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Intramolecular Electron Hopping in Double Carbazole Molecules Studied by the Fluorescence-Detected Magnetic Field Effect

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The intramolecular electron hopping in cation dimer radicals of 1,*n*-bis(*N*-carbazolyl) alkanes for $n = 3,4$ that are produced via photoinduced electron transfer to 1,4-dicyanobenzene (DCNB) has been studied by means of the exciplex fluorescence detected magnetic field effect (MFE) in a 18 vol % mixture of dimethylformamide with tetrahydrofuran. It has been found that on passing from a single cation radical of *N*-methylcarbazole to the cation dimers, the parameter $B_{1/2}$ decreases from ca. 50 G to ca. 26 G, while saturation values of MFE (at $B = 300$ G) are almost the same (ca. 3.0% for MeCz and CzB) but strongly decreased for CzP (ca. 0.5%). The experimental results obtained are in fair agreement with the Schulten theory of intramolecular electron exchange. In contrast to the well-known pyrene/*N*,*N*-dimethylaniline exciplex system, the carbazole derivatives/DCNB system exhibits a two-exponential decay of exciplex fluorescence and a significantly smaller MFE that might result from the fact that in the latter exciplex system the radical ion pair state is the lowest energy state above the ground state.

Introduction

The origin of magnetic field effects (MFE) detected by exciplex fluorescence is due to cage recombination of radical ions generated by photoinduced electron transfer.[1] External magnetic fields ($B \approx 100$ G) can affect intersystem crossing in the spin-correlated radical-ion pair (RIP). They remove the degeneracy of three triplet-state sublevels of RIP, T_0 and $T_\pm$, by virtue of the Zeeman effect. When the energy gap between them exceeds the size of the hyperfine interaction (HFI) of the unpaired electrons with their nuclei, $T_\pm$ cannot mix with the RIP singlet state, i.e., external magnetic fields diminish the probability of intersystem crossing in the radical ion pair and, therefore, change the relative concentration of both the singlet and triplet states of the RIP. The functional dependence of the singlet RIP concentration can be monitored conveniently through the intensity of the exciplex fluorescence produced during the course of the RIP cage recombination. A characteristic feature of the above MFE is that a variation in the width of RIP spin sublevels leads to a change in the characteristic parameter $B_{1/2}$, the field strength at which the MFE reaches half its saturation value.

The example of this type of process influencing the width of spin sublevels is electron hopping between a cation-radical and its diamagnetic molecule,

$$D^{\bullet +} + D \Leftrightarrow D + D^{\bullet +} \qquad (1)$$

that was successfully studied experimentally[2] and theoretically[3] a decade ago. It was found that on increasing the rate of electron hopping (1), which can be varied by a change in the concentration of donor molecules, the magnitude of $B_{1/2}$ increases while the saturation value of MFE decreases. Among other things, the theory predicts that on further increasing the exchange rate, broadening sublevels, i.e., increasing $B_{1/2}$ should be followed by their narrowing, i.e., decreasing $B_{1/2}$. However, this feature hardly could be observed in exciplex systems containing freely diffusing molecules because increasing the donor concentration cannot be done without changing other physical parameters of the system (e.g., polarity, viscosity, etc.) that also might affect the measured MFE.

To safely increase an effective donor concentration, donor molecules can be linked pairwise by methylene chains. The shorter their length, the higher the rate of electron exchange. Although the theoretical consideration of hopping in a linked system was made by Knapp and Lersch,[4] and Schulten,[5] who have predicted significant narrowing of RIP sublevels, there are almost no experimental studies of this feature. It is worth noting, rather as an exception, a paper by Hayashi and co-workers[6] that dealt with a complex triad donor−acceptor supramolecular system modeling the bacterial reaction center. They observed the influence of weak external magnetic fields on the absorption of the photoinduced intramolecular RIP containing a porphyrin radical-cation and diimide radical-anion. In particular, when a porphyrin donor moiety was replaced by a diporphyrin moiety, then $B_{1/2}$ of the observed MFE was reduced by a factor of ca. 1.4. This was attributed to electron hopping between double porphyrin donor moieties that might be considered as the porphyrin dimer cation.

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The purpose of the present work is to study the influence of intramolecular electron hopping on the MFE detected by exciplex fluorescence in a relatively simple and well-studied exciplex system, polar solutions of 1,*n*-bis(*N*-carbazolyl) alkanes for $n = 3,4$ in the presence of 1,4-dicyanobenzene as electron acceptor, i.e.,

$$\mathrm{D} - (\mathrm{CH}_2)_n - \mathrm{D}^{\bullet +} \Leftrightarrow \mathrm{D}^{\bullet +} - (\mathrm{CH}_2)_n - \mathrm{D} \qquad (2)$$

Photoinduced electron transfer from carbazole derivatives to an appropriate acceptor (dimethylterephalate), which results in exciplex fluorescence, has been studied in the systems of such a type since the end of the 1960s.[7] In addition, double carbazole molecules have been used as model compounds in studying the formation of intramolecular excimers in poly-*N*-vinylcarbazole.[8] It is worth noting that Aich and Basu[9] have recently reported about the observation of the MFE detected by exciplex fluorescence in solutions of *N*-ethylcarbazole in the presence of 1,4-dicyanobenzene as an electron acceptor.

Experimental Section

Fluorescence spectra were measured with a Perkin-Elmer LS-50 spectrophotometer, absorption spectra with a Cary 5E spectrophotometer. Fluorescence lifetimes were determined with a single photon counting fluorometer (Edinburgh Instruments). The relative change in exciplex fluorescence yield, φ, caused by the external magnetic field B is defined as $(\varphi(B) - \varphi(0))/\varphi(0)$ and in what follows is called magnetic field effect (MFE).[1,2] It was detected under steady-state conditions during photoexcitation of carbazole derivatives with a 150 W xenon lamp (cutoff filters BG18 + UG2). Magnetic fields, provided by a Bruker electromagnet and applied to the sample, were measured with a Hall-type gaussmeter.

As a solvent we used an 18% mixture of *N*,*N*-dimethylformamide (DMF) with Tetrahydrofuran (THF); these components were of spectroscopic grade (Merck, Uvasol). The electron donor compounds 1,3-bis(*N*-carbazolyl)propane (CzP) and 1,4-bis(*N*-carbazolyl)butane (CzB), synthesized according to ref 10, and *N*-methylcarbazole (MeCz) (Merck, Schuchardt) were purified by HPLC; electron acceptor 1,4-dicyanobenzene (DCNB) (Merck, Schuchardt) was purified by recrystallization from benzene. A typical concentration of carbazole derivatives was of the order of 10^{-4}mol/L; that of DCNB, ca. 4×10^{-2} mol/L. In this work we normally used air-saturated samples except in a few cases where samples were deoxygenated by bubbling the solutions with nitrogen for ca.15 min before measurements (see below). All experiments were carried out at room temperature.

Results and Discussion

Quenching of photoexcited carbazole derivatives by DCNB molecules resulted in a decrease of the monomer fluorescence (at the 352 nm band) by approximately 1 order of magnitude (i.e., by a factor of 13.5 for MeCz, 8 for CzP, and 13 for CzB) and concomitantly in the appearance of a structureless exciplex fluorescence band at the 500−600 nm. It is worth noting that in the case of a double carbazole donor it is more resonable to speak about triple complex formation exactly in the sense proposed by Beens and Weller.[11]

For all air-saturated solutions of carbazole derivatives, the application of an external magnetic field increases the fluorescence intensity in the exciplex band (see Figure 1). The saturation value of the MFE for MeCz is 2.9%; $B_{1/2} = 50 \pm 8$ G. In the case of CzB, the saturation value is almost the same (2.8%) while a value of $B_{1/2}$ is significantly lower, 26 ± 3 G.

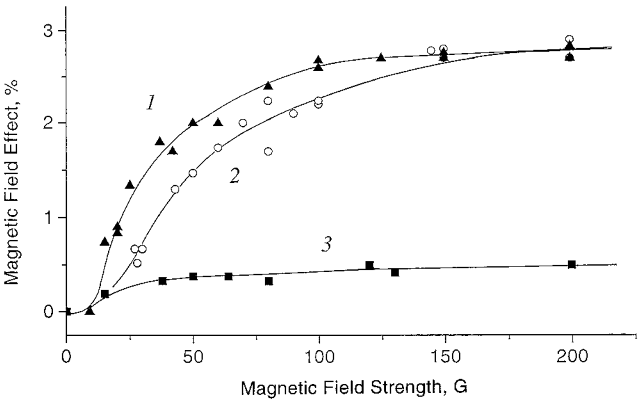

Figure 1. Relative external magnetic field effect (MFE) on exciplex fluorescence: (1) CzB + DCNB, (2) MeCz + DCNB, and (3) CzP + DCNB.

TABLE 1: Exciplex Fluorescence ($\lambda = 526$ nm) Decay Times, MFE Saturation Values (at 300 G), and Fields of Half Saturation for Air-Saturated Solutions of Carbazole Derivatives with an Access of DCNB in a 18% Mixture of DMF with THF

system	τ_1, ns[a]	τ_1, ns[a]	MFE, %	$B_{1/2}$, G
MeCz + DCNB	5.3	25	2.9	50
CzB + DCNB	6.9	25	2.8	26
CzP + DCNB	3.4	20.5	0.5	≈26

[a] The measurements of the exciplex fluorescence lifetimes were carried out in a zero external magnetic field.

For CzP, the MFE is strongly diminished, ca. 0.5%. This is rather small for $B_{1/2}$ to be determined accurately, but it seems almost the same as for CzB.

A distinctive feature of the exciplex system, carbazole derivatives with excess of DCNB, is that the decay of exciplex fluorescence (band maximum at 526 nm) was found to be fitted adequately by a two-exponential function corresponding to a shorter lifetime τ_1, of about 5 ns, and a significantly longer lifetime τ_2, of about 25 ns. When samples were not deoxygenated, τ_2 values decreased slightly, whereas shorter times remained almost the same (see Table 1). Under similar conditions, the pyrene/*N*,*N*,-dimethylaniline deoxygenated solution in a 18 vol % DMF mixture in THF, another well-known exciplex system, shows a single-exponential decay of 32 ns.

For the purpose of illustration, we consider the obtained results in the framework of a simple kinetic scheme suitable for describing photoinduced electron transfer in polar solutions (see Figure 2). After excitation of the donor molecule to the first electronically excited singlet state, the system goes from the ground state A + D to the electronically excited-state A + ^{1}D*. The mutual diffusional association of excited chromophore ^{1}D* and acceptor A makes the electron transfer possible. This results in the production of the $^1\{\mathrm{A}^{\bullet -}\cdots\mathrm{D}^{\bullet +}\}$singlet state of the RIP. There is an intersystem crossing transition to the $^3\{\mathrm{A}^{\bullet -}\cdots\mathrm{D}^{\bullet +}\}$ triplet RIP state with a rate constant k_{ST} (the reverse of this process is designated by k_{ST}). Upon cage recombination, the singlet and triplet RIPs lead to products of the same multiplicity with rate constants $k_{\mathrm{s}} = k_{\mathrm{sg}} + k_{\mathrm{se}}$ and k_{T}, respectively. Here k_{se} denotes the rate constant of transition to the fluorescent exciplex $^1(\mathrm{A}^{-}\mathrm{D}^{+})$* and k_{sg} that to the ground state; the rate constant k_{T} describes transition to a locally excited triplet state (in Figure 2 suitably located in terms of energy; see below).

Let us estimate the energy of the above states. According to Weller, the Gibbs energy of the RIP states with respect to the ground state in polar solution is $\Delta G \approx e(E_{\mathrm{D}}^{\mathrm{ox}} - E_{\mathrm{A}}^{\mathrm{red}}) = 2.75$

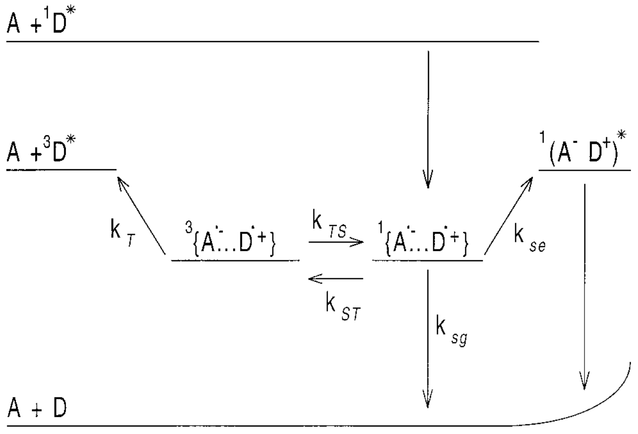

Figure 2. Kinetic scheme describing photoinduced electron transfer in polar solutions (see explanation in the text).

eV, where the electronic charge $e = 1$, $E_D^{ox} = 1.1$ V and $E_A^{red} = 1.65$ V[12] are redox potentials (vs SCE) of the donor and acceptor for the MeCz/DCNB system, respectively. Note that in the case of the Py/DMA exciplex system (there the acceptor pyrene is the primary excited species; $E_S = 3.3$ eV[13]) this energy, $\Delta G \approx 2.80$ eV,[14] is indeed very close to the above one. The energy of triplet and singlet states of MeCz can be estimated on the basis of spectroscopic data for carbazole ($E_T = 3.0$ eV and $E_S = 3.58$ eV[15]) and for poly(vinylcarbazole) films[16] ($E_T = 3.02$ eV and $E_S = 3.55$ eV). Thus, the lowest state of the system is that of the RIP with the locally excited triplet state of carbazole derivatives (ca. 3.0 eV) in the neighborhood of it. The lowest excited triplet state of DCNB is 3.16 eV.[17] Note for comparison that in the Py/DMA system the pyrene triplet state is at $E_T = 2.1$ eV[13] which is well below the RIP state, making the triplet channel of cage recombination very effective. This distinction seems to make these two exciplex systems qualitatively different and manifests itself in a two-exponential decay of the exciplex fluorescence as well as in a small MFE as compared with the Py/DMA system. Qualitatively, the same scheme is also valid for the double carbazole derivatives, D implying the double donor.

Consider the differences between two similar exciplex systems on the basis of the above kinetic scheme (Figure 2). The set of kinetic equations that describes the intersystem crossing in the RIP is as follows:

$$\frac{d[S]}{dt} = -(k_{ST} + k_S)[S] + k_{TS}[T]$$
$$\frac{d[T]}{dt} = -k_{ST}[S] - (k_{TS} + k_T)[T] \qquad (3)$$

Here [S] and [T] denote concentrations of singlet and triplet states of RIP, respectively. From eqs 3, it follows that

$$\frac{d^2[S]}{dt^2} + p\frac{d[S]}{dt} + q = 0 \qquad (4)$$

where $p = (k_{ST} + k_S) + (k_{TS} + k_T)$ and $q = [(k_S + k_{ST})(k_T + k_{TS}) - k_{ST}k_{TS}]$. The general solution of eq 4 is of the following type:[18]

$$[S] = C_1 \exp(\beta_1 t) + C_2 \exp(\beta_2 t) \qquad (5)$$

where $\beta_{1,2} = -p/2 \pm ((p^2/4) - q)^{1/2}$ and $C_{1,2}$ are constant values that are determined from boundary conditions. For our purpose, it is not necessary to give here the exact expression for it. From a formal point of view, it is completely analogous to any two-site kintetic scheme, for example, to the process of producing and decaying excimers (see for details[8]).

Nevertheless, it is worth noting that

$$\left(\frac{p^2}{4} - q\right) = \left(\frac{[(k_S + k_{ST}) + (k_T + k_{TS})]^2}{4} - (k_S + k_{ST})(k_T + k_{TS}) + k_{ST}k_{TS}\right) = \left(\frac{[(k_S + k_{ST}) - (k_T + k_{TS})]^2}{4} + k_{TS}k_{ST}\right) > 0 \qquad (6)$$

From eq 6 it follows that real and negative values of $\beta_{1,2}$ always exist for any reasonable rate constants of the kinetic scheme. Equation 5 predicts that the decay of the singlet state of RIP is described by the sum of two exponential functions of time. Note that this feature is observed easily, provided $(k_T + k_{TS}) \approx (k_S + k_{ST})$. If, for example, $(k_T + k_{TS}) \gg (k_S + k_{ST})$, then C_2/C_1 might become too small for the second term to be traced experimentally.[8] Therefore, the decay of exciplex fluorescence may be fitted well to a single-exponential function also.

There is a significant difference in the magnitudes of the observed MFE for these systems. In the case of the Py/DMA system, we observed about 12%, whereas in the MeCz/DCBN system, only about 3% under similar conditions. This can be rationalized as follows. One of the general principles of MFE theory[19] is that the RIP should be in nonequilibrium with respect to the S−T conversion in order for MFE to be observed. In the Py/DMA case, the RIP is almost out of equilibrium during its lifetime (32 ns) because of the effective triplet channel of the RIP recombination. For MeCz/DCNB, however, the shorter τ_1 is the time of establishing equilibrium. So only during this period out of τ_2 the RIP state can be affected by external magnetic fields. Thus, the observed MFE should be reduced by a factor of τ_1/τ_2 as compared with that of Py/DMA, i.e., (5 ns/25 ns) 12% ≈ 2.4%; in good agreement with the experiment.

The observed significant chemical instability of the systems carbazole derivatives/DCNB might be another consequence of the fact that the RIP is the lowest state of the system. A detailed study of the mechanism of such chemical changes is outside of the scope of this report so that we limit ourselves only to some remarks, bearing in mind that the experiment shows that air-saturated samples are stable enough to allow quantitative measurements of the MFE. The presence of oxygen can lead to quenching of relatively long-lived triplet states that might be produced via the cage recombination of the RIP triplet (analogous to the exciplex formation) and that might also be involved in irreversible photochemical changes in the system. Note that after exposing to light during a half hour (a typical time of one MFE experimental run), a new weak absorption band at 325−425 nm appeared in MeCz/DCNB deoxygenated solutions as compared to that containing oxygen.

Having measured the lifetime of MeCz fluorescence in a DMF/THF mixture with (8.6 ns) and without (14.1 ns) oxygen and assuming that quenching of fluorescence occurs at a diffusion-controlled rate, we estimate by the Stern−Volmer formula the oxygen concentration in the samples to be ca. 5×10^{-3} mol/L. Note that according to solubility data[20] the concentration of oxygen in THF at room temperature is about 2×10^{-3} mol/L so that oxygen can actually affect the states with lifetime longer than 20 ns.

The $B_{1/2}$ value observed experimentally is determined theoretically via the effective hyperfine interaction of donor and acceptor B_1 and B_2, respectively. They are defined as follows:[21]

$$B_i^{\,2} = \sum_k a_{ik}^2 I_{ik}(I_{ik} + 1), \quad i = 1,2$$

Here a_{ik} are the isotropic hyperfine coupling constants and I_{ik} are the nuclear spin quantum numbers for each unpaired electron of the RIP.

For DCNB, $B_2 = 4.6$ G.[2b] Assuming that intermolecular electron exchange between acceptor molecules does not lead to a strong broadening of RIP levels and using one of the empirical formulas, i.e.,[6]

$$B_{1/2} = \sqrt{3(B_1^{\,2} + B_2^{\,2})} \qquad (7)$$

one can estimate the B_1 parameter for carbazole derivatives. These are 28.5 G and 14.3 G for MeCz and CzB, respectively. The value for CzP seems to be close to the latter. Thus, B_1 decreases approximately by a factor of 2 on passing over from the single to the double donor. Although this factor rather should be closer to 1.4, these results seems to correspond pretty well to case (1) of strong exchange interaction between donor moieties for CzP, and case (2) of fast exchange (CzB) in the Schulten theory;[5] the discrepancy may be attributed to not high precision because of the chemical instability of the system. As for saturation values of the MFE, the theory also predicts the diminution of the observed MFE, although it seems not so strong as we observed it experimentally for CzP, unlike CzB, for which MFE is almost the same as for MeCz. A more qualitative comparison is not possible since particular numerical calculations were done by Schulten for double dimethylaniline molecules, another well-known electron donor. There is an obvious correlation with results obtained by Masuhara et al. on absorption of cation dimer,[22] i.e., CzP is associated with producing the carbazole sandwich cation radical as CzB, with the second dimer cation radical.

Conclusion

On passing from single to double carbazole derivatives as electron donors (the electron acceptor is DCNB), the $B_{1/2}$ parameter of the MFE detected by exciplex fluorescence decreases by a factor of ca. 2 due to a significant increase in the rate of electron hopping in the dimer cation radicals produced in the course of photoinduced electron transfer. The saturation values of the MFE are almost the same for MeCz and CzB, whereas that of CzP is strongly decreased. These experimental results are in qualitative agreement with the Schulten theory of intramolecular electron exchange.

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