# Photochemical Reactions of Aromatic Compounds. Part 49.[1] An Exciplex Chain Mechanism for the 1,4-Dicyanonaphthalene-photosensitised Isomerisation of Hexamethyl-(Dewar Benzene)

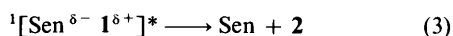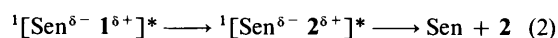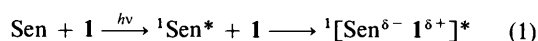**Yasuhiro Masaki, Yoshikazu Uehara, Shozo Yanagida and Chyongjin Pac***
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Mechanistic studies have been performed on the isomerisation of hexamethyl-(Dewar benzene) **1** to hexamethylbenzene **2** photosensitised by 1,4-dicyanonaphthalene (DCN). Analysis of the emission spectra of the DCN–1 and DCN–2 pairs demonstrates that the adiabatic isomerisation of the DCN–1 exciplex to that of DCN–2 occurs with the probabilities 0.53 in cyclohexane and 0.40 in dibutyl ether. The limiting quantum yields for the net isomerisation are 1.5 in cyclohexane and 0.77 in dibutyl ether. Extensive kinetic analyses suggest that the isomerisation proceeds mostly through the adiabatic pathway from the DCN–1 exciplex to DCN–2 followed by sensitisation of the **1** isomerisation by the product (DCN–2) exciplex *via* the putative DCN–2–1 triplex, while the participation of the non-adiabatic isomerisation from the DCN–1 exciplex is not important.

The chemistry of bicyclo[2.2.0^{1,4}]hexa-2,5-diene ('Dewar benzene') and its derivatives has received much attention from synthetic,[2] mechanistic[3] and theoretical[4] points of view because of the unique strained structure as well as from the historical background of benzene chemistry. Hexamethyl-(Dewar benzene) **1** is one of the stable Dewar benzene derivatives because of the relatively high activation barrier for the thermal isomerisation to hexamethylbenzene **2**,[5] and its ionisation potential, 7.8 eV,[6] is low enough for exciplex formation as well as for electron transfer to occur with electron-accepting molecules in electronically excited states. Accordingly, extensive investigation[7–13] has been addressed to the isomerisation of **1** to **2** photosensitised by electron acceptors. In non-polar solvents, the isomerisation of **1** to **2** is photosensitised by

1   **2**
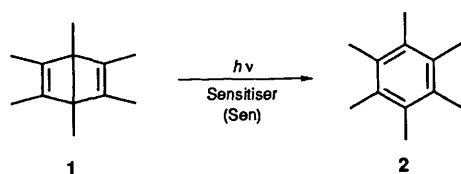
aromatic nitriles in high quantum yields, usually with unit efficiencies.[8,9] The reaction mechanism has been discussed in terms of the adiabatic and non-adiabatic pathways from sensitiser–1 exciplexes [eqns. (2) and (3)], while the decay to the

$$\text{Sen} + \textbf{1} \xrightarrow{h\nu} {}^1\text{Sen*} + \textbf{1} \longrightarrow {}^1[\text{Sen}^{\delta-} \, \textbf{1}^{\delta+}]* \quad (1)$$

$${}^1[\text{Sen}^{\delta-} \, \textbf{1}^{\delta+}]* \longrightarrow {}^1[\text{Sen}^{\delta-} \, \textbf{2}^{\delta+}]* \longrightarrow \text{Sen} + \textbf{2} \quad (2)$$

$${}^1[\text{Sen}^{\delta-} \, \textbf{1}^{\delta+}]* \longrightarrow \text{Sen} + \textbf{2} \quad (3)$$

ground-state precursors is negligible independently of the aromatic nitriles used.[9] In other words, the adiabatic and non-adiabatic pathways should be mutually counterbalanced to disallow the significant decay of the exciplexes to the ground-state precursors so that the net quantum yields of the isomerisation might become invariably *ca.* 100%. Therefore, it is of mechanistic significance to confirm which properties of the exciplexes might control the mechanistic channels and whether or not other mechanistic channels can participate in the photosensitised isomerisation of **1** by other aromatic nitriles.

From these viewpoints, the authors have investigated the isomerisation of **1** to **2** photosensitised by 1,4-dicyanonaphthalene (DCN), since the charge-transfer character of the DCN–1 exciplex should—as a consequence of the very positive reduction potential of excited singlet DCN (2.17 V in acetonitrile *vs.* SCE)[14]—be very considerable. It has been found that the limiting quantum yield for the DCN-photosensitised isomerisation in cyclohexane is greater than unity and that the Stern–Volmer constants for the quenching of DCN fluorescence in cyclohexane and dibutyl ether reveal substantial discrepancies from the intercept-to-slope ratios in the double-reciprocal plots of quantum yield *vs.* concentration of **1**. Detailed kinetic analysis of the DCN-photosensitised isomerisation of **1** demonstrates that the mechanism involves the adiabatic pathway from the DCN–1 exciplex to DCN–2 and the 'photosensitisation' by the product DCN–2 exciplex, presumably *via* the hypothesised DCN–2–1 triplex, while the participation of the non-adiabatic isomerisation is negligible.

Results

Fluorescence Measurements.—Quenching of DCN fluorescence by either **1** or **2** occurs at a diffusion-controlled limit, accompanied by the appearance of exciplex emission. Fig. 1 shows the exciplex emission spectra for the DCN–1 and DCN–2 pairs at 300 K, which are essentially superimposable with each other. A minor difference at longer wavelength for cyclohexane solution should be due to the appearance of another emission from the DCN–1 pair, as revealed by the emission spectrum of the DCN–1 pair in methylcyclohexane at 228 K [Fig. 1(*a*)]. In the case of the DCN–1 pair, the appearance of exciplex emission associated with quenching of DCN fluorescence showed an isoemissive point to reach a maximum at *ca.* 0.01 mol dm^{-3} in **1**, but a further increase in concentration of **1** resulted in quenching of the exciplex emission (*vide infra*). Therefore, the quantum yield of the exciplex emission ($\varphi_{Ex}^F\textbf{1}$) for the DCN–1 pair was determined by extrapolation of emission intensities at [**1**] ≤ 0.01 mol dm^{-3} to infinite concentration. On the other hand, the exciplex emission of the DCN–2 pair showed a continuous increase of intensity accompanied by retention of an isoemissive point without concentration quenching to reach a constant intensity at [**1**] = 0.1–0.3 mol dm^{-3}. In this case, therefore, the quantum yield of exciplex emission ($\varphi_{Ex}^F\textbf{2}$ was directly estimated from the emission intensity at [**2**] = 0.2 mol
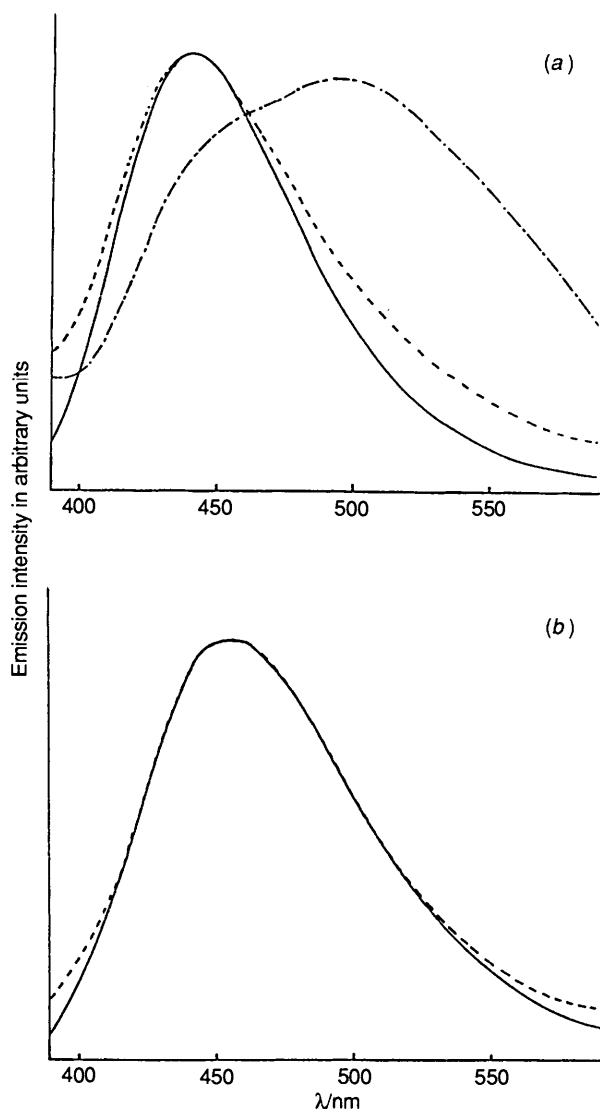
Fig. 1 Normalised exciplex emission spectra: (a) for cyclohexane solutions of the DCN-1 (– – – –) and DCN-2 (———) pairs at 300 K and for methylcyclohexane solution of the DCN-1 pair (— · — · —) at 228 K; (b) for dibutyl ether solutions of the DCN-1 (– – – –) and DCN-2 (———) pairs at 300 K. [DCN] = 2 × 10⁻⁴ mol dm⁻³, [1] = 0.8 mol dm⁻³ at 300 K or 0.35 mol dm⁻³ at 228 K and [2] = 0.20 mol dm⁻³ in dibutyl ether or 0.25 mol dm⁻³ in cyclohexane. The spectra were recorded by excitation at 330 nm after correction for the spectral response of the instrument.

Table 1 Kinetic parameters for fluorescence quenching and properties of exciplex emissions

	Solvent[a]	
	C_6H_{12}	Bu_2O
$K_{SV}^{S\,b}/dm^3\ mol^{-1}$	48.0	39.2
$k_1{}^c/10^9\ dm^3\ mol^{-1}\ s^{-1}$	14.5	14.5
$\lambda_{max}^{EX\,d}/nm$	441	454
$\tau_{E1}{}^e/ns$	12.1	7.8
$\tau_{E2}{}^e/ns$	57.9	59.3
$\varphi_{EX}^{F\,f}$ 1	0.19	0.068
2	0.35	0.17
α^g	0.53	0.40

[a] C_6H_{12} = cyclohexane and Bu_2O = dibutyl ether. [b] Stern–Volmer constants for quenching of DCN fluorescence by 1. [c] Quenching rate constants obtained by dividing K_{SV}^{S} values by the lifetimes of DCN fluorescence (3.3 ns in C_6H_{12} and 2.7 ns in Bu_2O). [d] Exciplex emission maxima. [e] Exciplex emission lifetimes for the DCN-1 and DCN-2 pairs. [f] Exciplex emission quantum yields for the DCN-1 and DCN-2 pairs. [g] $\varphi_{EX}^{F}1/\varphi_{EX}^{F}2$.
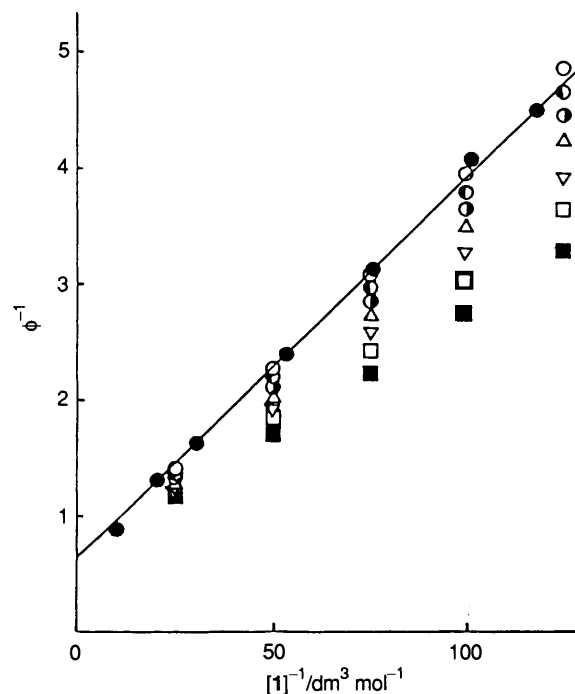
Fig. 2 Observed double-reciprocal plot of quantum yields for the photosensitised formation of 2 vs. concentration of 1 in cyclohexane (●) and calculated values at a = 0.0 (○), 0.1 (◐), 0.2 (◑), 0.3 (△), 0.5 (▽), 0.7 (□) and 1.0 (■); [DCN] = 1.0 mmol dm⁻³; irradiation at 313 nm

Table 2 Photosensitised isomerisation of 1 by DCN[a]

	Solvent	
	C_6H_{12}	Bu_2O
$S/mol\ dm^{-3}$	0.033	0.062
I	0.66	1.3
$I/S/dm^3\ mol^{-1}$	20	21
φ_{iso}^{lim} (1/I)	1.5	0.77

[a] The slopes (S) and intercepts (I) of the observed plots in Figs. 2 and 3 and the limiting quantum yields (φ_{iso}^{lim}) for the formation of 2.

dm⁻³, where DCN fluorescence is completely quenched. It was found that the exciplex emission of the DCN-2 pair in the presence of 0.25 mol dm⁻³ 2 is quenched by 1 with Stern–Volmer constants (K_{SV}^{E2}) of 20.7 dm³ mol⁻¹ in dibutyl ether and 35 dm³ mol⁻¹ in cyclohexane. Table 1 summarises the Stern–Volmer constants (K_{SV}^{S}) and rate constants (k_1) for the quenching of DCN fluorescence by 1, the exciplex emission maxima (λ_{max}^{EX}), the observed lifetimes (τ_{E1} and τ_{E2}) and quantum yields ($\varphi_{EX}^{F}1$ and $\varphi_{EX}^{F}2$) of exciplex emission, and the probabilities for the exciplex isomerisation of DCN-1 to DCN-2 ($\alpha = \varphi_{EX}^{F}1/\varphi_{EX}^{F}2$).

Photosensitised Isomerisation of 1.—Irradiation of cyclohexane or dibutyl ether solutions of DCN and 1 at 313 nm gave 2 as the only detectable product with >95% material balance at ≤20% conversions of 1. Figs. 2 and 3 show double-reciprocal plots of quantum yield for 2 formation vs. 1 concentration in cyclohexane and dibutyl ether, respectively. Table 2 lists the intercepts (I), slopes (S), intercept-to-slope ratios (I/S) and limiting quantum yields (φ_{iso}^{lim} = 1/I). It was found that 1 disappears upon irradiation in the presence of a large excess of 2 (0.25 mol dm⁻³) under the conditions where DCN fluorescence is exclusively quenched by an excess of 2 but not appreciably by
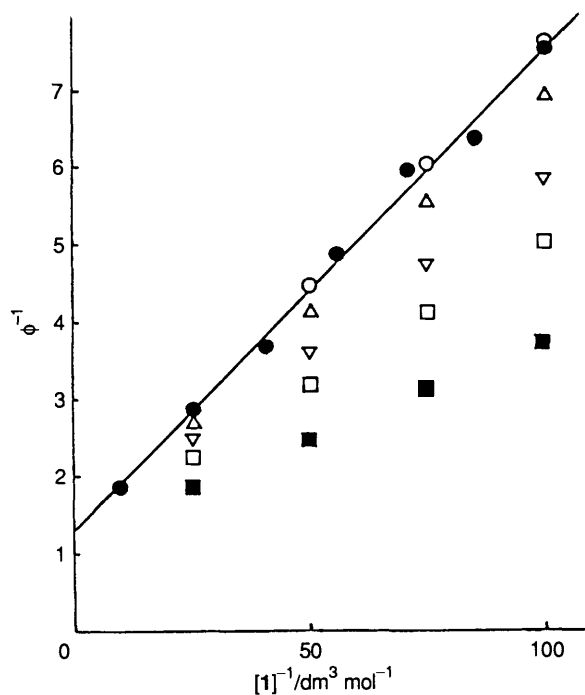
Fig. 3 Observed double-reciprocal plot of quantum yields for the photosensitised formation of **2** vs. concentration of **1** in dibutyl ether (●) and calculated values at $a = 0.0$ (○), 0.1 (△), 0.3 (▽), 0.5 (□) and 1.0 (■); [DCN] = 1.0 mmol dm⁻³; irradiation at 313 nm

Fig. 5 Observed Stern–Volmer plot for quenching of the photosensitised isomerisation of **1** by **3** in cyclohexane (●) and calculated values at $a = 0.0$ (○), 0.1 (◐), 0.2 (◑), 0.3 (△), 0.5 (▽), 0.7 (□) and 1.0 (■); [DCN] = 1.0 mmol dm⁻³ and [**1**] = 0.1 mol dm⁻³; irradiation at 313 nm
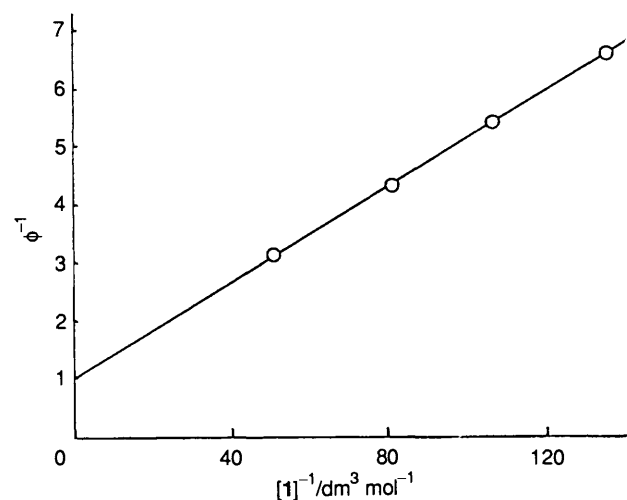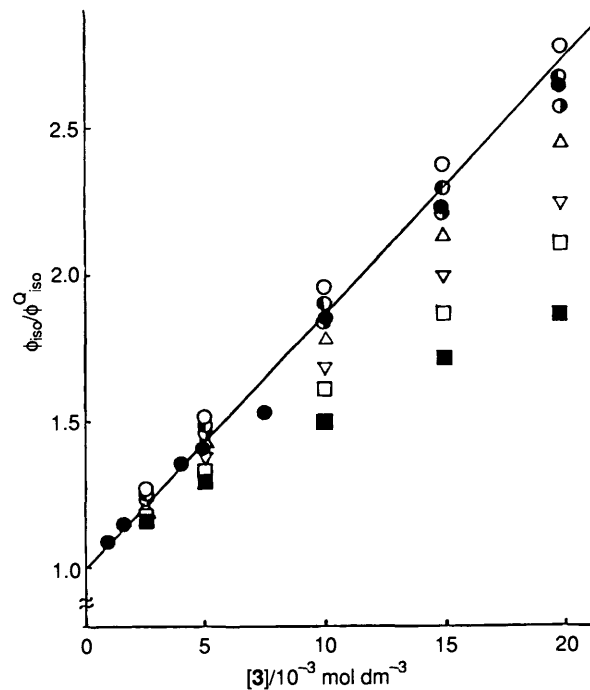

Fig. 4 Double-reciprocal plot of quantum yields for the photosensitised disappearance of **1** vs. concentration of **1** in dibutyl ether; [DCN] = 1.0 mmol dm⁻³ and [**2**] = 0.25 mol dm⁻³; irradiation at 313 nm
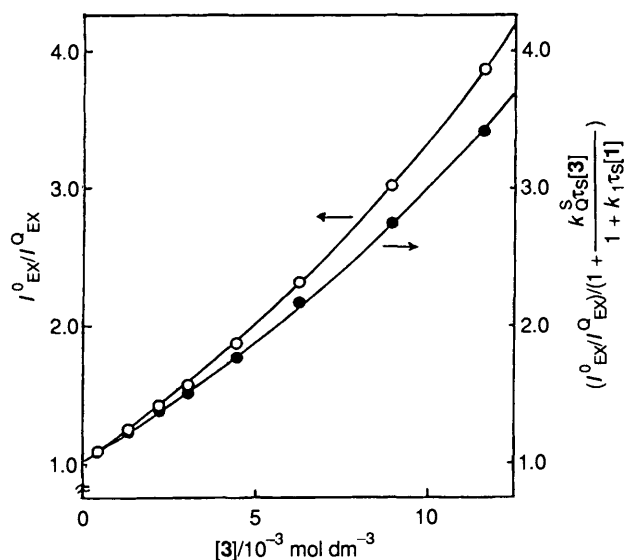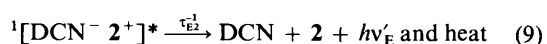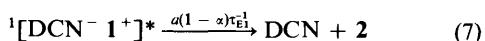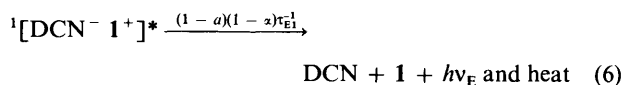

Fig. 6 Stern–Volmer plot for net quenching of the exciplex emission of the DCN–1 pair by **3** at [**1**] = 0.1 mol dm⁻³ (○) and one calculated by subtracting the contribution of ¹DCN* quenching (●)

1. The isomerisation of **1** to **2** should be responsible for the disappearance of **1** since no other products were detected by GLC. Fig. 4 shows a double-reciprocal plot of quantum yield for the disappearance of **1** vs. concentration of **1** ($\leqslant 0.02$ mol dm⁻³) for the photoreaction in the presence 0.25 mol dm⁻³ **2** in dibutyl ether.

Quenching by 1,2,4-Trimethoxybenzene.—The DCN-photosensitised isomerisation of **1** was efficiently quenched by 1,2,4-trimethoxybenzene **3**. A Stern–Volmer plot is shown in Fig. 5. Quenching of either DCN fluorescence or the exciplex emission of the DCN–2 pair by **3** also occurred efficiently to give linear Stern–Volmer plots with respective slopes of 65 and 690 dm³ mol⁻¹ in cyclohexane. On the other hand, a Stern–Volmer plot for the quenching of the exciplex emission of the DCN–1 pair

by **3** is deviated upwards from a linear correlation, as shown in Fig. 6.

Discussion

General Mechanistic Considerations.—The major and minor emissions of the DCN–1 pair at room temperature [Fig. 1(a)] can be attributed to the DCN–2 and DCN–1 exciplexes, respectively. It was confirmed that the contamination by **2**, present in the purified sample of **1** used, is below GLC detection limits and also that the addition of 1.0 mol% **2** to a solution of **1** did not affect the emission spectrum. It is therefore evident that the DCN-photosensitised isomerisation of **1** involves the adiabatic pathway from the DCN–1 to the DCN–2 exciplex.

The probabilities of the adiabatic pathway (α) can be represented by $\varphi_{EX}^{F}1/\varphi_{EX}^{F}2$ and are listed in Table 1. Usually, the photosensitised isomerisation of 1 by aromatic nitriles has been discussed in terms of the adiabatic and non-adiabatic reactions of a sensitiser–1 exciplex followed by the radiative and non-radiative decays of the product exciplex [eqns. (4)–(9)].

$$DCN \xrightarrow{h\nu} {}^{1}DCN^{*} \xrightarrow{\tau_{S}^{-1}} DCN + h\nu' \text{ and heat} \quad (4)$$

$${}^{1}DCN^{*} + 1 \xrightarrow{k_{1}} {}^{1}[DCN^{-}\ 1^{+}]^{*} \quad (5)$$

$${}^{1}[DCN^{-}\ 1^{+}]^{*} \xrightarrow{(1-a)(1-\alpha)\tau_{E1}^{-1}}$$
$$DCN + 1 + h\nu_{E} \text{ and heat} \quad (6)$$

$${}^{1}[DCN^{-}\ 1^{+}]^{*} \xrightarrow{a(1-\alpha)\tau_{E1}^{-1}} DCN + 2 \quad (7)$$

$${}^{1}[DCN^{-}\ 1^{+}]^{*} \xrightarrow{\alpha\tau_{E1}^{-1}} {}^{1}[DCN^{-}\ 2^{+}]^{*} \quad (8)$$

$${}^{1}[DCN^{-}\ 2^{+}]^{*} \xrightarrow{\tau_{E2}^{-1}} DCN + 2 + h\nu_{E}' \text{ and heat} \quad (9)$$

However, this simple mechanism cannot explain the marked discrepancies between I/S and K_{SV}^{S} or the limiting quantum yield in cyclohexane, which is larger than unity. Moreover, it is of mechanistic importance to note that the isomerisation of 1 does occur in the presence of 2 in large excess where 1 cannot interact with ${}^{1}DCN^{*}$ but only with the DCN–2 exciplex that has been primarily formed by exclusive quenching of ${}^{1}DCN^{*}$ by 2. The intercept/slope value obtained from Fig. 4 is 23 dm³ mol⁻¹, which is in excellent agreement with the Stern–Volmer constant ($K_{SV}^{E2} = 21.7$ dm³ mol⁻¹) for quenching of the DCN–2 exciplex emission by 1 in the presence of 2 at 0.25 mol dm⁻³ in dibutyl ether.†

On the basis of these observations, the mechanism shown in eqns. (4)–(11) is taken into consideration for kinetic analysis.

$${}^{1}[DCN^{-}\ 2^{+}]^{*} + 1 \xrightarrow{\beta k_{2}} {}^{1}[DCN^{-}\ 2^{+}]^{*} + 2 \quad (10)$$

$${}^{1}[DCN^{-}\ 2^{+}]^{*} + 1 \xrightarrow{(1-\beta)k_{2}}$$
$$DCN + (1+b)2 + (1-b)1 \quad (11)$$
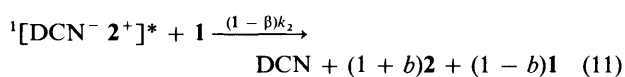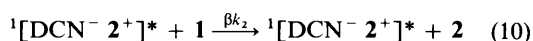
The rate parameters given in these equations are defined as follows: k_{1} = rate constant for quenching of DCN fluorescence by 1 (i.e. formation of the DCN–1 exciplex); τ_{E1} = lifetime of the DCN–1 exciplex; α = probability for the adiabatic isomerisation of DCN–1 to DCN–2; a = fraction for the non-adiabatic isomerisation of the DCN–1 exciplex; τ_{E2} = lifetime of the DCN–2 exciplex; $(1-\beta)k_{2}$ = rate constant for net quenching of the DCN–2 exciplex by 1; β = probability for the 1→2 isomerisation catalysed by the DCN–2 exciplex without its decay; b = fraction for the 1→2 isomerisation occurring in net quenching of the DCN–2 exciplex by 1. A steady-state assumption gives eqn. (12) for the quantum yield of the DCN-photosensitised isomerisation of 1, eqn. (13) for the quenching of DCN fluorescence by 1, eqn. (14) for the quenching of DCN–2 exciplex emission by 1 in the presence of 0.25 mol dm⁻³ 2, and

† For cyclohexane solution, the intercept/slope value in a double-reciprocal plot of quantum yield for the disappearance of 1 vs. concentration of 1 is 18 dm³ mol⁻¹, which is substantially different from the Stern–Volmer constant (35 dm³ mol⁻¹) for quenching of the DCN–2 exciplex emission by 1. This discrepancy is reproducible, suggesting the participation of other unreclaimed pathway(s) in cyclohexane. Unfortunately, all attempts to explore the mechanistic origin failed.

eqn. (15) for the quantum yield of 1 disappearance by the photoreaction in the presence of 0.25 mol dm⁻³ 2.

$$\varphi_{iso} = \left(\frac{k_{1}\tau_{S}[1]}{1 + k_{1}\tau_{S}[1]}\right)\left[(1-\alpha)a + \right.$$
$$\left. \alpha\left\{\frac{1 + (1 + b - b\beta)k_{2}\tau_{E2}[1]}{1 + (1 - \beta)k_{2}\tau_{E2}[1]}\right\}\right] \quad (12)$$

$$\frac{I_{0}^{S}}{I_{1}^{S}} = 1 + K_{SV}^{S}[1] = 1 + k_{1}\tau_{S}[1] \quad (13)$$

$$\frac{I_{0}^{E2}}{I_{2}^{E2}} = 1 + K_{SV}^{E2}[1] = 1 + (1 - \beta)k_{2}\tau_{E2}[1] \quad (14)$$
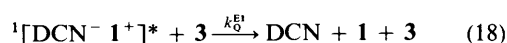
$$\varphi_{iso}^{E2} = \frac{(b - b\beta + \beta)k_{2}\tau_{E2}[1]}{1 + (1 - \beta)k_{2}\tau_{E2}[1]} \quad (15)$$

Kinetic Analysis.—Although the probabilities (α) of the adiabatic isomerisation of the DCN–1 exciplex to DCN–2 have been experimentally determined, the contributions of the non-adiabatic pathway (a) cannot be directly obtained from the experimental data. In order to estimate the values of a, numerical calculations of φ_{iso} were performed with various sets of arbitrary values of a, b and β using the observed values of $K_{SV}^{S}(k_{1}\tau_{S})$, $K_{SV}^{E2}[(1-\beta)k_{2}\tau_{E2}]$ and $\varphi_{EX}^{F}1/\varphi_{EX}^{F}2(\alpha)$ and eqn. (16)
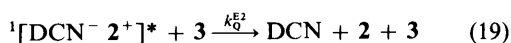
$$\varphi_{iso}^{lim} = 1/I = (1 - \alpha)a + \alpha\left(\frac{1 + b - b\beta}{1 - \beta}\right) =$$
$$\begin{cases} 1.5 \text{ in cyclohexane} \\ 0.77 \text{ in dibutyl ether} \end{cases} \quad (16)$$

for the limiting quantum yields of the isomerisation of 1. The calculated values of φ_{iso} at various concentrations of 1 are in good agreement with the observed values when $a \leqslant 0.2$ with any sets of b and β for cyclohexane solution and when $a = 0.0$ with any sets of b and β for dibutyl ether solution, as shown in Figs. 2 and 3. It should be noted that discrepancies between the calculated and the observed values increase with the increase of a independently of b and β. That is to say, the contribution of the non-adiabatic isomerisation [eqn. (7)] should be unimportant or negligible in the mechanistic pathways from the DCN–1 exciplex. Calculations with $a \leqslant 0.2$ in cyclohexane indicate that $0.4 \leqslant \beta \leqslant 0.65$ depending on b, suggesting the significant participation of eqn. (10), which might be mainly responsible for $\varphi_{iso}^{lim} > 1.0$ in cyclohexane. In dibutyl ether, β ranges from 0.0 with $b = 1.0$ to 0.5 with $b = 0.0$.

Either DCN fluorescence or the exciplex emission of the DCN–2 pair is quenched by 3 at a diffusion-controlled limit [$(1.2–2.2) \times 10^{10}$ dm³ mol⁻¹ s⁻¹] in cyclohexane and dibutyl ether. In cyclohexane solution, however, quenching of the exciplex emission of the DCN–1 pair by 3 in the presence of 0.1 mol dm⁻³ 1 gives a non-linear Stern–Volmer plot even after the contribution of ${}^{1}DCN^{*}$ quenching has been substracted, indicating the participation of two more quenchable species— probably DCN–1 and DCN–2 exciplexes. If we assume eqns. (17)–(19) for the quenching, we obtain eqn. (20) for quenching of the exciplex emission of the DCN–1 pair and eqn. (21) for quenching of the DCN-photosensitised isomerisation.

$${}^{1}DCN^{*} + 3 \xrightarrow{k_{0}^{S}} DCN + 3 \quad (17)$$

$${}^{1}[DCN^{-}\ 1^{+}]^{*} + 3 \xrightarrow{k_{0}^{E1}} DCN + 1 + 3 \quad (18)$$

$$^1[DCN^- \ 2^+]^* + 3 \xrightarrow{k_Q^{E2}} DCN + 2 + 3 \qquad (19)$$

$$\frac{I_{EX}^0}{I_{EX}^Q} = \left(1 + \frac{k_Q^S \tau_S[3]}{1 + k_1 \tau_S[1]}\right)(1 + k_Q^{E1}\tau_{E1}[3]) \times$$
$$\left(1 + \frac{k_Q^{E2}\tau_{E2}[3]}{1 + (1-\beta)k_2\tau_{E2}[1]}\right) \qquad (20)$$

$$\varphi_{iso}^Q = \left(\frac{k_1\tau_S[1]}{1 + k_1\tau_S[1] + k_Q^S\tau_S[3]}\right)\left(\frac{1}{1 + k_Q^{E1}\tau_{E1}[3]}\right) \times$$
$$\left[(1-\alpha)a + \alpha\left\{\frac{1 + (1 + b - b\beta)k_2\tau_{E2}[1] + k_Q^{E2}\tau_{E2}[3]}{1 + (1-\beta)k_2\tau_{E2}[1] + k_Q^{E2}\tau_{E2}[3]}\right\}\right]$$

$$(21)$$

Analysis of the non-linear Stern–Volmer plot in Fig. 6 gives values for $k_Q^{E1}\tau_{E1}$ and $k_Q^{E2}\tau_{E2}$ of 12 ± 2 dm³ mol⁻¹ and 745 ± 10 dm³ mol⁻¹, respectively. The latter is in reasonable agreement with the value (690 dm³ mol⁻¹) obtained from quenching of the exciplex emission of the DCN–2 pair by 3. If the DCN–1 exciplex is quenched by 3 at a diffusion-controlled limit, the lifetime of the exciplex should be *ca.* 1 ns at room temperature, which might be in line with the appearance of a very weak emission from the DCN–1 exciplex at room temperature. In dibutyl ether, on the other hand, quenching of the exciplex emission of the DCN–1 pair by 3 gives a linear Stern–Volmer plot after correction for ^{1}DCN* quenching. In this solvent, therefore, the lifetime of the DCN–1 exciplex should be much shorter than 1 ns, perhaps reflecting the lack of DCN–1 exciplex emission in the total emission of the DCN–1 pair, as shown in Fig. 1(*b*). At any rate, however, contributions from quenching of the DCN–1 exciplex should be negligible in the net quenching of the photosensitised reaction at $[3] \leqslant 0.01$ mol dm⁻³. On the basis of eqns. (12) and (21), numerical calculations of $\varphi_{iso}/\varphi_{iso}^Q$ in cyclohexane were performed with various sets of a, b and β using the known kinetic parameters. Reasonable agreements were obtained between the calculated and observed values of $\varphi_{iso}/\varphi_{iso}^Q$ at various concentrations of 3 when $a \leqslant 0.2$ with any sets of b and β, as shown in Fig. 6. Unfortunately, the exact values of β cannot be obtained from the available data, since both φ_{iso} and φ_{iso}^Q are almost independent in any given sets of b and β because of mutual compensation.

Further Considerations on Mechanism and Reactivities.—It should be noted that the adiabatic isomerisation of the DCN–1 exciplex is relatively efficient ($\alpha = 0.53$ or 0.40), while the contribution of the non-adiabatic pathway is minor or negligible ($a \ll 1$). This behaviour of the DCN–1 exciplex would arise from the high charge-transfer character [as expected from the very positive reduction potential of ^{1}DCN* (2.17 V *vs.* SCE)[14]] compared with the excited singlet state of other aromatic nitriles such as 1-cyanonaphthalene (1.77 V) and 9,10-dicyanoanthracene (1.99 V). Consequently, the population density of positive charge on 1 might be high enough to bring about a large skeletal distortion of the molecule,[12] thereby lowering the activation barrier for the adiabatic isomerisation. On the other hand, charge-transfer stabilisation of the DCN–1 exciplex should be also large enough to result in a small energy gap between an exciplex minimum and the ground-state surface which might open up decay channels to the ground-state precursors. The estimated lifetimes of the DCN–1 exciplex in cyclohexane (*ca.* 1 ns) and in the more polar dibutyl ether ($\ll 1$ ns) might reflect the faster non-radiative decay of the exciplex in the latter solvent as the consequence of greater solvation stabilisation.

Another notable observation of mechanistic significance is that the isomerisation of 1 to 2 is 'photosensitised' by the

product exciplex formed through the adiabatic pathway, presumably *via* the hypothesised triplex $^1[DCN^- \ 2^{(1-\delta)+} \ 1^{\delta+}]^*$, as suggested for the photosensitised reactions of diarylcyclobutanes and quadricyclane by DCN in arene solvents.[15] This triplex is a particular case of DCN–arene–1 triplexes assumed for the photosensitised isomerisation of 1 associated with quenching of DCN–arene exciplexes.[1] The adiabatic isomerisation of the triplex should regenerate the DCN–2 exciplex accompanied by the formation of 2. The kinetic analysis suggests that the DCN–2 exciplex is regenerated after catalysis of the 1 isomerisation—particularly in cyclohexane, since the possible value of β should be 0.4–0.65. Unfortunately, the possible contribution of the non-adiabatic 'triplex' isomerisation cannot be discussed since the values of b have not been determined.

An alternative mechanism for termolecular interaction between the DCN–2 exciplex and 1 would be the exciplex substitution[16] that gives the DCN–1 exciplex in place of DCN–2 in eqn. (10). Numerical calculations on the basis of this mechanism again indicate that the increase of a leads to an increase in discrepancies between the calculated and observed values of φ_{iso}. However, the minimum value of a in cyclohexane is limited to 0.38 with the maximum value of β (1.0) (*i.e.* the complete exciplex substitution). Even with these extreme values, calculations still indicate 12–15% discrepancies between the calculated and observed values of φ_{iso} at various concentrations of 1. In the case of dibutyl ether solution, the calculated values are still higher by *ca.* 10% than the observed quantum yields at various concentrations of 1 when $a = 0.11$ and $\beta = 1.0$. The complete exciplex substitution of DCN–2 with 1 is therefore an unacceptable mechanism.

Alternatively, the photosensitised isomerisation would proceed by an electron-transfer mechanism which involves the isomerisation of the cation radical of 1 to that of 2, followed by electron exchange between the latter and a neutral molecule of 1.[7,10,11] However, this mechanism is very unlikely to operate in non-polar cyclohexane solvent and cannot explain why the limiting quantum yield in more polar dibutyl ether is substantially lower than that in non-polar cyclohexane. Another possible explanation for the limiting quantum yield of larger than unity in cyclohexane and for the discrepancy between I/S and K_{SV}^S is that the isomerisation of 1 would be catalysed in the dark by photogenerated acidic impurities. However, this is clearly not the case, since the photosensitised isomerisation is not appreciably affected by added pyridine at 0.01 mol dm⁻³ where quenching of either DCN fluorescence or exciplex emission by pyridine is negligible.

Experimental

Materials.—Hexamethyl-(Dewar benzene) (Aldrich) was distilled under vacuum from LiAlH₄ according to a published method.[11] Hexamethylbenzene (Nakarai Tesque) was purified by recrystallisation from methanol followed by vacuum sublimation. 1,2,4-Trimethoxybenzene (Nakarai Tesque) was distilled under vacuum from sodium. 1,4-Dicyanonaphthalene was prepared from 1,2-bis(cyanomethyl)benzene and N,N'-di-t-butylglyoxaldiamine according to a literature method[17] and was purified by repeated recrystallisation from benzene.

Fluorescence Measurements.—A solution (4 cm³) of DCN (*ca.* 2.0×10^{-4} mol dm⁻³) and 1 or 2 at the requisite concentration was introduced into a quartz cell and deaerated by being bubbled with argon for 15 min; the cell was then sealed with a septum. Fluorescence measurements were performed on a Hitachi 850 spectrofluorimeter after correction of the spectral response of the instrument. The fluorescence lifetimes were determined on a Horiba NAES-1100 time-resolved spectrofluorimeter after deconvolution.

Photoreactions and Determination of Quantum Yields.—All the flasks, pipettes and irradiation tubes were soaked in dilute ammonia water, thoroughly washed with distilled water and then dried in a desiccator *in vacuo.* Solutions (4 cm^3) of DCN (*ca.* 1.0 mmol dm^{-3}) and **1** at 8×10^{-3}–0.1 mol dm^{-3} (and **2** at 0.25 mol dm^{-3}) in cyclohexane or dibutyl ether were deaerated by being bubbled with argon and then irradiated through a 10 mm path-length of potassium chromate filter solution (0.2 g dm^{-3}) with an Eikosha PIH-300 high-pressure mercury lamp under cooling with water using a 'merry-go-round' turntable. Photoreactions were followed by GLC on a Shimadzu GC-7A gas chromatograph using a 1 m column of 3% Silicone OV-17 on Chromosorb W after treatment with pyridine. A potassium tris(oxalato)iron(III) actinometer was used for the determination of quantum yields.

Acknowledgements

References

1 Part 48, Y. Masaki, Y. Uehara, S. Yanagida and C. Pac, *Chem. Lett.*, 1990, 1339.
2 E. E. Van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, 1962, **84**, 3789; 1963, **85**, 3297.
3 M. J. Goldstein and R. S. Leight, *J. Am. Chem. Soc.*, 1977, **98**, 8112.
4 M. D. Newton, J. M. Schulman and M. M. Manus, *J. Am. Chem. Soc.*, 1974, **96**, 7579; M. J. S. Dewar, S. Kirschner and H. W. Kollmar, *J. Am. Chem. Soc.*, 1974, **96**, 7579.
5 W. J. le Noble, K. Brower, C. Brower and S. Chang, *J. Am. Chem. Soc.*, 1982, **104**, 3510.
6 G. Bieri, E. Heilbronner, T. Kobayashi, A. Schmelzer, M. J. Goldstein, R. S. Leight and M. S. Lipton, *Helv. Chim. Acta*, 1976, **59**, 2657.
7 T. R. Evans, R. W. Wake and M. M. Sifrain, *Tetrahedron Lett.*, 1973, 701.
8 G. N. Taylor, *Z. Phys. Chem. Neue Folge*, 1976, **101**, 237.
9 G. Jones and S.-H. Chiang, *J. Am. Chem. Soc.*, 1979, **101**, 7421; *Tetrahedron*, 1981, **37**, 3397.
10 G. Jones and W. G. Becker, *J. Am. Chem. Soc.*, 1981, **103**, 4360; 1983, **105**, 1276.
11 N. J. Peacock and G. B. Schuster, *J. Am. Chem. Soc.*, 1983, **105**, 3632.
12 H. D. Roth, M. L. M. Schilling and K. Raghavachari, *J. Am. Chem. Soc.*, 1984, **106**, 253.
13 E. Roman, S. Hernandez and M. J. Barrera, *J. Chem. Soc., Chem. Commun.*, 1984, 1067.
14 S. L. Mattes and S. Farid, *Org. Photochem.*, 1983, **6**, 233.
15 C. Pac, *Pure Appl. Chem.*, 1986, **58**, 1249.
16 R. A. Caldwell, D. Creed, D. C. DeMarco, L. A. Melton, H. Ohta and P. H. Wine, *J. Am. Chem. Soc.*, 1980, **102**, 2369.
17 L. Heiss, E. F. Paulus and H. Lehling, *Liebigs Ann. Chem.*, 1980, 1583.