Photochemical Reactions of Aromatic Compounds. XLII.[1] Photosensitized Reactions of Some Selected Diarylcyclobutanes by Aromatic Nitriles and Chloranil. Implications of Charge-Transfer Contributions on Exciplex Reactivities

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Photosensitized reactions of *cis*- and *trans*-1,2-diphenylcyclobutane and *cis-transoid-cis*-cyclobuta[1,2-*a*:4,3-*a'*]diindene by 1-cyanonaphthalene, 9,10-dicyanoanthrancene, 1,4-dicyanonaphthalene, and chloranil, which mainly give the ring-splitting product (styrene or indene), have been investigated to explore steric and electronic requirements of the reactions associated with charge-transfer and excitation-resonance contributions of exciplex intermediates. The reaction efficiencies increase with an increase in the electron-accepting power of the sensitizers irrespective of the spin states. The formation of 1-phenyltetralin in the photosensitized reactions of the diphenylcyclobutanes occurs from the polar singlet exciplex with the dicyanoarenes but not at all from the less polar exciplex with 1-cyanonaphthalene nor from the triplet chloranil exciplex of high charge-transfer nature. Exciplex reactivities are discussed in terms of roles of charge-transfer contributions in exciplex decay channels as well as in terms of configurational and conformational effects on orbital interactions in the cyclobutanes.

Splitting of the cyclobutane ring is a typical prototype for theoretical predictions of chemical reaction courses.[2] More importantly this reaction can provide an excellent probe to explore chemical and dynamic behaviors of reactive states and/or intermediates as well as to manifest steric and electronic factors operating reaction courses.[1,3—12] Recently we reported the redox-photosensitized ring-splitting reactions of some diarylcyclobutanes,[7a—c] a novel type of photosensitization that is initiated by photochemical electron transfer from an aromatic hydrocarbon (ArH) to an electron acceptor, typically *p*-dicyanobenzene (DCNB).[7a—c,13] A key mechanistic pathway is the formation of a π complex between a cyclobutane (CB) and the cation radical of ArH, by which a positive charge is populated on CB to effect the cleavage of the cyclobutane ring in cases where the both ends of a ring sigma bond bear π or *n*-electron systems as substituents.

$$\mathrm{ArH}+\mathrm{DCNB} \xrightarrow{h\nu} {}^1\mathrm{ArH}^*+\mathrm{DCNB} \longrightarrow \mathrm{ArH}^{+\cdot}+\mathrm{DCNB}^{-\cdot}$$

$$\mathrm{ArH}^{+\cdot}+\mathrm{CB} \longrightarrow [\mathrm{ArH}\cdot\mathrm{CB}]^{+\cdot} \longrightarrow \mathrm{ArH}^{+\cdot}+\mathrm{Products}$$

Likewise the population of a positive charge on CB can be achieved by the exciplex formation with an electron-accepting molecule, thus resulting in a ring-splitting reaction of CB depending on charge-transfer (CT) contributions.[7d,8c] Since exciplexes are electronically excited species unlike the π complexes, however, chemical behaviors should be different between them. In other words exciplex decays are associated with exciplex reactivities that may be controlled by electronic properties of exciplexes, i.e., CT and excitation-resonance (ER) contributions, as has been discussed for the exciplex isomerization of quadricyclane to norbornadiene.[11—12a]

$$\mathrm{S}+\mathrm{CB} \xrightarrow{h\nu} \mathrm{S}^*+\mathrm{CB} \longrightarrow [\mathrm{S}\cdot\mathrm{CB}]^* \longrightarrow \mathrm{S}+\mathrm{Products}$$

(S = electron acceptors and CB = cyclobutanes.)

$$[\mathrm{S}\cdot\mathrm{CB}]^* \equiv \mathrm{S}^*\mathrm{CB} \longleftrightarrow \mathrm{S}\cdot\mathrm{CB}^* \longleftrightarrow \mathrm{S}^-\mathrm{CB}^+ \qquad (1)$$

Table 1. Excitation Energies and Reduction Potentials of the Sensitizers

S[a]	τ[b]/ns	E^*[c]/eV	$-E_{1/2}^{\mathrm{red}}$[d]/V	E^*_{red}[e]/V
CNN	12.3	3.75[f]	2.33	1.42
DCN	10.5	3.45[f]	1.05	2.40
DCA	12.4	2.88[f]	1.12	1.76
CHL		2.83[g]	0.28	2.55

a) CNN=1-cyanonaphthalene, DCN=1,4-dicyanonaphthalene, DCA=9,10-dicyanoanthracene, and CHL=chloranil. b) Fluorescence lifetimes. c) Excitation energies of the excited-singlet aromatic nitriles and triplet chloranil. d) Half-wave reduction potentials vs. Ag/AgNO$_3$ in acetonitrile. e) Reduction potentials of the excited states calculated from E^* plus $E_{1/2}^{\mathrm{red}}$. f) S. L. Mattes and S. Farid, *Org. Photochem.*, **6**, 233 (1983). g) M. Kasha, *Chem. Rev.*, **47**, 401 (1947).

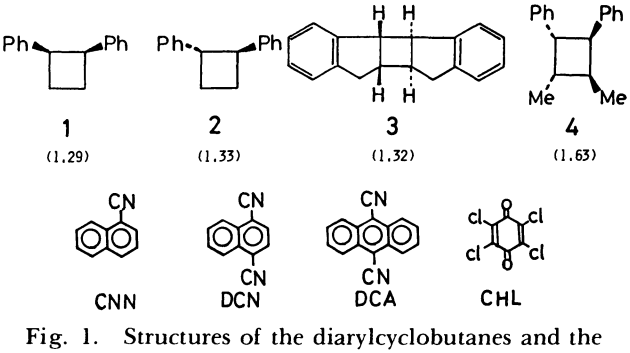
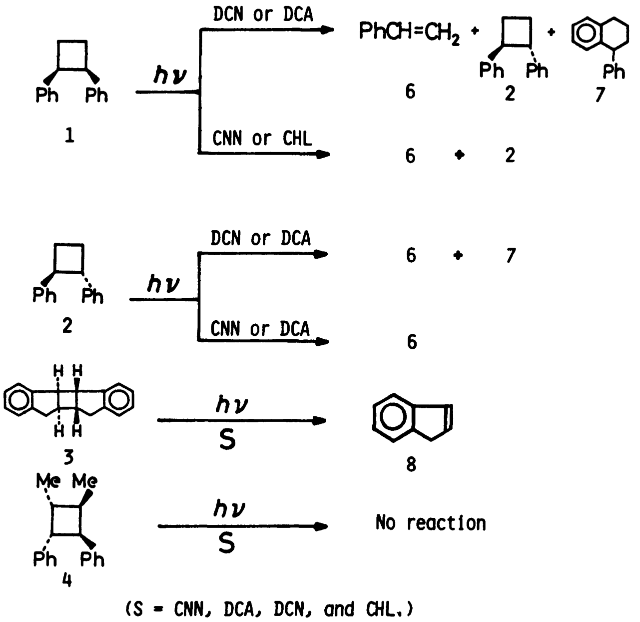


Fig. 1. Structures of the diarylcyclobutanes and the sensitizers. In parentheses are oxidation potentials of the cyclobutanes vs. Ag/Ag$^+$ in acetonitrile.

From this point of view, we attempted photosensitized reactions of some diarylcyclobutanes (CB; **1**—**4**) by 1-cyanonaphthalene (CNN), 1,4-dicyanonaphthalene (DCN), 9,10-dicyanoanthracene (DCA), and chloranil (CHL); these sensitizers (S) are typical electron acceptors which have different excitation energies (E^*) and reduction potentials in the ground and excited states ($E_{1/2}^{\mathrm{red}}$ and E^*_{red}) (Table 1). Figure 1 shows the structures of S and CB together with the observed oxidation potentials of CB. Major aims of the present investigation are focussed on (1) relative importance of CT and ER contributions of putative exciplex intermediates in bond-cleavage reactions of CB, (2) spin effects on the photoreactions, and (3) relationships of reactivities with structures of CB in the exciplex chemistry.

Results

Photoproducts. Photoreactions were carried out by irradiation of benzene solution at 313 nm for the CNN and DCN runs or at 366 nm for the DCA and CHL runs, and the progress of the photoreactions was followed by gas chromatography. The photoproducts are shown in Scheme 1.



(S = CNN, DCA, DCN, and CHL.)

Scheme 1.

Styrene (**6**) was mainly formed by the photosensitized reactions of either **1** or **2**. All the photosensitizers (S) commonly effected the photoisomerization of **1** to **2** but not at all the reverse isomerization, whereas the rearrangement of either **1** or **2** to 1-phenyltetralin (**7**) occurred with DCN or DCA but not at all with CNN or CHL. In the case of **3**, all the sensitizers effected the ring-splitting reaction to give indene (**8**) as the sole product. At low conversions (<10%), material balances were better than 90% without any consumption of the sensitizers, though other unreclaimed reactions increasingly occurred at higher conversions. Interestingly, **4** remained virtually unchanged even upon extensive irradiation in the presence of any of the sensitizers, a puzzling observation that is hardly expected from the configurational similarity to **2** and **3**.

Quantum Yields. Limiting quantum yields that are significant for discussions of exciplex reactivities were determined for the olefin formation from **1** or **3** by usual double-reciprocal plots of quantum yield vs. concentration of CB (Fig. 2) in the case of CHL and in cases where fluorescence quenching is inefficient (vide infra). Such plots were not taken for the formation of **2** and **7** from **1** as well as for the photosensitized reactions of **2** because of poor reproducibilities of data, particularly at low concentrations of CB due to low quantum efficiencies. In the case of the DCN-**1** or **3** pair, the observed quantum yield at [**1**] or [**3**]= 0.3 M[†] was used in place of the limiting quantum yield, since the fluorescence quenching was complete at [CB]≥0.2 M. Table 2 lists the intercepts (*I*) and the intercept-to-slope ratios (*I*/*S*) of the plots in Fig. 2 together with the limiting quantum yields for the olefin formation ($\phi_{\mathrm{ol}}^{\infty}$). In Table 3 are shown the observed quantum yields of the products in the photosensitized reactions of **1** at [**1**]=0.3 M.

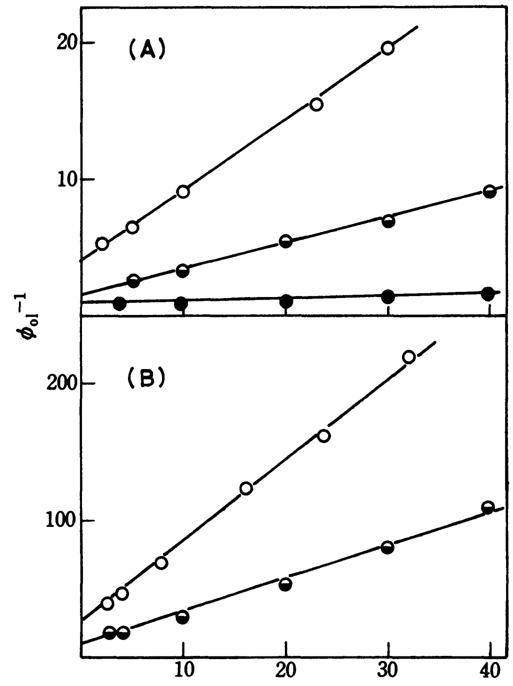


Fig. 2. Double-reciprocal plots of quantum yield for the olefin formation vs. concentration of CB: (A) CNN-**3** (—○—), DCA-**3** (—◒—), and CHL-**1** (—●—) pairs; (B) CNN-**1** (—○—) and DCA-**1** (—◒—) pairs.

Fluorescence Quenching. The fluorescence of the aromatic nitriles was quenched by CB following linear Stern-Volmer relationships. Table 2 includes the Stern-Volmer constants (K_{SV}) and the fluorescence-quenching rate constants (k_{q}) calculated from K_{SV} and the fluorescence lifetimes (τ). It is of mechanistic significance to note that the quenching of the CNN fluorescence by either **1** or **2** is accompanied by the appearance of weak exciplex emission at longer wavelength as is shown in Fig. 3A. A very weak exciplex

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[†] $1\,\mathrm{M}=1\,\mathrm{mol\,dm^{-3}}$.

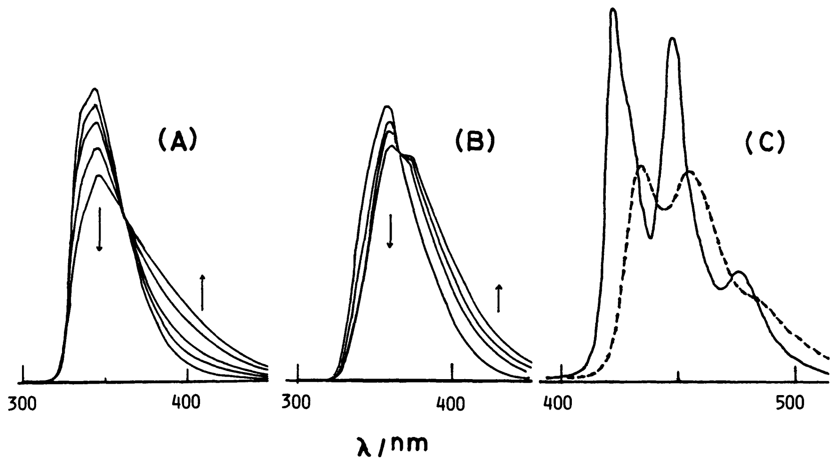


Fig. 3. Fluorescence spectra of the aromatic nitriles. (A) The CNN fluorescence in benzene at [**1**]=0.0, 1×10^{-2}, 4×10^{-2}, 9×10^{-2}, and 1.2×10^{-1} M. (B) The DCN fluorescence in cyclohexane at [**4**]=0.0, 5×10^{-3}, 1×10^{-2}, 1.5×10^{-2}, and 2×10^{-2} M. (C) The DCA fluorescence in cyclohexane in the presence of **1** (0.2 M) (dashed line) and in its absence (solid line).

Table 2. Limiting Quantum Yields for the Olefin Formation ($\phi_{\mathrm{ol}}^{\infty}$) and Fluorescence-Quenching Rate Constants (k_e)

CB[a]	S[a]	I[b]	I/S[c]/dm³ mol⁻¹	$\phi_{\mathrm{ol}}^{\infty}$	K_{SV}/dm³ mol⁻¹	k_e/dm³ mol⁻¹ s⁻¹
1	CNN	12	4.0	0.083	3	2.4×10^{8}
	DCA	4.0	3.3	0.25	5	4.0×10^{8}
	DCN			0.90	46	4.4×10^{9}
	CHL	1.0	≳100	1.0		
3	CNN	4.0	7.0	0.25	5	4.0×10^{8}
	DCA	1.3	7.0	0.77	9	7.3×10^{8}
	DCN			1.3	42	4.0×10^{9}

a) For abbreviations see Table 1 and Fig. 1. b) The intercepts of the plots in Fig. 2. c) The intercept-to-slope ratios of the plots in Fig. 2.

Table 3. Quantum Yields of the Photosensitized Reactions of **1**[a]

S[b]	ϕ_6[c]	ϕ_2	ϕ_7	ϕ_6/ϕ_2
CNN	0.05	0.007[d]	$<10^{-4}$	7.0
DCA	0.11	0.01[d]	0.007[d]	10
DCN	0.90	0.10[c]	0.025[d]	9.0
CHL	1.0	0.18[c]	$<10^{-4}$	5.6

a) Mean values for 3—5 runs at [**1**]=0.3 mol dm⁻³. b) For abbreviations see Table 1 and Fig. 1. c) ≤±10%. d) ≤±30%.

emission was also detected in the case of the DCA-**1** pair. Interestingly, the quenching of the DCN fluorescence by the unreactive cyclobutane, **4**, was accompanied by a relatively strong exciplex emission (Fig. 3B), though no exciplex emission was detected in the quenching of the DCN fluorescence by the reactive cyclobutanes. Moreover, it should be noted that the fluorescence quenching by **3** revealed no exciplex emission at all in any case.

Discussion

Mechanism. It is no doubt that the photosensitization by the aromatic nitriles proceeds via the excited-singlet state, since the fluorescence of DCN is quenched by either **1** or **3** near a diffusion-controlled limit and since the intercept-to-slope ratios obtained from quantum-yield measurements for the CNN and DCA-**1** or **3** pairs show reasonable agreements with the K_{SV} values for the fluorescence quenching. Moreover, the appearance of exciplex emissions strongly suggests that singlet exciplexes are involved as the intermediates of the photoreactions. In this regard, it should be noted that relatively strong exciplex emissions were detected with the unreactive DCN-**4** pair and also with the least reactive CNN-**1** pair, whereas the more reactive DCA-**1** pair shows a much weaker exciplex emission. In contrast, no exciplex emission was detected at all with the very reactive DCN-**1** pair as well as in the fluorescence quenching by **3** which is more reactive than **1**. These opposite behaviors between exciplex-emission efficiencies and reactivities suggest that the chemical reaction of CB occurs as a nonradiative decay of the sensitizer-CB exciplexes in competition with the emission pathway.

On the basis of these arguments, essential mechanistic pathways for the photosensitized reactions of CB by the aromatic nitriles are shown in Scheme 2. A usual kinetic treatment gives Eqs. 2—4.

$$\begin{aligned}
&\mathrm{S} \xrightarrow{h\nu} {}^1\mathrm{S}^* \\
&{}^1\mathrm{S}^* \xrightarrow{\tau^{-1}} \mathrm{S} \\
&{}^1\mathrm{S}^* + \mathrm{CB} \xrightarrow{k_e} {}^1[\mathrm{S\cdot CB}]^* \\
&{}^1[\mathrm{S\cdot CB}]^* \xrightarrow{k_{o1}} \mathrm{S} + 2\ \text{Olefin } (\mathbf{6} \text{ or } \mathbf{8}) \\
&{}^1[\mathrm{S\cdot CB}]^* \xrightarrow[(\mathrm{CB}=\mathbf{1})]{k_i} \mathrm{S} + \mathbf{2} + \mathbf{7} \\
&{}^1[\mathrm{S\cdot CB}]^* \xrightarrow{k_f} \mathrm{S} + \mathrm{CB} + h\nu' \\
&{}^1[\mathrm{S\cdot CB}]^* \xrightarrow{k_d} \mathrm{S} + \mathrm{CB}
\end{aligned}$$

(S = CNN, DCA, and DCN.)

Scheme 2.

$$\frac{1}{\phi_{o1}} = \frac{1}{\phi_{o1}^{\infty}}\left(1+\frac{1}{k_e\tau[\mathrm{CB}]}\right) \tag{2}$$

$$\phi_{o1}^{\infty} = \frac{2k_{o1}}{k_{o1}+k_i+k_d+k_f} \tag{3}$$

$$I_F^0/I_F = 1 + K_{SV}[\mathrm{CB}] = 1 + k_e\tau[\mathrm{CB}] \tag{4}$$

On the other hand, a triplet mechanism should operate in the CHL-photosensitized reaction of **1**, since the intersystem crossing of excited-singlet CHL to the triplet is extremely fast ($>10^{10}\,\mathrm{s}^{-1}$).[14] However, classical excitation transfer from triplet CHL to **1** is unlikely to occur, since no photoreaction of **1** was effected at all by the photosensitization using acetophenone which has a much higher triplet energy (309 kJ mol^{-1})[15] than CHL (261 kJ mol^{-1}).[16] Consequently, a triplet exciplex mechanism seems to be a reasonable choice. The high reduction potential of triplet CHL may give a benefit to the formation of an exciplex. Scheme 3 shows a possible mechanism for the CHL-photosensitized reaction of **1**, which is very similar to Scheme 2 except for the spin state.

$$\begin{aligned}
&\mathrm{CHL} \xrightarrow{h\nu} {}^1\mathrm{CHL}^* \xrightarrow{>10^{10}\,\mathrm{s}^{-1}} {}^3\mathrm{CHL}^* \\
&{}^3\mathrm{CHL}^* \xrightarrow{\tau_T^{-1}} \mathrm{CHL} \\
&{}^3\mathrm{CHL}^* + \mathbf{1} \xrightarrow{k_e} {}^3[\mathrm{CHL\cdot}\mathbf{1}]^* \\
&{}^3[\mathrm{CHL\cdot}\mathbf{1}]^* \xrightarrow{k_{o1}} \mathrm{CHL} + 2\ \mathbf{6} \\
&{}^3[\mathrm{CHL\cdot}\mathbf{1}]^* \xrightarrow{k_i} \mathrm{CHL} + \mathbf{2} \\
&{}^3[\mathrm{CHL\cdot}\mathbf{1}]^* \xrightarrow{k_d} \mathrm{CHL} + \mathbf{1}
\end{aligned}$$

Scheme 3.

$$\frac{1}{\phi_{o1}} = \frac{1}{\phi_{o1}^{\infty}}\left(1+\frac{1}{k_e\tau_T[\mathrm{CB}]}\right) \tag{5}$$

$$\phi_{o1}^{\infty} = \frac{2k_{o1}}{k_{o1}+k_i+k_d} \tag{6}$$

Electronic Properties and Reactivities of Exciplexes. Electronic properties of exciplexes are approximately described by Eq. 1, in which CT and ER contributions can be qualitatively estimated by E_{red}^* and E^* respectively. Since the excitation energies of excited-singlet CB are commonly ≈440 kJ mol^{-1} (105 kcal mol^{-1} (1 cal=4.184 J)) as determined by the fluorescence spectra,[17] differences of excited-singlet excitation energy between CB and S are ≈66 kJ mol^{-1} for the CNN–CB pairs, ≈100 kJ mol^{-1} for the DCN–CB pairs, and ≈160 kJ mol^{-1} for the DCA–CB pairs. Since the energy differences for the DCA–CB pairs are too large to allow significant ER, the binding origin of the DCA exciplexes should exclusively come from CT contributions. For the DCN exciplexes, CT contributions are certainly dominant because of the high E_{red}^* value of DCN, whereas the CNN exciplexes have higher ER contributions but less CT contributions compared with the other exciplexes. Although the CHL-**1** exciplex appears to be of dominant CT nature, a significant ER contribution might be indicated by a relatively small energy difference between the triplets of CHL and **1** (37—62 kJ mol^{-1}).[18]

As shown in Tables 2 and 3, the quantum yields strongly depend on E_{red}^* but not significantly on E^*, thus demonstrating that reactivities of the exciplexes are mainly controlled by CT contributions irrespective of the spin states. Moreover, the formation of **7** occurs from the more polar exciplexes of DCN and DCA but not at all from the CNN exciplex of a less CT contribution. Interestingly, **7** is not formed again from the triplet CHL-**1** exciplex of polar nature. Presumably, the rearrangement to **7** would proceed via a very polar state on singlet hypersurface in a way different from the decay pathways for the formation of **6** and **2**, while no decay channel for the formation of **7** is available in the triplet state.

Comparisons of the exciplex chemistry with other types of photoreactions of CB may be diagnostic for discussing decay channels of the exciplexes which should depend on CT contributions. The redox-photosensitized reaction of **1** gives only **7** without any formation of **6** and **2**,[19] revealing behaviors different from the exciplex chemistry. This difference appears to reflect different reaction surfaces since key chemical events in the former reaction occur in the ground state. On the other hand, the ratios of ϕ_6 to ϕ_2 in the photosensitized reactions of **1** by the aromatic nitriles are similar to that of the direct photolysis (7.2)[18b] but still higher than those of the acetone-photosensitized reaction (2.6) and the thermal reaction (2.0).[18b] It is

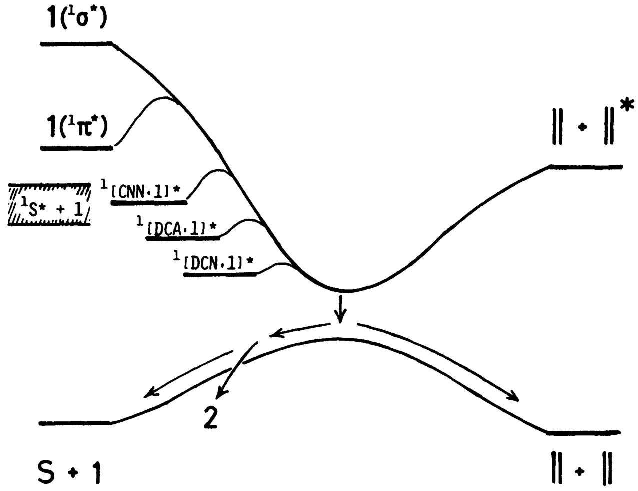
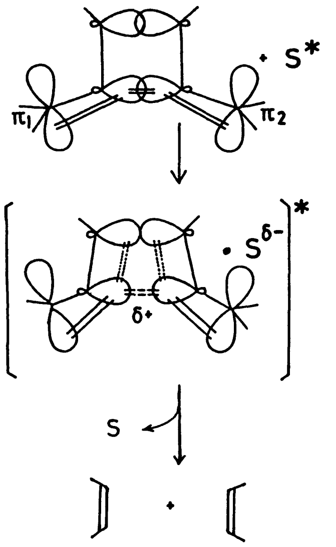


Fig. 4. A schematic potential hypersurface diagram for singlet photochemistry of **1**.

therefore suggested that the singlet exciplexes cross to the reaction surface involved in the direct photolysis to reach a common pericyclic minimum.

Figure 4 shows hypothetical reaction hypersurfaces for the singlet photochemistry of **1**, which are qualitatively illustrated on the basis of the Michl's prediction concerning [2+2] cycloaddition and cycloreversion.[20] The exciplex formation should lead to the population of a positive charge on **1** by CT contributions. As is shown in Scheme 4, this positive charge on CB is delocalized mostly on the π_1–C–C–π_2 orbital array since the π_1 and π_2-electron systems interact with each other through the ring C–C sigma orbitals.[7,21] This means that the ring sigma bond should be weakened by a decrease of electron density depending on CT contributions. As a result, an exciplex state of higher CT nature might be located closer to the reaction surface, and activation barriers for the crossing to the reaction surface would be decreased with an increase of CT contributions.



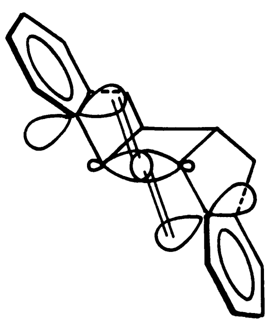
Scheme 4.

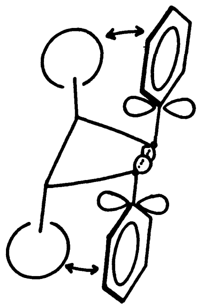
On the other hand, it is of interest to note that the direct photoexcitation of **1** is much less effective to cause the reaction than the exciplex formation; $\phi_6+\phi_2 \cong 0.02$ in the direct photolysis.[18b] Since the UV-absorption and fluorescence spectra of **1** and the other cyclobutanes are essentially identical with those of simple alkylbenzenes,[17] the electronic excitation of **1** in the spectroscopic state is almost localized on the isolated π-electron chromophore. In other words, little perturbation of the ring C–C bond might occur in the spectroscopic state, thus implying that crossing to the reaction surface perhaps requires a high activation barrier because of the extremely high σ^* level compared with the π^* level. This may also give a rationale to interpret minor roles of ER contributions in the exciplex chemistry.

On the other hand, the decay channels of the triplet CHL-**1** exciplex can not be straightforwardly interpreted, since the ϕ_6/ϕ_2 value is substantially greater than that of the acetone-photosensitized reaction and since **7** is not formed regardless of the polar nature of the exciplex. Although the triplet exciplex can efficiently go into reactive states, the decay pathways are not the same as those of the triplet state of **1**. A plausible interpretation is that the triplet exciplex would competitively cross to both singlet and triplet reaction surfaces. The former crossing requires a prior spin flip, which may be facilitated by high CT interactions[22] and/or by a considerable distortion of the cyclobutane ring in the exciplex state.[23]

Relationships of Exciplex Reactivities with Structures of CB. In previous papers,[7a–c] we demonstrated that through-bond interactions between vicinally substituted π or n-electron systems are essential to determine reactivities of cyclobutanes in the redox-photosensitized ring-splitting reactions. For example, **3** is very reactive because of the head-to-head structure favorable for efficient through-bond interactions, while no photosensitized reaction occurs at all with the head-to-tail isomer of **3** for which such interactions are configurationally forbidden. Interestingly, however, the complete lack of any reaction of **4** in the exciplex chemistry would apparently disagree with this concept, since this cyclobutane has a head-to-head structure. Actually, the methyl substituents sterically inhibit the phenyl groups from taking conformations favorable for through-bond interactions.[21] In other words, through-bond interactions are conformationally disallowed, a conclusion supported by the oxidation potential of **4** (1.63 V) which is considerably higher than those of the reactive cyclobutanes. Therefore, the through-bond-interaction concept is valid to interpret reactivities of CB in the exciplex chemistry as well.

Another significant feature in structure-reactivity relationships is that **3** is much more reactive than **1** and **2**, though they have similar oxidation potentials and fluorescence-quenching capabilities. Apparently,





this difference arises from the rigid tricyclic structure of **3** compared with the more flexible monocyclic structure of **1** and **2**, since free rotation around the C–Ph bond is certainly unfavorable for through-bond interactions. Moreover, conformational rigidity of **3** is again favorable for orbital interactions between the C1(C2) and C4(C3) sigma orbitals which are required for splitting of the cyclobutane ring to occur. In cases of **1** and **2**, on the other hand, the cyclobutane ring may be distorted unfavorably for such orbital interactions as the C1–C2 bond is elongated by the exciplex formation; the isomerization reactions of **1** and **2** perhaps occur as the consequences of ring distortion. As a result, the exciplexes of **3** can cross to the reaction surface with lower activation barriers than the exciplexes of **1** or **2** can do. This would also interpret why the CNN and DCA-**1** exciplexes can emit even in low efficiencies and why the exciplexes of **3** can not at all.

Conclusions

It is suggested that the photosensitized reactions of **1**—**3** proceed via the singlet exciplexes of the aromatic nitriles or the triplet CHL exciplex. CT contributions are essential to control the exciplex chemistry as the consequences of the population of a positive charge on the π_1–C1σ–C2σ–π_2 orbital array which weakens the ring C–C bond. It is speculated that such bond-weakening effects lower activation barriers for the crossing from the singlet-exciplex state to a reaction hypersurface involved in the direct photolysis, whereas the decay channels of the triplet chloranil exciplex are not the same as those of the triplet state of CB. On the other hand, a different pathway is indicated for the formation of **7** from the singlet exciplexes of **1** or **2**, involving a very polar state which is not realized from the triplet CHL exciplex.

The lack of any reaction of **4** by the exciplex formation is attributed to conformations unfavorable for through-bond interactions between the two π-electron systems. Higher reactivities of **3** compared with **1** and **2** are associated with the rigid tricyclic structure that facilitates orbital overlaps between the C1(C2)–C4(C3) sigma orbitals in the progress of the reaction.

Experimental

Instruments. Gas chromatography was performed on a Shimadzu GC-7A gas chromatograph using a 2-m column of 25% PEG 20M on Shimalite NAW for analyses of **6** and **8** and a 2-m column of 2% OV-17 on Chromosorb W for analyses of **7** and the cyclobutanes. Oxidation and reduction potentials were determined by cyclic voltammetry vs. Ag/AgNO$_3$ in acetonitrile using tetraethylammonium tetrafluoroborate as the supporting electrolyte; the instrument and methods are the same as those reported previously.[7a)] IR, UV, and ^{1}H NMR spectra were obtained on Hitachi 260-10, Hitachi 220-A, and JEOL JNM-PMX60 spectrometers, respectively. A Hitachi MPF-4 spectrofluorometer equipped with a data processor (612-0085) was used for fluorescence measurements; all the fluorescence spectra were recorded after the correction of spectral responses of the instrument.

Materials. Commercial 1-cyanonaphthalene (Tokyo Kasei) was thoroughly purified by the method described in a previous paper.[24)] Both chloranil and 9,10-dicyanoanthracene (Tokyo Kasei) were purified by repeated recrystallization from benzene followed by vacuum sublimation. 1,4-Dicyanonaphthalene was prepared according to the literature method[25)] and was purified by repeated recrystallization from benzene followed by vacuum sublimation. The indene dimer (**3**)[26)] and the diphenylcyclobutanes (**1** and **2**)[27)] were prepared according to the literature methods. The purification of **1** and **3** was performed by repeated recrystallization from methanol.

***r*-1,*t*-2-Dimethyl-*t*-3,*c*-4-diphenylcyclobutane (4).** Dimethyl *t*-3,*c*-4-diphenyl-*r*-1,*t*-2-cyclobutanedicarboxylate (dimethyl μ-truxinate), which had been prepared by the photoaddition of dimethyl fumarate to *trans*-stilbene,[28)] was reduced by an excess of LiAlH$_4$ in tetrahydrofuran to give *r*-1,*t*-2-bis(hydroxymethyl)-*t*-3,*c*-4-diphenylcyclobutane (mp 130—132 °C from a benzene-hexane mixture); ^{1}H NMR δ=1.6 (t, 2H, OH×2), 2.6 (m, 2H, H-1 and H-2), 3.5 (d-d, 4H, CH_2×2), 4.2 (m, 2H, H-3 and H-4), 8.2 (m, 10H, C_6H_5×2). This dialcohol was converted to the ditosylate, which was then reduced by an excess of LiAlH$_4$ in tetrahydrofuran to give the dimethyldiphenylcyclobutane in a 60% yield based on the truxinate (bp 108—110 °C/0.15 Torr[†]); ^{1}H NMR δ=0.9 (d, 6H, CH_3×2), 2.3 (m, 2H, H-1 and H-2), 4.1 (m, 2H, H-3 and H-4), 7.2 (m, 10H, C_6H_5×2).

Found: C, 91.14; H, 8.63%. Calcd for $C_{18}H_{20}$: C, 91.47; H, 8.53%.

Photoreactions and Determination of Quantum Yields. Photoirradiation was carried out with an Eikosha PIH-300 high-pressure Hg lamp under cooling with water using appropriate light filters and a "merry-go-round" turntable. A pottassium chromate solution (0.2 g dm^{-3}, 10-mm path length) was used to isolate the 313-nm light, whereas the 366-nm light was obtained by the passage through an uranyl glass and a solution (10-mm path length) obtained by the dissolution of $CoCl_2\cdot 6H_2O$ (45.2 g), $NiCl_2\cdot 6H_2O$ (22.7 g), and a concentrated hydrochloric acid (15 cm^3) in a mixture of ethanol (52.5 cm^3), acetone (37.5 cm^3), and water (60 cm^3).[29)] A 2-hexanone actinometer[30)] and a benzophenone–benzhydrol actinometer[31)] were used for the determination of quan-

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[†] 1 Torr≈133.322 Pa.

tum yields at 313 nm for the CNN and DCN-photosensitized reactions and at 366 nm for the DCA and CHL runs respectively. Concentrations of the aromatic nitriles and CHL were set in 5×10^{-4}—10^{-3} M and $\approx10^{-2}$ M, respectively, which were confirmed to be high enough for the complete absorption of the incident light under photoreaction conditions. Pyrex tubes (8 mm i.d.) were used as the common vessels for the photoreactions and for the actinometry. Benzene solutions of the reactants (3 cm^3) and actinometer solutions (3 cm^3) were irradiated, and the progress of the photoreactions was followed by gas chromatography.

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