# Evidence of an Ion-pair Charge-transfer Complex between 9,10-Dicyanoanthracene and 1,4-Dimethylnaphthalene in Acetonitrile, studied by Photoinduced Charge-recombination Luminescence and by Direct Photoexcitation Luminescence Techniques

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Photoinduced charge-recombination luminescence studies of preirradiated solid solutions of 9,10-dicyanoanthracene (DCA) and 1,4-dimethylnaphthalene (DMN) in acetonitrile at 77 K indicate that in this polar solvent the excited charge-transfer complex formed between DCA and DMN is an ion-pair form which dissociates into $DCA^{-\bullet}$ and $DMN^{+\bullet}$ upon irradiation at ≥420 nm. These results complement reported e.s.r. and optical absorption data and further support the postulate of photogeneration of radical ions ($DCA^{-\bullet}$ and $DMN^{+\bullet}$) as intermediates in polar solvents for the DCA-sensitized photo-oxygenation of DMN. Phosphorescence and fluorescence techniques give evidence of the formation of a charge-transfer complex upon excitation, with DMN as donor and DCA as acceptor. The formation of $O_2^{-\bullet}$ and $^1O_2{}^*$ proceeds from this excited charge-transfer complex.

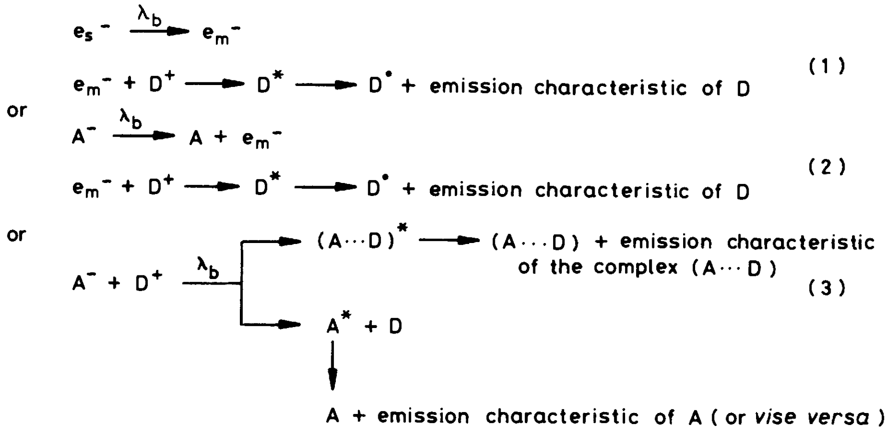
Electron-transfer quenching of singlet sensitizers such as 9,10-dicyanoanthracene (DCA) by aromatic compounds such as 1,4-dimethylnaphthalene (DMN) in photo-oxygenation reactions has aroused some interest.[1–6] In polar solvents such as acetonitrile, photogeneration of radical ions ($DCA^{-\bullet}$ and $DMN^{+\bullet}$) as intermediates has been postulated, and evidence for the photochemical formation of the sensitizer radical anion ($DCA^{-\bullet}$) has recently been obtained by e.s.r.[7] and optical absorption[8] analytical techniques.

Stimulated or photoinduced charge-recombination luminescence (r.l.) has also proved to be a good analytical technique,[9] which complements the two classical ones. In rigid matrices at 77 K, in the dark, transient species such as solvated electrons ($e_s^-$), acceptor anions ($A^{-\bullet}$), or donor cations ($D^{+\bullet}$) produced by irradiation are stabilized and their lifetime can be long (minutes or hours); this facilitates their detection. The photoinduced charge-recombination luminescence technique consists of photo-detaching solvated electrons and inducing charge-recombination luminescence (Scheme 1).

The bleaching wavelength $\lambda_b$ is situated in the optical absorption band of $e_s^-$ or of $A^{-\bullet}$. The r.l. excitation spectrum, $I_{r.l.} = f(\lambda_b)\lambda_{em}$ (em = emission), obtained by viewing the charge-recombination luminescence at a constant analytical wavelength, $\lambda_{em}$ (usually $\lambda_{max.}$ of the r.l. emission band), and recorded as luminescence intensity as a function of $\lambda_b$, provides information concerning *only* the negative stabilized species: $e_s^-$ or $A^{-\bullet}$. However, the r.l. emission spectrum, $I_{r.l.} = f(\lambda_{em})\lambda_b$, gives information concerning the neutralized cation.

One of us (J. S.),[5,10] in studies of DCA-sensitized photo-oxidations of aromatic compounds, has provided chemical evidence for the involvement of both $^1O_2$-mediated and electron-transfer mechanisms. Foote[11] has demonstrated directly by laser spectroscopy that DCA can sensitize the formation of $^1O_2$ in substantial yield by several mechanisms. More recently, Davidson,[12] in studies of DCA-sensitized photo-oxidation of di-t-butyl sulphide and citronellol, and Foote,[13] in studies of the photo-oxygenation of several alkyl-substituted olefins by using the solvent deuterium isotope effect, have presented evidence for the intermediacy of $^1O_2$ in these photo-oxidations. Although these results demonstrate that DCA acts as an $^1O_2$ sensitizer, the interpretation of these oxidation reactions (and of the formation of $^1O_2$ in particular) has not been substantially clarified.

We have studied the photochemical reaction of DCA with



**Scheme 1.** Photoinduced charge-recombination luminescence mechanism; m = mobile; $\lambda_b$ refers to bleaching; s = solvated

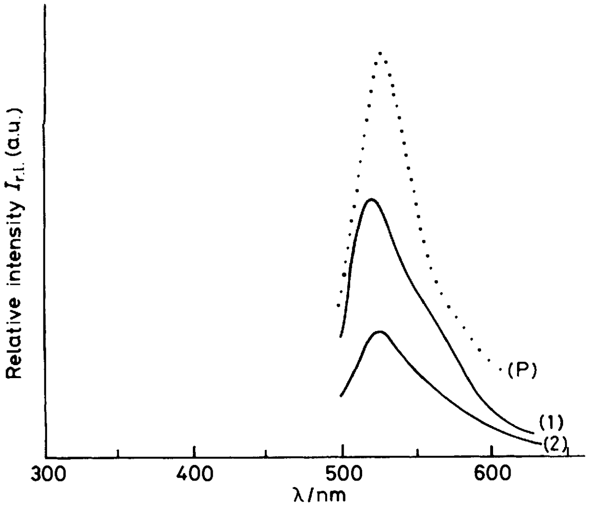


**Figure 1.** The r.l. emission spectrum $I_{r.l.} = f(\lambda_{em})\lambda_b$ of preirradiated DCA–DMN in acetonitrile at 77 K; $\lambda_b$ 480 nm: (1) 5 min after the irradiation is cut off; (2) after bleaching with $\lambda_b$ = 480 nm for 30 min; (P) phosphorescence of DCA–DMN solutions

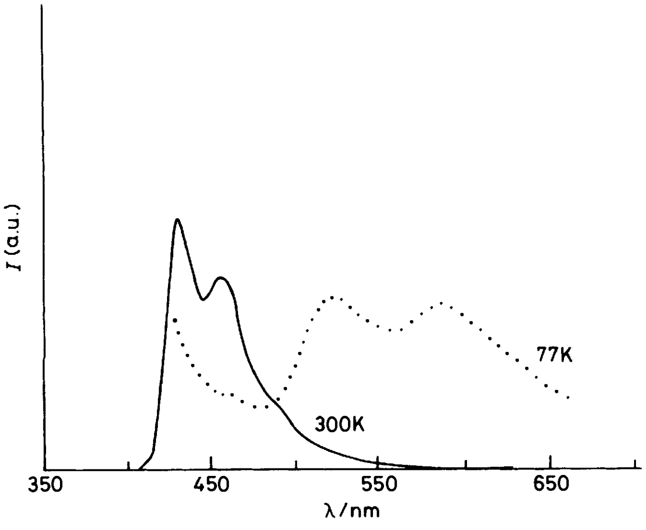


**Figure 2.** Direct luminescence emission spectra of DCA in acetonitrile at 300 and at 77 K ($\lambda_{ex}$ = 420 nm)

DMN by phosphorescence and fluorescence techniques combined with the r.l. technique. Our results provide evidence of an ion-pair charge-transfer complex between the donor DMN and the acceptor DCA upon excitation in acetonitrile. The formation of $O_2^{-\bullet}$ and $^1O_2$ proceeds from this excited charge-transfer complex.

## Results and Discussion

*Recombination Luminescence Spectra.*—Figure 1 presents the r.l. emission spectrum obtained by bleaching a preirradiated solid solution of DMN and DCA in acetonitrile kept in the dark at 77 K, with $\lambda_b$ = 480 nm ($\lambda_{max.}$ of the DCA$^{-\bullet}$ absorption).[8] The r.l. emission resembles that of the phosphorescence (curve P, Figure 1) of the exciplex (DCA ··· DMN)* and to some extent that of DCA*, which exhibits phosphorescence in the same region (Figure 2). Luminescence of DMN* can be excluded since there is not enough energy (irradiation $\geqslant$420 nm; DMN begins to absorb at $\leqslant$340 nm). Besides, the emission

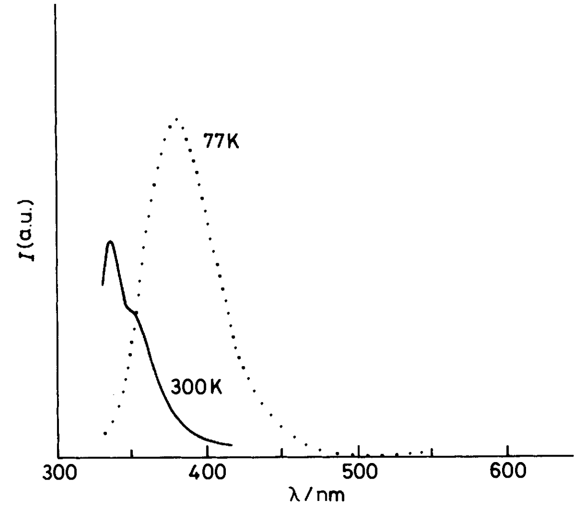


**Figure 3.** Direct luminescence emission spectra of DMN in acetonitrile at 300 and at 77 K ($\lambda_{ex}$ = 330 nm)

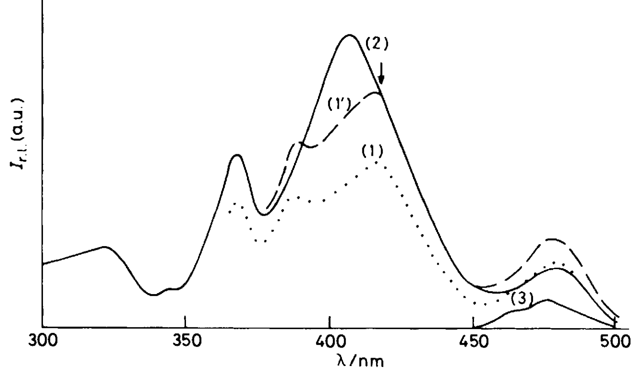


**Figure 4.** Corrected r.l. excitation spectra of preirradiated DCA–DMN in acetonitrile at 77 K; $\lambda_{em}$ = 530 nm (peak of the emission in Figure 3): (1) deaerated sample; (2) sample saturated with $O_2$; (1′) curve (1) normalized at point of curve (2) marked by arrow; (3) difference between curve (1′) and curve (2): DCA$^{-\bullet}$

of DMN at 77 K is at higher energy than the observed r.l. (Figure 3). Curve 2 in Figure 1 represents the r.l. emission after 30 min bleaching with $\lambda_b$ = 480 nm. The decrease in r.l. intensity with bleaching time indicates that there is a depletion of stabilized ionic species due to recombination [equation (3)].

Furthermore in irradiated DCA–DMN–MeCN at 77 K, the r.l. excitation spectrum $I_{r.l.} = f(\lambda_b)\lambda_{em}$ reveals the existence of the anion DCA$^{-\bullet}$ as only stabilized negative species (Figure 4). The curves in Figures 4 represent a combination of the excitation spectra of DCA$^{-\bullet}$ and (DCA···DMN)* exciplex, the luminescence and excitation spectra of which are located in this region (Figures 5 and 6). The presence of $O_2$ in the solutions scavenges the photoejected electrons; hence $O_2$ will be in competition with DCA for these electrons. The irradiated sample which contains $O_2$ therefore contains less DCA$^{-\bullet}$ than the one without $O_2$. The difference between the r.l. excitation spectra of the irradiated sample containing $O_2$ and that of the sample without $O_2$ gives the excitation spectrum of DCA$^{-\bullet}$ (curve 3, Figure 4, $\lambda_{max.}$ *ca.* 480 nm). It is interesting that DCA–DMN in non-polar solvents upon irradiation $\geqslant$420 nm at 77 K does not give any r.l. nor does the r.l. excitation spectrum reveal

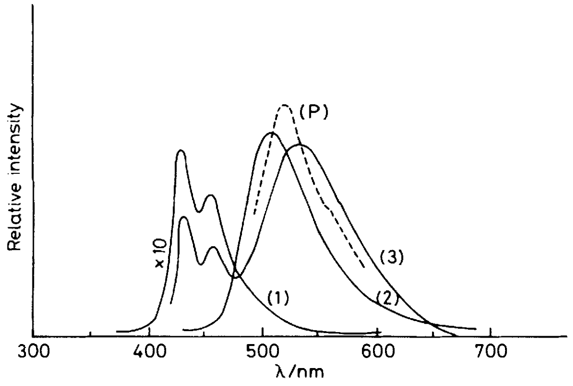


**Figure 5.** Emission spectra of deaerated solutions of DCA–DMN in acetonitrile at (1) 300 K and (2) 77 K and (3) in benzene at 300 K ($\lambda_{ex}$ = 420 nm); (P) phosphorescence (see text); [DCA] = $10^{-5}$M, [DMN] = 6.4 × $10^{-2}$M

any change in the band at *ca.* 480 nm.[14] Thus we conclude that the irradiation ⩾420 nm cannot photoionize the exciplex (DCA ··· DMN)* in non-polar solvents. In other words, in non-polar solvents, the exciplex is not in ion-pair form. The radical anion DCA$^{-\bullet}$ has an r.l. excitation band (hence an absorption band) at 480 nm, a result which is consistent with that of Spada and Foote[8] and is supported by e.s.r. data.[7] On the other hand, direct excitation luminescence studies at 300 and at 77 K of DCA–DMN solutions demonstrate that the exciplex formed by DCA and DMN upon direct excitation in the optical absorption region of DCA is a precursor state for the sensitized photo-oxygenation of DMN, as shown in Figures 5 and 6. The suggestion that a (DCA ··· DMN)* exciplex is a precursor for the sensitized photo-oxygenation of DMN has been mentioned.[15–17]

*Luminescence of DCA–DMN Solutions at* 300 *and at* 77 K.—(*a*) *Emission spectra.* Figure 5 shows the luminescence spectra of DCA–DMN upon excitation at 420 nm (the optical absorption band of DCA), at 300 and at 77 K. In the polar solvent acetonitrile the emission at 300 K consists mainly of the fluorescence of $^1$DCA* (Figure 5, curve 1) whereas in a non-polar solvent, benzene[14] for example, the emission is that of $^1$DCA* and of the exciplex $^1$(DCA ··· DMN)* (Figure 5, curve 3). In contrast, the luminescence of a rapidly frozen solution of DCA–DMN at 77 K contains only one band, centred at *ca.* 510 nm, and is independent of solvent polarity (curve 2, Figure 5). The emission band at *ca.* 520 nm is the luminescence of the exciplex, which at 77 K is shifted slightly to the blue (by *ca.* 20 nm) as compared with that at 300 K ($\lambda_{max.}$ 540 nm) because of the lack of solvent rotational reorientation in the relaxed excited state in rigid matrices.

In acetonitrile, the emission associated with $^1$DCA* observed at 300 K is completely suppressed at 77 K at the same excitation wavelength (420 nm). The phosphorescence spectrum of the exciplex at 77 K which is obtained by photon counting at each wavelength after a delay of 0.5 s after termination of the excitation (at 420 nm) is represented by curve P in Figure 5. The spectrum may also contain the phosphorescence of $^3$DCA*, the emission peaks of which are at 530 and 570 nm, *i.e.* in the same region (Figure 2).

(b) *Corrected excitation spectra.* Figure 6 presents the corrected excitation spectra at 300 and at 77 K of DCA–DMN solutions viewed at different emission wavelengths corresponding to various peaks in the emission spectra in Figure 5. When $\lambda_{em}$ = 430 or 460 nm (peak emission of $^1$DCA*), the corrected excitation spectra at 300 K resembles the optical absorption spectrum of DCA (Figure 6, curve 1). When $\lambda_{em} \simeq$ 540 nm (peak emission of the exciplex at 300 K) the excitation spectrum (curve 2 in Figure 6) is obtained. It looks similar to that of DCA except that the bands are less resolved and there is an extra band around 480 nm. The intensity of the latter (at *ca.* 480 nm) is more pronounced in acetonitrile. In non-polar solvents the 480 nm band is negligible.[14] At 77 K for non-polar as well as polar solvents only one excitation spectrum, which resembles that of the exciplex at 300 K, is obtained for any emission wavelength [430, 460, or 520 nm (the peak emission of the exciplex at 77 K)], indicating that only one excited species is responsible for the observed emission at 77 K: the exciplex (Figure 6, curve 3).

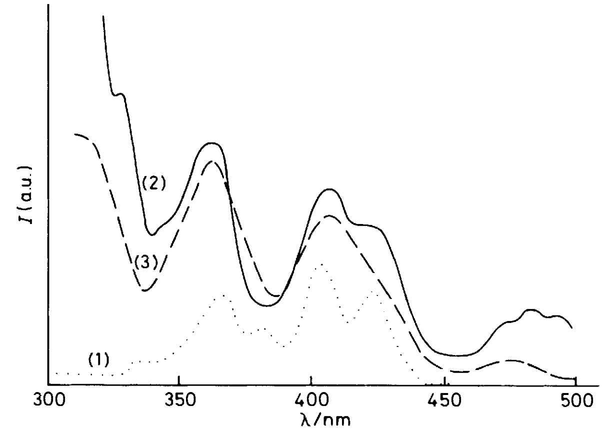
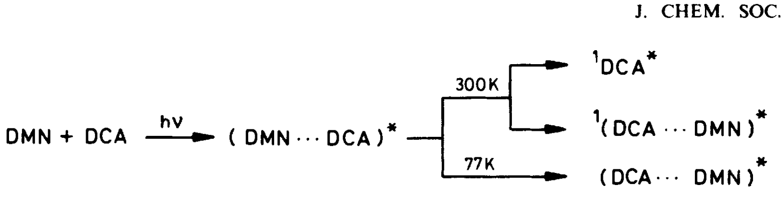


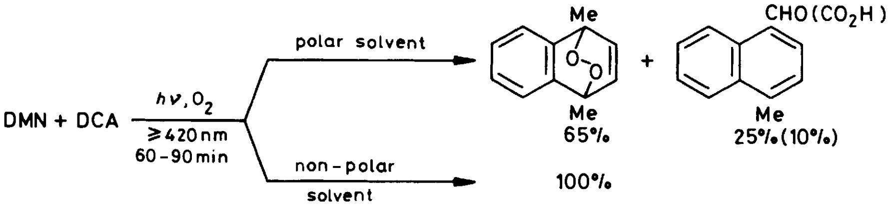
**Figure 6.** Corrected excitation spectra of DCA–DMN in various solvents: (1) $\lambda_{em}$ 430 or 460 nm ($^1$DCA* emission) at 300 K (similar to the DCA optical absorption spectrum); (2) $\lambda_{em}$ *ca.* 540 nm [$^1$(DCA ··· DMN)* emission] at 300 K in acetonitrile; (3) $\lambda_{em}$ 430, 460, or 520 nm at 77 K

One of the mechanisms which appears to operate in the electron-transfer reactions is the charge-transfer complex model,[5,12,15–19] which in some cases shows features are sensitive to solvent polarity.[5,12,15,17–19] Marcus[18] has pointed out the important role of solvent reorganization on the electron-transfer reactions in solution, and recently the importance has been demonstrated[19] of the influence of inner shell solvent reorganization on the variation of the electron-transfer rate constant with $\Delta G^\circ$, the standard free energy change of the electron-transfer reaction $D + A \longrightarrow D^{+\bullet} + A^{-\bullet}$. Truong[19] considers that the solute forms a charge-transfer complex within its solvent cage, and that any charge transfer from or to the solute will take place through this solvent cavity. In other words, in solutions the solute and its solvent cage are considered together as an unity.

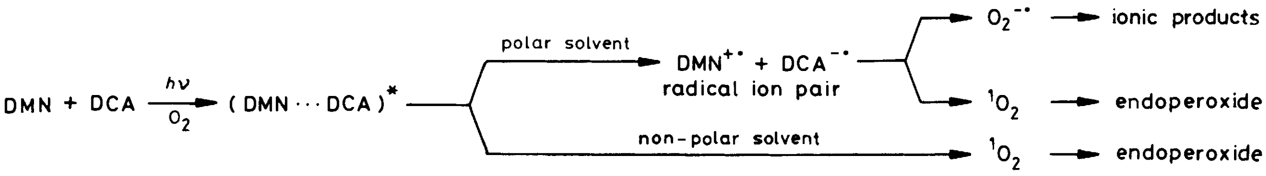
When rapidly frozen from 300 to 77 K, the solid solution of DCA–DMN retains the equilibrium solute–solvent cage configuration of the liquid solution at 300 K. The emission spectrum at 77 K upon excitation at 420 nm shows only one band, centred *ca.* 520 nm, which is associated with the exciplex (DCA ··· DMN)* (curve 2 in Figure 5), and the excitation spectrum at 77 K reveals only one emitting species, the (DCA ··· DMN)* exciplex, in polar as well as non-polar solvents. The observed results indicate that other species (dimer, trimer, *etc.* DCA or DMN itself, or corresponding species from both solutes) are absent when the solution is frozen rapidly from 300 to 77 K. Such species, if ever present, would not interfere in the investigated wavelength region. Hence, the difference between emission spectra of DCA–DMN solutions at 300 and at 77 K is due to the lack of solvent rotational reorientation during excitation at 77 K. This solvent rotational reorientation in the relaxed excited state of the solute causes rupture of outer-sphere solvent configuration which creates the activated complex and thus partially destroys the exciplexes. This gives rise to the



Scheme 2.



Scheme 3.[15]



Scheme 4.

fluorescence of the excited solvated DCA, *i.e.* DCA with its solvent cage (Figure 5). Thus there is formation and subsequent dissociation of the exciplex upon excitation. The exciplex (DCA ··· DMN)* is hence a precursor for the photo-oxidation reactions sensitized by DCA (Scheme 2).

In the case of DCA–DMN in acetonitrile, the exciplex is completely destroyed during excitation at 300 K. This is mainly due to dissociation into the ion-pair state: DCA ··· $\mathrm{DMN}^{+\cdot}$ as the r.l. results suggest [Figures 1 and 4 and equation (3)], partly due to solvent reorientation during excitation at 300 K.

Support for our results can be found in the recent work of Davidson and Pratt,[12] showing evidence of the ability of excimers and exciplexes to sensitize the photo-oxidation of di-t-butyl sulphide and citronellol, which are known to be reactive towards singlet oxygen.

*Effect of Solvent Polarity on the Ionization Energy of the Exciplex (DCA ··· DMN)* and Formation of* $^1O_2$.—Use of the photoinduced charge-recombination luminescence technique shows that the (DCA ··· DMN)* exciplex can be ionized by irradiation ≥420 nm only in the polar solvent acetonitrile, not in non-polar solvents (benzene or methylene dichloride).[14] Increasing the solvent polarity causes an increase in solute–solvent cage interactions, hence decreasing the solute ionization energy.[20] Consequently it is easier to ionize the complex (DCA ··· DMN) in acetonitrile than in benzene. Our results from photoinduced charge-recombination luminescence studies support previous suggestions that in acetonitrile the complex is in ion-pair form.[16,17,21]

As seen in Scheme 3,[15] for the DCA–DMN system in non-polar solvents the oxygenation product is the endoperoxide of the donor molecule DMN. The yield is 100%, whereas in polar solvents this yield is only 65%; the rest (35%) is oxidation products of DMN.

From these results, combined with the present observations, we suggest that, in polar solvents, the triplet species $^3$(DCA ··· DMN) and $^3$DCA are formed from charge-recombination of the radical ion pairs and not from $^1$DCA as proposed by Foote *et al.*[11,22] The work of Weller *et al.*,[23,24] giving evidence that triplet formation arises from the radical ions, further supports our conclusion. The formation of $O_2^{-\cdot}$ occurs by reaction of $O_2$ with the photodetached electron upon irradiation ≥420 nm. It is the reaction of $O_2^{-\cdot}$ with DMN which gives the ionic products. The absence of ionic products in non-polar solvents (Scheme 3[15]) is further support for this suggestion, because in non-polar solvents there is no dissociation upon irradiation ≥420 nm; hence there is no photoelectron ejection and therefore no $O_2^{-\cdot}$ formation.

In non-polar solvents, we suggest that the singlet exciplex gives rise to a triplet exciplex and triplet DCA (through dissociation; Scheme 2) by intersystem crossing. Singlet oxygen is then generated by action of $^3$DCA and/or $^3$(DCA ··· DMN) with $O_2$ in both polar and non-polar solvents.

Scheme 3, combined with photoinduced charge-recombination and direct excitation luminescence results, gives further evidence that endoperoxide formation is mediated mainly through $^1O_2$ (Scheme 4).

The exciplex (DCA ··· DMN)* is thus a precursor state for the DCA-sensitized photo-oxygenations. The formation of $O_2^{-\cdot}$ and $^1O_2$ proceeds from this excited charge-transfer complex.

## Experimental

Solutions of DMN ($6.4 \times 10^{-2}$M) and DCA ($10^{-5}$M) in various solvents were placed in Suprasil tubes and subjected to freeze–pump–thaw degassing cycles before being sealed and preserved for experiment. A spectrofluorometer (Jobin and Yvon type JY 3D) equipped with automatic programmer and plotter was used to measure the direct fluorescence intensity (excitation wavelength 420 nm). The phosphorescence spectra at 77 K were obtained by photon counting at each wavelength after a delay of 0.5 s subsequent to termination of the excitation ($\lambda_{ex}$ 420 nm). For r.l. experiments the degassed solutions were cooled rapidly in liquid $N_2$ and irradiated $\geqslant$420 nm with a high-pressure mercury lamp (Osram HBO; 500 W), equipped with a filter to cut off all shorter wavelengths, for 5 min (photon dose rate $6 \times 10^6$ $h\nu$ $cm^{-2}$ $s^{-1}$). 9,10-Dicyanoanthracene (DCA) (Eastman Kodak) was recrystallized from boiling acetonitrile; 1,4-dimethylnaphthalene (DMN) (reagent grade; Schuchardt) was purified by silica gel column chromatography.

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