.9, 129.0, 129.1, 132.6, 137.4, 141.8; MS (70 eV) *m/z* 422 (M$^+$), 228, 194; IR (KBr) 2248 cm^{-1} (CN). Anal. Calcd for $C_{31}H_{22}N_2$: C, 88.12; H, 5.25; N, 6.63. Found: C; 88.03, H; 5.05, N; 6.30.

6,7:8,9-Dibenzo-1,5-dicyano-*trans*-2,4-diphenylbicyclo[3.2.2]nona-6,8-diene (4d): mp 228.5–230.0 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.05 (t, 2 H, *J* = 6.7 Hz), 3.61 (t, 2 H), 6.94 (m, 4 H), 7.27 (m, 6 H), 7.40 (m, 4 H), 7.54 (dt, 2 H, *J* = 1.8 and 6.4 Hz), 8.04 (d, 2 H, *J* = 7.3 Hz); ^{13}C NMR δ 35.9, 48.8, 53.4, 119.0, 125.0, 127.6, 128.1, 128.4, 128.5, 128.5, 129.4, 132.3, 136.0, 140.5; MS (70 eV) *m/z* 422 (M$^+$), 228, 194; IR (KBr) 2248 cm^{-1} (CN). Anal. Calcd for $C_{31}H_{22}N_2$: C, 88.12; H, 5.25; N, 6.63. Found: C; 88.26, H; 5.54, N; 6.32.

DCA-Sensitized Photoisomerization of 1 and 2: General Procedure. An acetonitrile solution (4 cm^3) containing **2a** and DCA ([**2a**] = 1 × 10^{-2} mol dm^{-3}, [DCA] = 4 × 10^{-4} mol dm^{-3}) was irradiated with 405-nm light in a Pyrex tube (i.d. 10 mm) under various atmospheres. The progress of the reaction was followed by the GLC analysis of the reaction mixture. The photoreaction of (+)-**1a** and (−)-**1a** was monitored with the HPLC. The photoisomerization of **2a** to **1a** in an aerated acetonitrile solution in the absence of additive was used as a reference for the quantum yield determination of the photoisomerization in the presence of additives.

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