

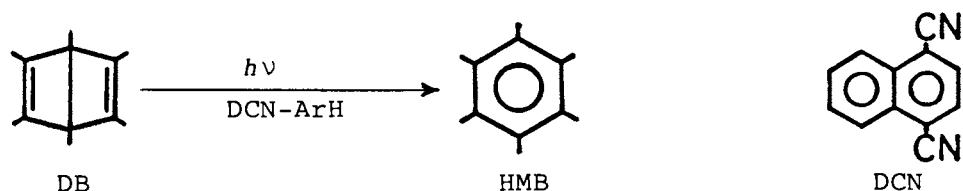
Photosensitized Isomerization of Hexamethyl(Dewar benzene) by
 Interactions with 1,4-Dicyanonaphthalene-Arene Exciplexes.
 An Adiabatic Triplex Pathway¹⁾

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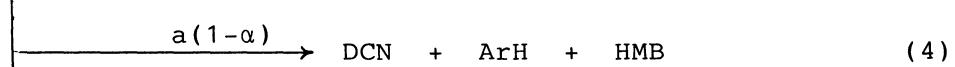
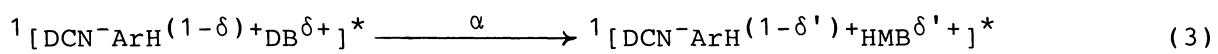
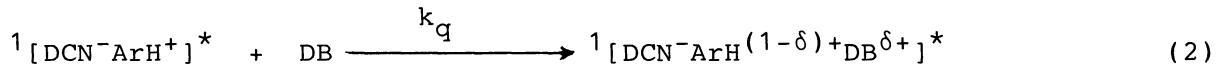
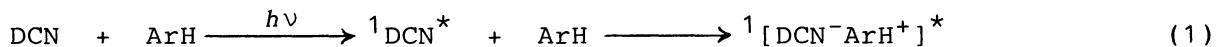
The isomerization of Hexamethyl(Dewar benzene) to hexamethylbenzene is photosensitized by 1,4-dicyanonaphthalene-arene exciplexes. Spectroscopic and quantum-yield studies suggest that the isomerization proceeds mostly through an adiabatic pathway from hypothetical termolecular excited complexes (triplexes).

Interactions of a ground-state molecule with bimolecular excited complexes (exciplexes) can give termolecular excited complexes,²⁾ so-called triplexes, which have been supposed to play important roles in a variety of photochemical events.¹⁻¹⁰⁾ In a previous paper,¹¹⁾ one of us reported a novel type of photosensitization that proceeds through hypothetical triplexes formed by interactions of a reactant molecule with 1,4-dicyanonaphthalene (DCN)-arene (ArH) exciplexes. It was indeed found that quenching of DCN-ArH exciplex emissions by aromatic olefins results in the appearance of new emissions attributable to DCN-ArH-olefin triplexes.¹²⁾ This type of photosensitization, which we call "triplex photosensitization", has been found to effect the valence isomerization of hexamethyl(Dewar benzene) (DB) to hexamethylbenzene (HMB) that proceeds mostly through an adiabatic pathway from hypothetical DCN-ArH-DB triplexes.



Emissive DCN-ArH exciplexes are exclusively formed in ArH solvents.^{11,13)} Quenching of the exciplex emissions by DB and by HMB gives

essentially superimposable new emissions (e.g., Fig. 1(B)). Table 1 lists properties of the new emissions. Since the ionization potential of DB is significantly lower than that of HMB,¹⁴⁾ the new emissions of the DCN-ArH-DB systems should not come from the excited complexes of DB but from those of HMB after the adiabatic isomerization of the former complexes. As shown in Fig. 1, the new emission maximum in benzene is considerably longer than the DCN-HMB exciplex emission in more polar dibutyl ether. Since an exciplex generally reveals the emission at longer wavelengths in more polar solvents, the new emission in benzene is very unlikely to come from DCN-HMB exciplex after the substitution of DCN-benzene exciplex with DB¹⁵⁾ followed by the adiabatic exciplex isomerization.^{14,16)} It is therefore reasonable to attribute the new emissions in ArH solvents to DCN-ArH-HMB triplexes. Furthermore, the new emission maxima depend on the ionization potentials of ArH to reveal a systematic blue shift from 478 nm in benzene to 454 nm in 1,2,4-trimethylbenzene. This behavior might arise from charge-transfer interactions of HMB with the positively charged ArH in the triplexes, which should result in greater stabilization of the triplexes with ArH of higher ionization potential. Consequently, the DCN-photosensitized isomerization of DB to HMB in ArH solvents can be described in terms of Eqs. 1 - 6.



It is of mechanistic significance to note that the probabilities (α) of the adiabatic pathway are almost identical with the net quantum yields (ϕ_R) of the photosensitized isomerization in ArH solvents within experimental errors. Namely, the triplex isomerism of DB in ArH solvents proceeds mostly through the adiabatic pathway (Eq. 3), while the nonadiabatic isomerization (Eq. 4) should be negligible, i.e., $\alpha \approx 0$. This is in sharp contrast to the exciplex isomerism of DB by such aromatic nitriles as 1-cyanonaphthalene and 9,10-dicyanoanthracene in nonpolar solvents, which occurs through both the adiabatic and the nonadiabatic pathways from the nitrile-DB exciplexes in unit combined quantum yields.^{14,16)} Although

Table 1. Properties of Triplex Emissions, Probabilities of the Adiabatic Triplex Isomerization (α), and Net Isomerization Quantum Yields (ϕ_R)

Solvents (DK) ^{a)}	IP/eV	$10^{-9}k_q$ ^{b)}	λ_{\max}^c /nm	τ^d /ns	$\phi_{\text{em}}^{\text{DB}}$ ^{e)}	$\phi_{\text{em}}^{\text{HMB}}$ ^{f)}	$\alpha^g)$	$\phi_R^h)$
Benzene (2.28)	9.24	9.8	478	20.4	0.039	0.17	0.23	0.22
Toluene (2.38)	8.82	8.4	476	31.1	0.074	0.25	0.29	0.27
<i>o</i> -Xylene (2.57)	8.56	4.7	476	37.8	0.055	0.20	0.27	0.32
<i>p</i> -Xylene (2.37)	8.44	4.9	475	34.0	0.066	0.22	0.32	0.43
1,3,5-TMB ⁱ⁾	8.41	3.4	460	36.4	0.063	0.19	0.32	0.36
1,2,4-TMB ⁱ⁾	8.27	2.5	454	43.0	0.040			
Dibutyl ether (3.06) ^{j)}	12.0 ^{k)}		457	23.1	0.068	0.17	0.40	0.77 ^{l)}

a) Dielectric constants at 20 or 25 C. b) Rate constants in $\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$ for Eq. 2. c) Triplex emission maxima in ArH solvents; ± 2 nm. d) Lifetimes of the triplex emissions at $[\text{DB}] = 0.6 - 0.8 \text{ mol dm}^{-3}$; ± 0.5 ns. e) Emission quantum yields for the DCN-ArH-DB systems extrapolated to infinite concentration of DB. f) Emission quantum yields for the DCN-ArH-HMB systems. g) $\phi_{\text{em}}^{\text{DB}}/\phi_{\text{em}}^{\text{HMB}}$. h) At 0.1 mol dm^{-3} DB where DCN-ArH exciplex emissions are almost completely quenched. i) Trimethylbenzene. j) For the DCN-DB or DCN-HMB exciplex system in this solvent. k) For quenching of DCN fluorescence by DB. l) Limiting quantum yield obtained from a double reciprocal plot of quantum yields vs. concentration of DB.

it is still unknown why the nonadiabatic pathway is negligible in the mechanistic pathways from the DCN-ArH-DB triplexes, further investigation on the triplex photosensitized isomerization might provide an important mechanistic clue to explore controlling factors for the adiabatic and nonadiabatic pathways from excited complexes of DB. For instance, the decrease of α with the increase in IP of ArH would be attributable to higher activation barriers for the adiabatic triplex pathway that might be imposed by greater charge-transfer stabilization of the triplexes associated with higher population densities of the positive charge on

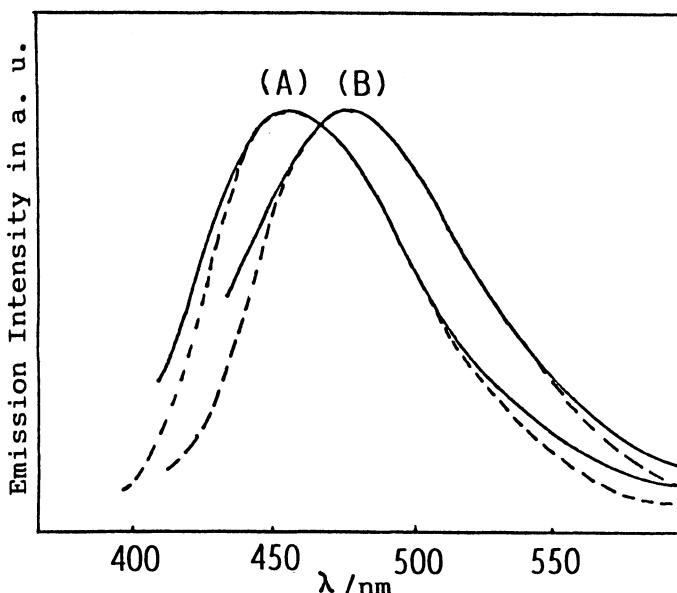


Fig. 1. (A) Exciplex emission spectra obtained upon quenching of DCN fluorescence by 0.8 M[†] DB (solid curve) or by 0.3 M HMB (broken curve) in dibutyl ether and (B) triplex emission spectra obtained upon quenching of DCN-benzene exciplex emission by 0.7 M DB (solid curve) or by 0.3 M HMB (broken curve) in benzene; $[\text{DCN}] = 2.0 \times 10^{-4}$ M. The spectra are corrected and normalized for comparison. [†]1.0 M = 1.0 mol dm^{-3} .

the DB (i.e., $\delta \rightarrow 1$).

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