Electron Transfer Photoisomerization of Norbornadiene to Quadricyclane Cosensitized by Dibenzoylmethanatoboron Difluoride and Aromatic Hydrocarbons

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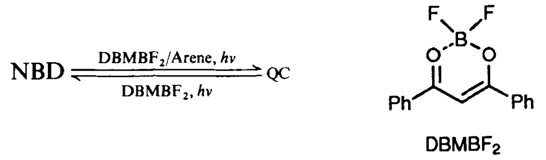
Chemically induced dynamic nuclear polarization (CIDNP) was used to study the valence isomerization of norbornadiene (NBD) to quadricyclane (QC) sensitized by dibenzoylmethanatoboron difluoride ($DBMBF_2$). While $DBMBF_2$ readily sensitized QC to NBD *via* an electron transfer mechanism, it did not promote the reverse isomerization. In contrast, in the presence of an aromatic co-sensitizer, such as toluene, ethylbenzene, biphenyl or durene, $DBMBF_2$ sensitized NBD isomerization to QC. The novel result is rationalized by invoking a photoinduced electron transfer mechanism, involving triplexes as the key intermediate which facilitates triplet recombination of the ion radical pair.

The photosensitized valence isomerization of norbornadiene (NBD) to quadricyclane (QC) has been the subject of intense experimental and theoretical investigation[1] in view of its significance in solar energy storage[2] and mechanistic interests.[3] Recently one of us has reported that dibenzoylmethanatoboron difluoride ($DBMBF_2$) sensitized, from its singlet excited state, the photoisomerization of QC to NBD with high efficiency, but did not sensitize the reverse conversion, NBD to QC.[4] It was proposed that the conversion of QC to NBD was initiated by photoinduced electron transfer between $DBMBF_2$ and QC, and that the failure of the reverse conversion was due to the unfavourable energetics of the $NBD^{\cdot+}$ to $QC^{\cdot+}$ transformation.[4]

We have probed the intermediate involved in the cation radical reaction of the $DBMBF_2$ sensitized NBD–QC valence isomerization by chemically induced dynamic nuclear polarization (CIDNP). In the process, we have found that certain aromatic compounds could also act as co-catalysts, driving $DBMBF_2$ sensitizing of NBD isomerization to QC (Scheme 1), causing CIDNP effects and NMR line-broadening of $DBMBF_2$ signals. Together with fluorescence quenching results, this evidence establishes a cooperative catalytic action of the aromatic hydrocarbons that suggests that the boron complex can sensitize the photoisomerization of NBD to QC *via* a triplex electron transfer mechanism. This is believed to be the first example of the aromatic hydrocarbon consensitized valence isomerization of NBD to QC and CIDNP effects.



Scheme 1

Results

Chemically Induced Dynamic Nuclear Polarization (CIDNP).—Irraidation of an $[^2H_3]$acetonitrile solution of $DBMBF_2$ (0.03 mol dm^{-3}) and QC (0.02 mol dm^{-3}) *in situ* with a 1000 W high-pressure Hg–Xe lamp through a Pyrex filter gave rise to a CIDNP spectrum which showed enhanced absorption for the bridgehead protons (Q_{bh} at 1.36 ppm) and emission for the cyclobutane protons (Q_o at 1.45 ppm) of the reactant (QC), as well as enhanced absorption for the olefinic protons (N_o at 6.77 ppm) and emission for the bridgehead protons (N_{bh} at 3.56 ppm) of the rearranged hydrocarbon (NBD). In addition, the signal of the sensitizer, $DBMBF_2$, was extensively broadened (Fig. 1). This spectrum unambiguously confirmed the previous assertion that singlet excited $DBMBF_2$ sensitized the valence isomerization of QC to NBD through an electron transfer mechanism[4] (*vide infra*). In contrast, irradiation of a $DBMBF_2$–NBD mixture under a range of similar conditions did not produce any spectral change, which is in agreement with the observed failure of $DBMBF_2$ to sensitize the transformation of NBD to QC.[4]

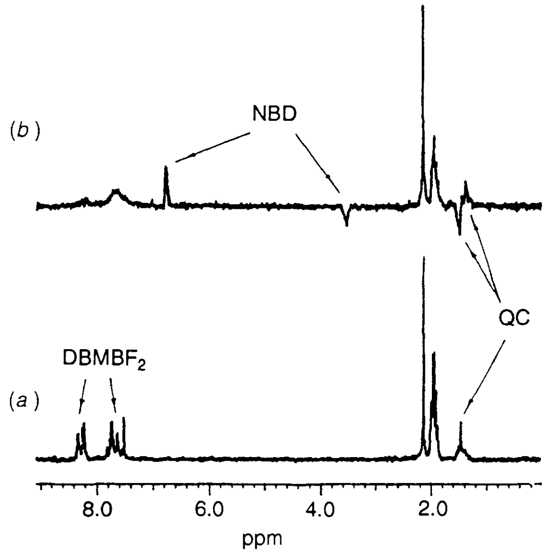


Fig. 1 ^1H NMR (80 MHz) spectra obtained (*a*) before and (*b*) during the irradiation of $DBMBF_2$ (0.03 mol dm^{-3}) and QC (0.02 mol dm^{-3}) in CD_3CN

Most strikingly, when a small amount of toluene (0.005–0.03 mol dm^{-3}) was added to the acetonitrile solution of $DBMBF_2$–NBD, upon irradiation, the mixture showed strong emission for NBD (N_o at 6.77 ppm, olefinic protons) and weak enhanced absorption for QC (Q_o at 1.45 ppm, cyclobutane protons). This

Table 1 CIDNP results observed during the photoreaction of DBMBF$_2$–QC and DBMBF$_2$–NBD–toluene systems in CD$_3$CN

			Polarization phase[a]	
Compound	Position	δ_H (ppm)	DBMBF$_2$–QC	DBMBF$_2$–NBD–Toluene
NBD	bridgehead	3.56	E	—[b]
	olefinic	6.77	A	E
	bridge	1.92	—[c]	—[c]
QC	bridgehead	1.35	A	—[b]
	cyclobutane	1.45	E	A
	bridge	1.94	—[c]	—[c]

[a] A and E denote enhanced absorption and emission respectively. [b] No observable change. [c] The signal was obscured by the solvent peak.

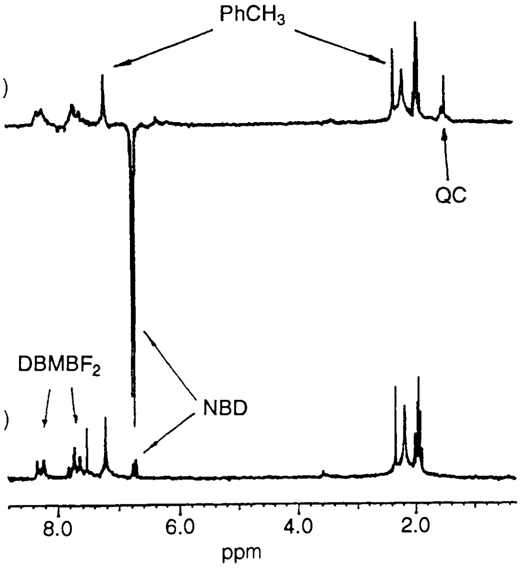


Fig. 2 ^{1}H NMR (80 MHz) spectra obtained (*a*) before and (*b*) during the photoreaction of DBMBF$_2$ (0.02 mol dm^{-3}) with NBD (0.02 mol dm^{-3}) in the presence of toluene (0.03 mol dm^{-3}) in CD$_3$CN. The signal at 2.2 ppm arises from H$_2$O.

Fig. 3 Concentration dependence of the ^{1}H NMR spectra during irradiation of the DBMBF$_2$–NBD–toluene system; (*a*) DBMBF$_2$ (0.03 mol dm^{-3}) and toluene (0.005 mol dm^{-3}); (*b*) DBMBF$_2$ (0.03 mol dm^{-3}) and toluene (0.02 mol dm^{-3}); (*c*) DBMBF$_2$ (0.2 mol dm^{-3}) and toluene (0.02 mol dm^{-3}) in CD$_3$CN containing NBD (0.02 mol dm^{-3}).

occurrence was accompanied by NMR line broadening of the DBMBF$_2$ signals, while the toluene signal remained sharp and unchanged (Fig. 2). The polarization phases are summarized in Table 1. It was also found that the polarization intensity was dependent upon the relative concentration of DBMBF$_2$ and toluene; the larger the concentration ratio of toluene to DBMBF$_2$, the more intense the resulting polarization (Fig. 3). The drop in intensity on increase in DBMBF$_2$ concentration [Fig. 3, spectrum (c)] no doubt arose from the competition excimer formation[4] which reduced the available singlet excited DBMBF$_2$ for interaction with NBD and toluene. Ethylbenzene, biphenyl or durene* could also act as cosensitizers with DBMBF$_2$ for the isomerization of NBD to QC, giving CIDNP spectra similar to those observed for the DBMBF$_2$–NBD–toluene system as shown in Figs. 2 and 3. However, if benzene was used in place of toluene, no NMR spectral change was observed during the irradiation.

Fluorescence Quenching.—DBMBF$_2$ shows strong fluorescence at 397 and 416 nm on excitation at 365 nm in dilute acetonitrile solution.[5]† Both NBD and QC reduced the fluorescence intensity effectively without showing new emission. The Stern–Volmer plots showed upward curvature, due to the transient effect, at substrate concentration $\geqslant 0.08$ mol dm^{-3}; the initial slope was extracted by a second order polynomial fit at dilute concentration[6] to give slopes $k_q\tau$ of 6.8 ± 0.2 and 10.6 ± 0.3 dm^3 mol^{-1} respectively.[4] Assuming the lifetime, τ, of DBMBF$_2$ to be 0.34 ns,[5] the quenching rate constants k_q were calculated to be 2.0×10^{10} and 3.1×10^{10} dm^3 mol^{-1} s^{-1} for NBD and QC respectively.[5] The aromatic hydrocarbons used as co-sensitizers also quenched DBMBF$_2$ fluorescence in acetonitrile, giving a good linear Stern–Volmer correlation with calculated k_q values shown in Table 2. Quenching of DBMBF$_2$ fluorescence in acetonitrile by concentrations of toluene up to 0.1 mol dm^{-3} was accompanied by a weak exciplex emission in the 500 nm region (Fig. 4); the exciplex fluorescence intensity was reduced significantly by the addition of a small amount of NBD ($\leqslant 0.008$ mol dm^{-3}), whereas DBMBF$_2$ fluorescence showed hardly any reduction. Since benzene forms a strongly

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* 1,2,4,5-Tetramethylbenzene.

† The lifetime of singlet excited DBMBF$_2$ was redetermined using biacetyl as the quencher with inner filter correction to be 0.34 ns which is in good agreement with $\tau_0 = 0.35$ ns determined by others (H.-D. Ilge, E. Birdener, D. Fassler, M. V. Kozmeuko, M. G. Kuzmin and H. Hartmann, *J. Photochem.*, 1986, **32**, 177. By fluorescence decay kinetics, the lifetime was determined to be 0.30 ns in acetonitrile (personal communication, J. Korppi-Tommola, University of Jyvskyla, Finland).

Table 2 Thermodynamic and quenching parameters in the $DBMBF_2$ sensitized photoisomerization of NBD to QC

Electron donor	$E_{(D/D^+)}$/ V *vs.* SCE	ΔG_{ET}/ kcal mol^{-1} [a]	E_{IRP}/ kcal mol^{-1} [b]	$k_q/10^{10}$ dm^3 mol^{-1} s^{-1}
NBD	1.81[c]	−12.2	61.3	2.0[f]
Benzene	2.62[d]	6.5	80.1	0.16
Toluene	2.25[d]	−2.1	71.5	0.78
Ethylbenzene	2.27[d]	−1.6	72.0	—
Biphenyl	1.96[e]	−8.8	64.8	2.2[f]
Durene	1.79[d]	−12.7	60.9	2.2[f]

[a] Calculated by Rehm–Weller equation,[19] $\Delta G_{ET} = 23.06\ [E_{(D/D^+)} - E_{(A^-/A)} - E_{0,0} - 0.06]$ (kcal mol^{-1}): $DBMBF_2$ possesses: $E_{(A^-/A)} = -0.91$ V *vs.* SCE, $E_{0,0} = 3.19$ eV, and $E_T = 62$ kcal mol^{-1}. [b] Calculated by,[19] $E_{IRP} = 23.06\ [E_{(D/D^+)} - E_{(A^-/A)} - 0.06] = \Delta G_{ET} + E_{0,0}$ (kcal mol^{-1}). [c] Ref. 3(*b*) and this work. [d] J. O. Howell, J. M. Goncalves, C. Amatore, I. Klasinc, R. M. Wightman and J. K. Kochi, *J. Am. Chem. Soc.*, 1984, **106**, 3968. [e] I. R. Gould, D. Ege, J. E. Moser and S. Farid, *J. Am. Chem. Soc.*, 1990, **112**, 4290. [f] For these electron donors, the initial slope at infinite dilution represents the Stern–Volmer constant.

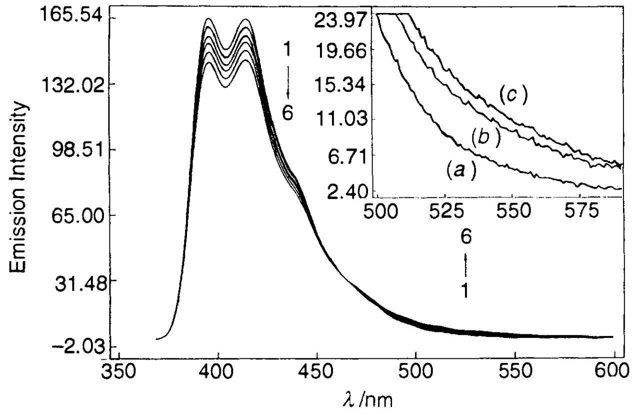


Fig. 4 Fluorescence spectra of $DBMBF_2$ (5×10^{-6} mol dm^{-3}) in acetonitrile with increasing concentrations of toluene (for spectra 1–6; 0, 0.01, 0.021, 0.029, 0.042 and 0.057 mol dm^{-3}) under air. {Inset: The expanded spectra of the above spectra at [toluene] (*a*) = 0.0 mol dm^{-3} and (*c*) 0.057 mol dm^{-3}; spectrum (*b*) was taken with the same solution as (*c*) but containing [NBD] = 0.0074 mol dm^{-3}, and recorded by multiplying by a factor of 1.05 to compensate for $DBMBF_2$ fluorescence quenching}.

fluorescing exciplex, the quenching of $DBMBF_2$ fluorescence in acetonitrile by benzene was masked by intense emission as reported previously.[5] In this case the quenching spectra were generated by elimination of exciplex emission curves which were obtained by spectral subtractions; the Stern–Volmer plot of these artificially generated quenching spectra gave $k_q = 1.6 \times 10^{-9}$ dm^3 mol^{-1} s^{-1}. It was immediately clear that quenching rate constants of these aromatics were generally smaller or equal to that of NBD.

Electron Paramagnetic Resonance (*EPR*) *Study*.—The EPR spectrum of the $DBMBF_2$ anion radical has not been reported previously. In spite of extensive attempts, a $DBMBF_2$ EPR signal was not observed on *in situ* irradiation of either $DBMBF_2$–NBD or $DBMBF_2$–NBD–toluene systems in acetonitrile. However, in the presence of *tert*-butyl-*N*,*N*-dimethylamine, similar irradiation in the EPR cavity gave a transient blue solution as well as a broad signal with a peak to peak width of 7.6 gauss and a *g* factor of 2.0033. A blue solution had been previously assigned as the colour of the $DBMBF_2$ anion radical produced by electrolysis.[7]

Discussion

Roth and co-workers[8] have elegantly demonstrated by use of CIDNP that $NBD^{\cdot +}$ and $QC^{\cdot +}$ are two distinct cation radicals (but not resonance forms) involved in the photosensitized valence isomerization of NBD and QC by electron transfer, work which was later supported by theoretical calculations.[9] The calculated hyperfine splitting constants obtained by using the 6-31G* basis set are annotated on the structures shown in Fig. 5, that have provided a basis for the previous CIDNP experimental assignment.[8] In the chloranil photosensitized reaction, QC was readily converted to NBD and showed strong polarization in the protons of both QC and NBD.[8] The present CIDNP observation in the $DBMBF_2$–QC system (Fig. 1 and Table 1) is compatible with that observed in the chloranil–QC system except that all of the polarization phases are opposite. Furthermore, the line-broadening of the $DBMBF_2$ signal indicates that the corresponding anion radical must be formed and undergo rapid electron exchange with the parent molecules. It is well-known that similar electron exchange could cause NMR line-broadening,[10] which in turn would obscure the polarization.[11] Both the observations in CIDNP and the NMR line-broadening provide unambiguous evidence for the electron transfer mechanism for the $DBMBF_2$ sensitized valence isomerization of QC to NBD as shown in Scheme 2.

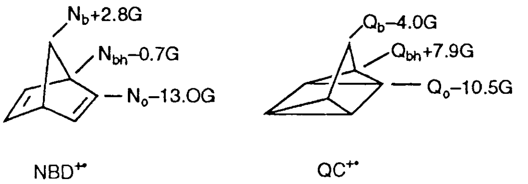


Fig. 5 The calculated hyperfine splitting constants obtained using the 6-31G* basis set for $NBD^{\cdot +}$ and $QC^{\cdot +}$

$$A \xrightarrow{h\nu} {}^1A$$

$${}^1A + QC \longrightarrow {}^1[A^{\cdot -}\ QC^{\cdot +}]$$

$${}^1[A^{\cdot -}\ QC^{\cdot +}] \longrightarrow A + QC\dagger$$

$${}^1[A^{\cdot -}\ QC^{\cdot +}] \longrightarrow A^{\cdot -} + QC^{\cdot +}$$

$$QC^{\cdot +} \xrightarrow{\Omega} NBD^{\cdot +}$$

$$A^{\cdot -} + NBD^{\cdot +} \longrightarrow A + NBD\dagger$$

$$A^{\cdot -} + A \longrightarrow A + A^{\cdot -}\ \text{(line-broadening)}$$

$A = DBMBF_2$
† Denotes polarized molecule

Scheme 2

According to the Kaptein rule[12] and subsequent amendment,[13] the net CIDNP effect depends on five parameters: the initial spin multiplicity of the radical pair (μ); the type of product formations (ε); the relative sign of g factors of the individual radicals (Δg); the sign of the hyperfine splitting constant (hfc) for the nucleus under observation (A_i); and the exit channel factor (γ).[13b] In the $DBMBF_2$–QC system, the signs of each factor are judged as follows: (i) $DBMBF_2$ is a singlet sensitizer[4,14] giving a negative value of μ; (ii) The **g** value of $QC^{\bullet +}$ (*ca.* 2.0025)[12b] is smaller than that of $DBMBF_2^{\bullet -}$ (2.0033) giving $\Delta g < 0$; (iii) The hfc of $QC^{\bullet +}$ are -10.5 for Q_o (A_i is negative) and $+7.9$ gauss for Q_{bh} (A_i is positive) respectively.[9] Therefore, the emission of the cyclobutane protons and the enhanced absorption of the bridgehead protons must mean that the polarized QC is an in-cage product (ε is positive). The enhanced absorption of the olefinic protons of NBD indicates that it must be an escape product (ε is negative) with singlet exit channel (γ is positive). In addition, the opposing polarization phases of the olefinic and bridgehead protons of NBD requires that the polarization must originate from $QC^{\bullet +}$, but not from the F-pair of $NBD^{\bullet +}$ and $DBMBF_2^{\bullet -}$; if the latter were true, the bridgehead protons of NBD would show a weak to negligible absorption due to the small negative value (-0.7 gauss) of its hfc[9] since the sign and the intensity of the polarization are hfc dependent. This is an example of the so-called memory effect in CIDNP.[15] It indicates that the diffusion of $QC^{\bullet +}$ from the solvent cage, the isomerization of $QC^{\bullet +}$ to $NBD^{\bullet +}$ and the formation of the encounter pair are all fast processes, allowing $QC^{\bullet +}$ to keep and transfer its polarization to $NBD^{\bullet +}$ well before the occurrence of spin-lattice relaxation which typically takes *ca.* 10^{-6} second.[12b] Similar memory effects have been reported previously.[15,16]

It is well-known that the energy level of $NBD^{\bullet +}$ lies significantly below that of $QC^{\bullet +}$ (by 9–11 kcal mol^{-1})[9,17] and that the excited singlet energy surface connecting NBD and QC delivers singlet excited molecules preferentially to NBD.[1,18] Therefore, it is expected that the singlet $DBMBF_2$ could not sensitize the isomerization of NBD to QC[4] even if the free energy difference calculated by the Rehm–Weller equation[19] favours the electron transfer and NBD quenches singlet excited $DBMBF_2$ with a near diffusion limited rate constant (see Table 2). Aside from the product formation, the absence of CIDNP in the $DBMBF_2$–NBD system during irradiation also suggests that either the ion radical pair (IRP) [$DBMBF_2^{\bullet -}$/$NBD^{\bullet +}$] was not formed or, more probably, the reverse electron transfer was so efficient that other chemical or photophysical processes were circumvented.

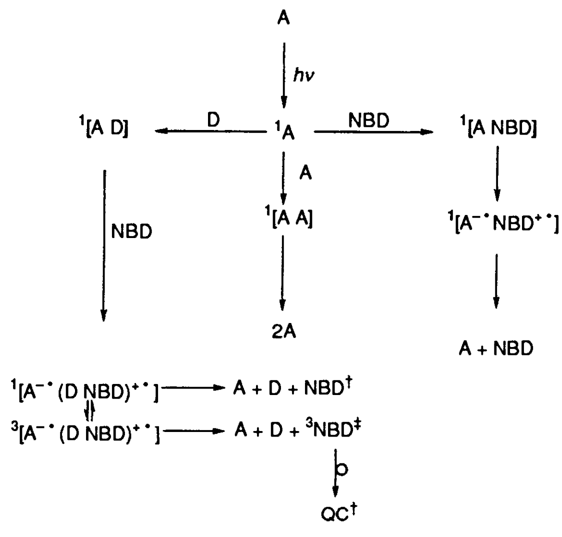
It has been well documented that NBD can be photoisomerized to QC irreversibly by triplet sensitizers with $E_T \geqslant 68$ kcal mol^{-1}. Alternatively, this process can be performed by singlet sensitization followed by a triplet IRP recombination provided $E_{IRP} \geqslant E_T$ (NBD).[8,18,20] Using 1-cyanonaphthalene as a singlet sensitizer, it can be shown that NBD is converted readily to QC and in the process, shows emissive polarization for olefinic protons of NBD (N_o) but enhanced absorption for cyclobutane protons of QC (Q_o); this implies that polarized QC is an in-cage product (ε is positive) and exits from a triplet pair (γ is negative).[8] In the present case, the estimated IRP energy of [$DBMBF_2^{\bullet -}$/$NBD^{\bullet +}$] (61.3 kcal mol^{-1}) is *ca.* 6–8 kcal mol^{-1} below the triplet energy of NBD (68–70 kcal mol^{-1}, see Table 2). This suggests that the triplet recombination pathway by $DBMBF_2$ sensitization is also energetically unfavourable. This energy mismatch has been used to explain the failure of singlet excited $DBMBF_2$ to sensitize the NBD→QC conversion[4] and can be used to explain the absence of a CIDNP effect during irradiation.

The surprising observation of CIDNP in the ternary system $DBMBF_2$–NBD–arenes (*e.g.*, Fig. 2) indicates that the NBD→QC rearrangement takes place with an arene as a co-sensitizer, opening up a new reaction pathway as well as an interesting mechanistic question. As only the olefinic protons of NBD (N_o) and cyclobutane protons of QC (Q_o) were polarized, the polarizations must stem from $NBD^{\bullet +}$ but not from $QC^{\bullet +}$, otherwise the bridgehead protons would also have been polarized (*vide supra*). Furthermore, the emission of N_o undoubtedly demonstrates that the polarized NBD must come from the in-cage reverse electron transfer of a singlet IRP (μ, Δg, and A_i are negative, ε is positive thus Γ is negative, emission). The absorption of Q_o (A_i is negative) means that QC may be derived from either a singlet out-of-cage rearrangement of $NBD^{\bullet +}$ (μ, ε are negative) or an in-cage recombination exited from a triplet IRP (μ, γ are negative, ε positive), *i.e.*, triplet recombination. The former possibility can be excluded by thermodynamics, as $NBD^{\bullet +}$ is known to be more stable than $QC^{\bullet +}$ and not likely to undergo the required uphill transformation.[1,9,18] If the triplet recombination mechanism is accepted, we must address the question of the function of the arene and the related mechanism.

The use of co-sensitizers to facilitate photochemical reactions mediated by electron transfer has been described. These catalysts (usually aromatic hydrocarbons) act as radical ion relays, in promoting a smooth radical ion chain sequence by virtue of favourable energetic relations or kinetic factors. For example, the biphenyl cation radical $BP^{\bullet +}$, due to its long lifetime, can diffuse out of cages and undergo electron transfer oxidation even in slightly endothermic reactions.[21]

With the exception of benzene, the arenes shown in Table 2 undoubtedly participate in the NBD→QC isomerization through molecular interactions. However, the absence of a CIDNP effect for toluene and other arenes indicates that the arene radical cation might not form by complete electron transfer between the arene and $DBMBF_2$, as described for the biphenyl radical cation mediated reactions mentioned above. Instead, the role of the arene may be only to insert into the [$DBMBF_2^{\bullet -}$/$NBD^{\bullet +}$] radical ion pair and stabilize it by delocalizing partial positive charge from the donor radical cation. Therefore, we propose an arene mediated electron transfer mechanism with triplexes as the key intermediate to rationalize the observed polarization (Scheme 3). Triplexes have been invoked as viable intermediates in a number of photochemical processes, but triplex emission could scarcely be detected, especially in polar solvents or when the two quenching species were different.[22–26]

According to Scheme 3 singlet excited $DBMBF_2$ (A), NBD and the arene (D) form a singlet triplex. In addition to the CIDNP result, which predicts an in-cage triplet recombination process, the proposed involvement of the intermediate triplex is supported by the facts that both NBD and toluene quench the fluorescence of $DBMBF_2$ efficiently (see Table 2) and $DBMBF_2$–toluene exciplex emission could be observed even in polar acetonitrile solvent, and was quenched by NBD (Fig. 4) which is an indication of involvement of a triplex.[22] The concentrations used in the experiment (*ca.* 0.02 mol dm^{-3} for each component) are high enough to ensure an effective combination of the three components in the ternary complex. The concentration dependence of the CIDNP intensity upon the relative concentration ratio of toluene–$DBMBF_2$ (Fig. 3) also reveals the participation of toluene in the exciplex and/or triplex formation, which may compete with the excimer formation of $DBMBF_2$.[4] Most importantly, the participation of the arene in the triplex may significantly stabilize the ion radical pair by delocalizing the positive charge and distortion of its molecular configuration, which, in turn, may alter its potential energy surface. This configuration distortion may lead to generation of a vibrationally excited triplet after intersystem crossing. The system may move initially along the triplex surface until, at some critical geometry, crossing to the triplet surface of NBD. Obviously, the energy of this distorted ternary IRP at the crossing point must be well below that of the vertical triplet



A = $DBMBF_2$
D = Arenes
† Denotes polarized molecule
‡ Denotes distorted triplet NBD

Scheme 3

state of NBD. This should make the triplet recombination energetically feasible. Indeed, Grutsch and Kutal[27] have used a similar argument to explain the successful photosensitized NBD→QC transformation, whose IRP energy is far lower than the vertical triplet energy of NBD. Furthermore, as exciplexes and charge transfer complexes are known to favour spin reversal,[21c] triplex formation must also facilitate the circumvention of the singlet reverse electron transfer and prompt the intersystem crossing that makes the triplet recombination predominant.

In conclusion, this work reveals that toluene and several other aromatic hydrocarbons can cosensitize with $DBMBF_2$ the valence isomerization of NBD to QC *via* an electron transfer triplet recombination mechanism with triplexes as the critical intermediates. The triplex formation may make feasible some seemingly energetically unfavourable electron transfer processes.

Experimental

Materials.—$DBMBF_2$ was prepared according to the published procedures.[28] NBD and QC were commercial products (Aldrich) and were purified by redistillation under reduced pressure before use. [$^2H_3$]Acetonitrile was used as obtained from Aldrich. Acetonitrile, toluene, ethylbenzene, biphenyl, durene and benzene were also commercial products and purified by standard methods before use.

General Procedure.—CIDNP experiments were performed at 80.131 MHz on a Bruker AC-80 spectrometer equipped with a photo-CIDNP probe as described previously.[29] The fluorescence quenching experiments were carried out at room temperature in solutions under air with a PTI LS-100 fluorescence spectrophotometer by Photon Technology International (South Brunswick, N.J., USA).

The redox potentials of NBD and the sensitizer, $DBMBF_2$, were determined by cyclic voltammetry with a Princeton Applied Research (PAR Model 173) potentiostat equipped with a high-impedance voltage amplifier (PAR Model 178). The cyclic voltammetric measurements were performed with a three-electrode system, with a platinum wire (φ 0.5 mm) as counterelectrode, glassy carbon as working electrode and saturated calomel electrode as reference. The experiments were carried out in oxygen-free, dry acetonitrile containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate as the supporting electrolyte and ferrocene/ferrocenium couple [$E^{ox}_{\frac{1}{2}}$ = 0.33 V (SCE)][30] was employed as an internal standard.

The EPR spectrum of the radical anion $DBMBF_2^{•-}$ was obtained by *in situ* photolysis of the oxygen-free dry acetonitrile solution of $DBMBF_2$ and *tert*-butyl-*N*,*N*-dimethylamine with a Bruker ER 200D EPR spectrometer operating in the X-band with 100 kHz modulation. The *g* value was measured by exact field calibration using an EIP 371 microwave counter and a Bruker RF 80X gaussmeter.

Fluorescence Quenching.—Unpurged acetonitrile solutions of $DBMBF_2$ (4.2×10^{-6} mol dm^{-3}) with increasing amounts of toluene (0.010–0.057 mol dm^{-3}) were used to record the fluorescence spectra shown in Fig. 4. The expanded fluorescence spectra of the 500–600 nm region for toluene concentrations 0.0 [for (*a*)] and 0.57 mol dm^{-3} [for (*c*)] are also shown in the inset. The latter solution containing additional NBD (0.007A mol dm^{-3}) was used to determine the fluorescence spectrum (*b*) which was multiplied by a factor of 1.05 to compensate for $DBMBF_2$ quenching by NBD.

Fluorescence spectra of $DBMBF_2$ in acetonitrile with increasing amounts of benzene had been recorded.[5a] A fluorescence curve of the benzene exciplex was generated by subtracting a fraction of the $DBMBF_2$ fluorescence. The exciplex fluorescence was subtracted from the observed spectra for a given benzene concentration to give the intensity reduced fluorescence spectrum of $DBMBF_2$. The value of I_0/I at all wavelengths should be the same.

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