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Evidence for the Formation of Emissive A-D-D' Triplexes in Quenching of 1,4-Dicyanonaphthalene-Arene Exciplexes by Olefins[1)]

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Evidence for the intervention of emissive triplexes has been presented for quenching of 1,4-dicyanonaphthalene-arene exciplexes by aromatic olefins. Chemical implications of the triplexes are discussed in relation with reactivities of olefins in geometric isomerization and dimerization reactions by charge transfer.

Termolecular interactions in an electronically excited state are important in a variety of photophysical and photochemical phenomena, e.g., selective quenching of exciplexes,[2,3)] enhanced charge separation of exciplexes,[4-6)] photosensitized dimerization reactions,[7-9)] and photosensitized Diels-Alder reactions.[10)] One of us (C.P.) also reported that the photosensitized reactions of diarylcyclobutanes and quadricyclane by 1,4-dicyanonaphthalene (DCN) in aromatic hydrocarbon (ArH) solvents proceed via DCN-ArH-substrate termolecular interactions in the excited singlet state involving the intervention of hypothetical triplexes $^1[\mathrm{A{\cdot}D{\cdot}D'}]^*$ different from usual A-D-D and A-A-D triplexes supposed in the other reactions.[11)] Although a few reports have appeared on emissive A-D-D triplexes,[12,13)] there has been no convincing evidence for the formation of discrete A-D-D' or A-A'-D triplexes. In this paper, we wish to show evidence for the formation of emissive A-D-D' triplexes in quenching of DCN-ArH exciplexes by aromatic olefins.

Excited-singlet DCN ($^1\mathrm{DCN}^*$) forms emissive exciplexes with benzene and methylated and methoxylated benzenes.[11,14)] The exciplex emissions were quenched by a variety of olefins at rate constants increasing with the decrease of ionization potential of the olefins or with the increase of ionization potential of ArH.[15)] Quenching of the DCN-ArH exciplex emissions by several aromatic olefins accompanied the appearance of new emissions at longer wavelength as shown in Fig. 1. It is reasonable to presume that the new emissions are assignable to either DCN-ArH-olefin triplexes or DCN-olefin exciplexes formed by the substitution of DCN-ArH exciplexes with the olefins.[16]

$$\mathrm{DCN} \xrightarrow{h\nu} {}^{1}\mathrm{DCN}^{*} \xrightarrow{\mathrm{ArH}} {}^{1}[\mathrm{DCN}^{-}\mathrm{ArH}^{+}]^{*}$$

$$ {}^{1}[\mathrm{DCN}^{-}\mathrm{ArH}]^{*} + \mathrm{D} \longrightarrow \left\{ \begin{array}{l} \longrightarrow {}^{1}[\mathrm{DCN}^{-}\mathrm{ArH}^{(1-\delta)+}\mathrm{D}^{\delta+}]^{*} \\ \longrightarrow {}^{1}[\mathrm{DCN}^{-}\mathrm{D}^{+}]^{*} + \mathrm{ArH} \end{array} \right.$$

(D = olefin)

In order to identify the origin of the new emissions, therefore, we determined emission properties of DCN-trans-β-methylstyrene and DCN-trans-anethole exciplexes in either cyclohexane or

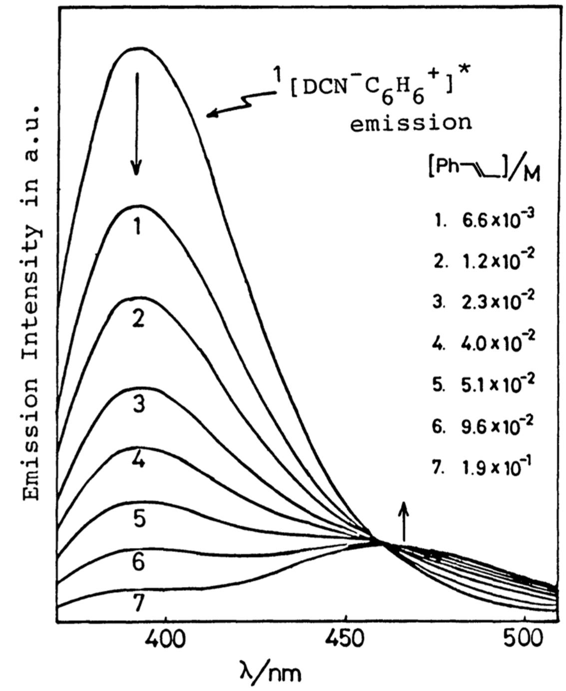


Fig. 1. Corrected emission spectra of the DCN-benzene-trans-2-methylstyrene system following concentration of the olefin; [DCN]=2×10^{-4} mol dm^{-3} in deaerated benzene.

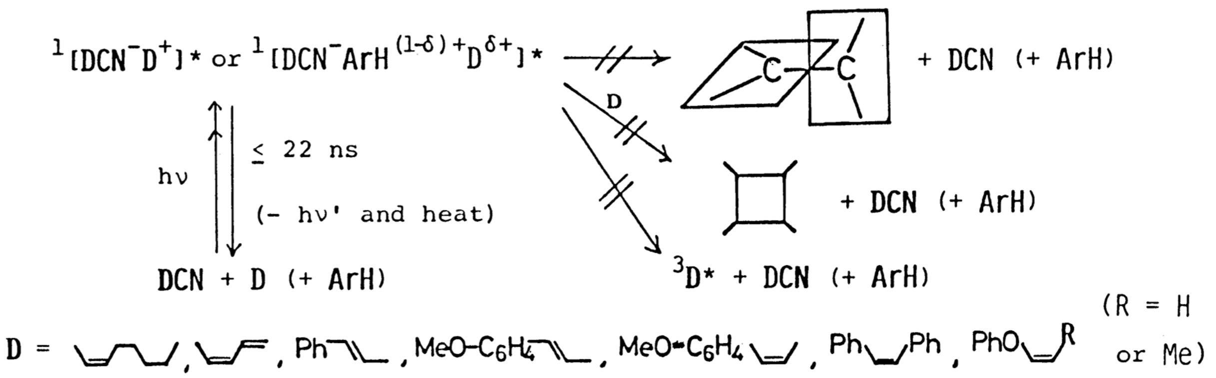
Table 1. Properties of Emissions from DCN-Olefin Exciplexes and from DCN-ArH-Olefin Triplexes

Olefin (D)	Emission source	Solvent a)	λ_{max}^{EM}/nm b)	τ_{EM}/ns c)	ϕ_{EM} d)	τ_{EM}^{0}/ns e)
trans-β-Methylstyrene	$^{1}[\mathrm{DCN}^{-}\mathrm{D}^{+}]^{*}$	C_6H_{12}	437	6.0	0.079	76
		Bu_2O	448	10.7	0.068	157
	$^{1}[\mathrm{DCN}^{-}\mathrm{ArH}^{(1-\delta)+}\mathrm{D}^{\delta+}]^{*}$	PhH	462	22.3	0.13	172
		PhMe	456	22.1	0.13	170
		$C_6H_3Me_3$	449	17.9	0.091	197
trans-Anethole	$^{1}[\mathrm{DCN}^{-}\mathrm{D}^{+}]^{*}$	C_6H_{12}	502	20.0	0.057	350
		Bu_2O	565	12.5	0.028	440
	$^{1}[\mathrm{DCN}^{-}\mathrm{ArH}^{(1-\delta)+}\mathrm{D}^{\delta+}]^{*}$	PhH	530	17.0	0.022	778
		PhMe	524	19.3	0.026	753
		$C_6H_3Me_3$	530	20.8	0.029	715

a) C_6H_{12} = cyclohexane, Bu_2O = dibutyl ether, PhH = benzene, PhMe = toluene, and $C_6H_3Me_3$ = 1,3,5-trimethylbenzene. b) Emission maxima. c) Observed emission lifetimes. d) Emission quantum yields. e) Natural radiative lifetimes.

dibutyl ether as well as those of the new emissions from the DCN-ArH-olefin systems in neat ArH. The observed quantum yields (Φ_{EM}) and lifetimes (τ_{EM}) give the natural radiative lifetimes ($\tau^0_{EM} = \tau_{EM}/\Phi_{EM}$) which are essential for the assignment of the new emissions. As shown in Table 1, the τ^0_{EM} values of the new emissions are substantially longer than those of the DCN-olefin exciplexes in cyclohexane and even in dibutyl ether, which is a more polar solvent than any of ArH, thus demonstrating that the new emissions should be assignable to DCN-ArH-olefin triplexes. The triplex formation appears to be rather general in quenching of DCN-ArH exciplex emissions by aromatic olefins.[15)]

It was confirmed that neither geometric isomerization nor cyclodimerization of the olefins shown in Scheme 1 is photosensitized by DCN in cyclohexane, dibutyl ether, or neat ArH (benzene, toluene, xylenes, and mesitylene) under conditions where the DCN fluorescence or the DCN-ArH exciplex emission was completely quenched by the olefins.[15)] It is therefore evident that the singlet exciplexes and triplexes do not undergo intersystem crossing to generate olefin triplets. The lack of any chemical reaction in the present photosensitization is in sharp contrast to the stereomutation of 1-phenoxypropene[17)] and the cyclodimerization of phenyl vinyl ether[18)] and anethole[19)] via cation-radical species. Presumably population densities of positive charge and/or excitation energy on the olefins in the exciplexes and triplexes are not high enough to effect twisting of the C=C bonds nor to allow the addition of a neutral olefin molecule to the charged one in the excited complexes. It should be also taken into consideration that the lifetimes of the exciplexes and triplexes ($\leq$ 22 ns) are much shorter than those of photogenerated free cation radicals (usually $\gtrsim$ 1 μs).



Scheme 1.

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References

1) Photochemical Reactions of Aromatic Compounds. Part 47. Part 46: C. Pac, Y. Go-An, and S. Yanagida, in contribution.

2) R. A. Caldwell, D. Creed, D. C. DeMarco, L. A. Melton, H. Ohta, and P. H. Wine, J. Am. Chem. Soc., 102, 2369 (1980) and references cited therein.

3) C. Pac and H. Sakurai, Chem. Lett., 1976, 1067; T. Majima, C. Pac, and H. Sakurai, Bull. Chem. Soc. Jpn., 51, 1811 (1978).

4) N. C. Yang, R. Gerald II, and M. R. Wasielewski, J. Am. Chem. Soc., 107, 5531 (1985) and references cited therein.

5) W. Hub, S. Schneider, F. Dorr, J. D. Oxman, and F. D. Lewis, J. Am. Chem. Soc., 106, 701 (1984) and references cited therein.

6) N. Mataga, A. Karen, T. Okada, S. Nishijima, N. Kurata, Y. Sakata, and S. Misumi, J. Phys. Chem., 88, 5138 (1984).

7) R. O. Campbell and R. S. H. Liu, Mol. Photochem., 6, 207 (1974).

8) J. Saltiel, D. E. Townsend, B. D. Watson, P. Shannon, and S. L. Finson, J. Am. Chem. Soc., 99, 884 (1977).

9) K. Mizuno, H. Hashizume, and Y. Otsuji, J. Chem. Soc., Chem. Commun., 1983, 772.

10) G. C. Calhoun and G. B. Schuster, J. Am. Chem. Soc., 108, 8021 (1986).

11) C. Pac, Pure Appl. Chem., 58, 1249 (1986).

12) H. Beens and A. Weller, Chem. Phys. Lett., 2, 140 (1968).

13) J. Saltiel, D. E. Townsend, B. D. Watson, and P. Shannon, J. Am. Chem. Soc., 97, 5688 (1975).

14) H. F. Davis, S. K. Chattopadhyay, and P. K. Das, J. Phys. Chem., 88, 2798 (1984).

15) Details will be published in a full paper.

16) H. Ohta, D. Creed, P. H. Wine, R. A. Caldwell, and L. A. Melton, J. Am. Chem. Soc., 98, 2002 (1976).

17) T. Majima, C. Pac, and H. Sakurai, Chem. Lett., 1979, 1133.

18) S. L. Mattes, H. R. Luss, and S. Farid, J. Phys. Chem., 87, 4779 (1983).

19) N. L. Bauld and R. Pabon, J. Am. Chem. Soc., 105, 633 (1983).

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