Magnetic Field Dependent Reaction Yields from Radical Ion Pairs Linked by a Partially Rigid Aliphatic Chain

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The electron donor-acceptor compound pyrene- $(CH_2)_3$ -cyclohexane- $(CH_2)_3$ -dimethylaniline, abbreviated as Py3(C6)3DMA, has been investigated. Photoinduced electron transfer leads to the singlet radical ion pair Py-3(C6)3DMA⁺. An extraordinary large and distinct magnetic field effect is observed in the yield of the locally excited triplet state of the pyrene moiety, the recombination product of the triplet radical ion pair. The half-width of the "J-resonance" maximum in the magnetic field dependent triplet yield curve is just 66 G, corresponding to 7.7×10^{-7} eV or 6.2×10^{-3} cm⁻¹. This is due to the influence of the rigid *trans*-cyclohexane part in the aliphatic chain, which leads to a reduced intramolecular mobility and to a narrow probability distribution of the radical ion pair distance, as predicted by Monte-Carlo computer simulations. The magnetic field dependence of the triplet generation is further transmitted to secondary reactions like triplet-triplet annihilation, thus leading to a magnetic field dependent delayed fluorescence and to a delayed excimer fluorescence.

Introduction

Magnetic fields can influence the reaction yields of radical ion pair recombination reactions by modifying the electron spin evolution of the initially formed radical ion pair species, thus affecting the competition between spin-state-dependent decay pathways. In past years, a series of experimental and theoretical investigations have led to a wealth of interesting new information on magnetic field effects, particularly of the hyperfine type.¹⁻¹⁰

Spin-correlated radical ion pairs (RIPs), i.e., pairs from precursors that are in a certain spin state, in our case a singlet state, are often prepared by photoinduced electron-transfer reactions taking place between electron donor (D) and acceptor (A). In particular, instead of radical ions which can diffuse freely in solution, compounds have been investigated with donor and acceptor linked by an alkane chain of variable length. Generally, this increases the influence of a magnetic field since the radical ion pairs remain a geminate pair, and at low concentration homogeneous reactions of ions are absent.

Furthermore, A-D systems linked by a $(CH_2)_n$ chain with n between 6 and 11 exhibit a new shape of magnetic field curves of the hyperfine type. In such cases, one observes at a certain magnetic field strength a maximum of the triplet yield (and/or a minimum of the exciplex fluorescence),¹¹⁻¹³ in contrast to the monotonic saturation-type curve, which approaches a final value at high field strength. With increasing magnetic field strength, after passing through the maximum at field strength B_{max} , the effect reverses and approaches a new saturation value at high field strengths (B_{∞}) with a triplet yield below that found at B =0. This resonance-type behavior is discussed in terms of the energy splitting 2J between the radical ion pairs with overall singlet multiplicity ${}^{1}{}^{2}A^{-}-{}^{2}D^{+}$ and RIPs with triplet multiplicity ${}^{3}{}^{2}A^{-2}D^{+}$, due to the exchange interaction (J) between the respective unpaired electrons of the intramolecular RIPs, where $2J > \Delta E_{\rm hfc}$ ($\Delta E_{\rm hfc}$ is the hyperfine coupling energy). When the magnitude of the applied magnetic field is just sufficient to achieve degeneracy between a triplet sublevel (generally T_{-1}) and the singlet level, due to Zeeman interaction between unpaired electrons and the magnetic field, i.e., $g\mu B = 2J$, then an enhanced transition probability between singlet and triplet radical ion pair states results. This behavior is not amenable to direct experimental

determination of the exchange interaction, since the carbon chains do not ensure a fixed spacing between the unpaired electrons, while the exchange interaction is strongly distance-dependent. A detailed investigation has shown that even knowledge about the equilibrium distribution of the distances does not necessarily result in a certain distribution of the exchange interaction. Rather, the exchange interaction is stochastically modulated by the chain dynamics. Thus, even if the equilibrium distribution is achieved, the chain dynamics (i.e., the transition rate between conformations of differing distances) leads to sizable displacements in the distribution of these exchange interactions.^{11,14}

One approach to specify an exchange interaction energy is a rigid chain with fixed donor-acceptor distance. Closs et al.¹⁵ and Paddon-Row and Verhoeven¹⁶ have synthesized and characterized such rigid molecular structures for determining the distance and spacer dependence on electron transfer (ET). However, investigation of the spin dynamics by way of magnetic field effects requires molecules with a relatively large donoracceptor distance, which makes it possible to achieve a level mixing $(S \times T_{-1})$ with magnetic field strengths in the readily available range 100-1000 G. On the other hand, such large molecular distances result in a diminishing rate of ET, so only low concentrations of RIPs are available for studying the magnetic field effect (MFE). Our present approach, achieved through a partial rigidity of the donor-acceptor linkage, provides the desired restriction of energetically favorable conformations while only minimally affecting the folding dynamics of the chain. This yields a narrower probability distribution of the exchange interaction. The incorporation of a rigidifying structure must provide both an ET and RET (return electron transfer) over shorter distances and the evolution of the electron spin system at greater distances. The average length of such partially flexible chains should be comparable to the $(CH_2)_8$ to $(CH_2)_{10}$ chains which have been used repeatedly for establishing donor-acceptor combinations for the level-crossing MFE studies.^{3g,3h,11-13,18} Shorter chains usually show no MFE, while longer chain systems only show saturation behavior.

After extensive computer simulation studies of pair distribution functions of a large number of chain-linked A–D molecules,^{17,19} we have selected and synthesized a compound with electrondonor N,N-dimethylaniline (DMA) and electron-acceptor pyrene (Py), linked by a partially rigid chain of *trans*-1,4-di-*n*-propyl-

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Figure 1. The molecule investigated (in stretched conformation, front view, and side view, according to PCModel): 1-pyrene-(CH₂)₃-cyclohexane-(CH₂)₃-N,N-dimethylaniline. It is abbreviated Py3(C6)-3DMA or 3(C6)3.

cyclohexane. This molecule, shown in Figure 1, is referred to as Py3(C6)3DMA or simply as 3(C6)3.

Selection of the Trans-Isomer. Variably substituted cyclohexane in the 1,4-position has two isomers, namely, the transand the cis-form, each allowing three conformations. Of these conformations, the boat-shape conformer, undesirable for the present study, is only a brief intermediate at room temperature because of its high conformational energy.²⁰ It is assumed that at least 95% remained in the trans-form at the end of the synthesis equivalent to the starting substance. An indication is derived from an earlier substance, pyrene-(CH₂)-cyclohexane-(CH₂)-DMA (abbreviated Py1(C6)1DMA), which was once synthesized from a cis-trans mixture (approximately 50%/50%) and another time synthesized from a 95% trans starting material (see Experimental Section). The electron transfer rate of both compounds was distinctly different.

In the chair conformations, the cis-isomer has one substituent in an axially oriented position and the other one is equatorially oriented. This conformation would readily result in A-D distances which are too short when large substituents and rotational degrees of freedom are involved in the alkane chains, like in the present material. In contrast, the trans-form has both substituents in the equatorial position in one conformation. This conformer is energetically more advantageous ($\Delta E = 3.6 \text{ kcal/mol}$) than the axial-axial form.²⁰ Therefore, the trans-isomer will predominantly attain the conformation in which the cyclohexane substantially represents a rigid and straight portion between two short flexible or mobile chain segments.

The extended or stretched chain length of 3(C6)3 is calculated by a molecular mechanics program (PCModel,²¹ with MMX algorithm) at 13.0 Å between the first carbon atoms of the end groups. By comparison a distance of 12.1 Å is calculated for the $(CH_2)_9$ chain and 14.0 Å for the $(CH_2)_{10}$ chain. The calculated distance distribution, derived from a Monte-Carlo simulation,¹⁷ indicates that virtually no conformations for $3(C6)_3$ are found with a central distance in the end groups of less than 10 Å. Comparative values are as follows: for Py(CH₂)₉DMA 27%, for Py(CH₂)₁₀DMA 14%, while for Py3(C6)3DMA with cyclohexane in the trans-form, as discussed above, only 0.05% of the distribution falls within this range of narrow conformations at room temperature. Due to the specific conformation distribution, this molecule was chosen for the investigations described here.

We investigated and characterized the spectral, kinetic, and magneto-chemical properties of the 3(C6)3 compound and compared these properties with $Py(CH_2)_nDMA$, n = 9-10.

Experimental Section

Synthesis of the Compound Pyrene- $(CH_2)_3$ -Cyclohexane-(CH₂)₃-DMA (Figure 1). trans-1,4-Cyclohexanedicarboxylic acid dimethyl ester was prepared from commercial 95% trans-1,4-cyclohexanedicarboxylic acid by methanol/HCl. The diester was transformed with NaOH to the monoester. From thionyl chloride the acid chloride was obtained, which reacted with methylzinc chloride to the *trans*-1-acetylcyclohexanecarboxylic acid monoethyl ester. The obtained ketone was converted with 1-pyrenecarboxaldehyde to an unsaturated ketone, which was hydrogenated in the presence of Pd/C. After reduction of the keto group by the Huang-Minlon process, the obtained *trans*-4-(1-pyrenyl-*n*-propyl)cyclohexanecarboxylic acid was transformed with thionyl chloride to the acid chloride, which, with methylzinc chloride, provides the ketone. This ketone reacted with p-(N,N-dimethylamino)benzaldehyde in alcoholic NaOH to form an unsaturated ketone, which was hydrogenated. Finally, the ketone was transformed by the Huang-Minlon process to the *trans*-1-(1-pyrenyl-*n*-propyl)-4-(4-N,N-dimethylamino)phenyl)-cyclohexane.

The 12 synthesis steps were controlled by MS, NMR, and IR spectroscopy. The intermediates were purified by column chromatography. The final product was additionally purified by HPLC.

Sample Preparation. Samples with concentrations of about 10^{-4} M were prepared directly from the HPLC machine into the degassing bulb of the quartz cuvette. The solvent (isooctane and chloroform) was evaporated in vacuo, and the purified and dried solvent was distilled in vacuo into the degassing bulb cooled in a liquid N₂ bath. About six freeze-pump-thaw cycles were applied before sealing off the glass-quartz system from the vacuum line.

Instruments. The spectroscopic instrumentation used in this work, in particular instrumentation for MODESC spectroscopy (magneto-optically detected spin conversion), is described in the relevant sections that follow. The lasers used were an EMG 500, an EMG 102 MSC, and a dye laser FL 2000 operating with stilbene 1, all from Lambda Physik. Magnetic field strengths were measured with a Hall-type Gauss-meter (Bell 620).

Results

Electronic Transitions and Reactions. The states and transitions of the molecule 3(C6)3 are shown in Figure 2. The primary excitation by a pulsed N₂-laser at 337 nm falls within the pyrene (actually methylpyrene) absorption. We have found that methylpyrene is hardly affected in its electronic properties by the additional chain substitution and, therefore, is promoted into its first excited singlet state (2), (¹A*-D). From this excited state, there are at least three pathways leading to states of lower energy.

1. The emissive transition to the ground state (1) provides prompt fluorescence with a rate constant $k_{\rm f}$ independent of external magnetic fields; the fluorescence spectrum is shown in Figure 3. This transition is characterized by the emission at 360–450 nm, corresponding to fluorescence bands of methylpyrene.

2. The lowest triplet state (6) of the pyrene is arrived through intersystem crossing with k_{isc} . This step results in triplets, independent of an external magnetic field.

3. The dominant competitive process in polar solvents is the electron transfer (k_{et}) from the donor DMA to the acceptor pyrene by generating an intramolecular RIP (3). The total spin multiplicity is conserved: the RIP is formed in an overall-singlet state.

The possibility of direct transition to the exciplex (4), which can occur when DMA approaches pyrene within an encounter distance during the lifetime of the excited pyrene, would lead to an exciplex fluorescence, independent of a magnetic field. Exciplex fluorescence of pyrene/DMA systems generally appears as a broad band between 460 and 620 nm. However, it is not distinguishable spectrally from those exciplexes which are formed through the pathway $(2) \rightarrow (3) \rightarrow (4)$ of the RIP generation; the yield of the latter exciplexes is magnetic field dependent.^{11,12} In 3(C6)3, the emission intensity of the exciplex band is very weak, but still detectable, in the solvent acetonitrile (ACN) but is pronounced in tetrahydrofuran (THF); see Figure 3.



Figure 2. Energy level diagram. (a) Reaction pathways after excitation from the ground state (1): (2) primary excited singlet state, (3) singlet RIP, (4)-intramolecular exciplex, (5) triplet RIP, (6) locally excited triplet product. (b) Reaction pathways of the triplet products (6): delayed formation of the first excited singlet state (7) and the excimer (8) leading to delayed fluorescence and delayed excimer fluorescence.



Wavelength /nm

Figure 3. Photostationary prompt fluorescence of Py3(C6)3DMA in ACN and THF.

In the case of methylpyrene in the solvent ACN, only k_f and k_{isc} are effective, and the lifetime is $\tau_0 = 190$ ns. By comparison, the lifetime of the excited pyrene in 3(C6)3 is $\tau_f = 36$ ns in ACN, from which the RIP yield is computed:

$$\Phi_{\rm RIP} = \frac{1/\tau_{\rm f} - 1/\tau_{\rm 0}}{1/\tau_{\rm f}} \tag{1}$$

This is valid in polar solvents since direct exciplex formation is

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negligible. In ACN, Φ_{RIP} is 80%. The remaining 20% of excited singlet-state concentration is distributed between prompt monomer fluorescence and to a smaller extent by the direct triplet formation (k_{isc}) , as already mentioned. The efficiency of further possible reaction channels (radiationless charge recombination to the ground state and the formation of the triplet RIPs (5)) depends on the evolution of the respective relative position of the donor and acceptor moieties: when the distance between donor and acceptor is reduced after RIP formation, then the contact ion pair, i.e., the exciplex (4), can be formed. At greater distance (in the course of diffusional separation), the exchange interaction between the two unpaired electrons in the RIP, resulting in a S-T splitting of 2J, may become smaller than the hyperfine interaction energy, $\Delta E_{\rm hfc}$. In that case, spin coherence may be lost and a new population of spin states according to the relevant selection rules may take place.^{14,11}

In the presence of an applied external magnetic field, another population change is possible, in particular if a J-resonance is active, i.e., when the exchange interaction is equal to the Zeeman energy. An externally applied magnetic field displaces the triplet sublevels T_{+1} and T_{-1} from their energy state T_0 by the Zeeman interaction, whereby the equilibrium is changed between singlet and triplet RIPs. All cases imply that a certain fraction of originally generated singlet RIPs reaches the triplet RIP state (5). This reaction step $k_{st}(B)$ is the only *directly* magnetic field dependent process in the scheme of Figure 2.

Singlet RIPs can recombine to the ground state (1) through return electron transfer (RET). From triplet RIPs, the locally excited triplet state (6) of pyrene evolves; in subsequent reaction steps, these triplet pyrene molecules behave much like unlinked triplet pyrenes. For reasons of conformational restrictions in the 3(C6)3 chain, the formation of emissive contact ion pairs (singlet exciplexes) from the singlet ion pairs and of triplet exciplexes from triplet ion pairs is possible only with low yield, contrary to compounds having a flexible alkane chain, $(CH_2)_n$ e.g., n = 10.^{11,12}

The prompt fluorescence spectrum in Figure 3 exhibits the characteristic appearance of donor-acceptor molecules. In the range 360-450 nm, the emission bands of the initially excited pyrene are evident, and the exciplex band between 460 and 620 nm is red-shifted. It is quite weak with this compound (3(C6)3), clearly recognizable only in the low-polarity solvent THF and virtually absent in ACN. In both solvents, the relative intensity of the exciplex emission is lower by about a factor of 20 than that in the comparable alkane-linked compound Py10DMA.

Thus, depending on the distribution of triplet and singlet RIPs, respectively, different intermediates or final states result whose yield can be influenced by applied external magnetic fields. After about 200 ns, all primary processes are completed. A fraction of the initially excited molecules has returned to the ground state, while another fraction appears as triplet pyrene, linked with DMA. The lifetime of the latter state is of the order of several hundred microseconds. Pyrene triplets can return to their ground state by several pathways: encounter with quenching molecules (e.g., molecular oxygen), phosphorescence, radiationless monomolecular deactivation, and finally the triplet-triplet annihilation, shown in Figure 2b. The latter process subsequently exhibits a readily observable MFE which derives from the magnetic field dependence of the [³Py*-D] yield. A different kind of MFE, namely, the influence on the T-T-annihilation described by Labhard et al.,²² is only expected at higher magnetic fields and higher solvent viscosity. Additionally, this effect is much smaller than the one found with the present compound.

Two parallel reactions can be observed in the current study:

$${}^{3}Py^{*}-D + {}^{3}Py^{*}-D \rightarrow {}^{1}Py^{*}-D + Py-D$$
 (2)

In this reaction, one of the molecules is found again in the first locally excited singlet state (7), from which, at least in principle, all previously described processes can be repeated. Clearly



Figure 4. Delayed fluorescence spectrum of Py3(C6)3DMA in ACN, 0.3 ms after excitation, at different magnetic field strengths. An intermediate field at $B \approx 90$ G intensifies the signal compared to that of B = 0, and a stronger field impairs the signal.

observable, however, is only the fluorescence from ${}^{1}Py^{*}$, appearing *delayed* and with half of the lifetime of the triplet pyrene, as to be expected.

The excimers (8), also generated with delay, are well-known as promptly-formed excimers in unlinked pyrene at higher concentrations. They appear in the spectrum of delayed fluorescence in a band around 480 nm, in Figure 4. It should be noted that in the present compound 3(C6)3 excimers (8) appear with *delayed* excimer fluorescence only and not with prompt excimer fluorescence.

$$^{3}Py^{*}-D + ^{3}Py^{*}-D \rightarrow D^{-1}(PyPy)^{*}-D$$
 (3)

During the long triplet lifetime, the probability of an encounter, initiating the annihilation, is much higher. After the encounter and the energy transfer, both pyrenes are closely adjacent.

Both processes (eqs 2 and 3) occur simultaneously and result in the spectrum of delayed fluorescence. The number of triplet molecules (6) generated via reaction paths [(2), k_{et} , (3), $k_{st}(B)$, (5), k_{rt} , (6)], cf. Figure 2, depends on the magnetic field, due to reaction step $k_{st}(B)$; this dependence is transferred to the entire emission spectrum of delayed fluorescence, as shown in Figure 4. Lavrik et al. investigated the MFE of unlinked donor-acceptor systems by using delayed excimer emission as a monitor.²³ Since T-T annihilation is a bimolecular process, triplet concentration and MFE enter as squared terms.

Decay Times. The deconvoluted decay curve of the primary fluorescence, measured at 377 nm with the time-correlated single photon counting method (excitation, 337 nm; half-width, 3 ns), is not a simple exponential function. A reasonable fit leads to a sum of three exponentials which can be assigned to three species: one component with a decay time of 190 ns but very small initial amplitude is due to unquenched pyrene which is disconnected from the quencher moiety. The main fraction of the emission with a decay time of 36 ns is attributed to the transisomer of 3(C6)3. The short decay time of 6-9 ns with small initial amplitude is assigned to the cis-isomer, whose shorter donoracceptor distances promote a stronger quenching. The latter fraction contributes little to the total emission yield, and moreover, it lies essentially in the convolution range of the excitation pulse; therefore, the molar fractions of the isomers cannot be obtained from the curve-fitting procedure. The value of the 5% cis-isomer, starting at the synthesis of 3(C6)3, is well within the range of allowable variation of the fit. The lifetime of the trans-isomer is long in comparison with that of the alkane-linked compounds (Py10DMA, 1.7 ns; Py9DMA, 1.5 ns). The above observations as well as the low exciplex yield both confirm the results obtained



Figure 5. Triplet absorbance of Py3(C6)3DMA in ACN as a function of an applied external magnetic field. The curve is normalized to 1.0 at B = 0.

from the Monte-Carlo calculations of pair distribution functions,¹⁷ namely, that short intramolecular distances at the end groups in 3(C6)3 appear far less frequently than they do in the alkanelinked compounds. Still, the quenching by ET is sufficiently strong that about 80% of the initially excited molecules end up in the RIP state. In the highly viscous solvent diethylene glycol (DEG), the prompt fluorescence decay time of 3(C6)3 is 131 ns, with a small component of 54 ns.

The observed very weak exciplex emission at 577 nm in ACN shows a rise time of 29 ns followed by a decay time of 56 ns; this decay time is identified with the decay time of the radical ion pair.¹² Due to the weak signal, the functional dependence of the rising signal cannot be resolved as biexponential: it possibly appears as the average of 6.6 and 35.7 ns (see above). Considering the possible origin of species (4) (cf. Figure 2), it is likely that the functional dependence of the rise is correlated with the decay of the initially excited state (2).

Magnetic Field Effect (MFE). A. MFE of the Triplet Absorption. The most direct observation of the MFE is obtained by measuring the absorption of the triplet pyrene, which has a typical absorption at 415 nm. For optimal detection of the effect, a time delay of at least 100 ns is required between excitation and absorbance measurement. That is achieved via two electronically synchronized lasers. The excitation laser, a N₂-laser ($\lambda = 337$ nm, $t_{\rm HW} = 5$ ns), is focused along the front face of the sample cuvette into a narrow line. The quartz cuvette is positioned between the pole pieces of an ESR magnet. The dye laser beam, generated by a second N₂-laser, is narrowed through a microscope objective located in one of the pole pieces, the beam running parallel to the front face of the sample cuvette throughout the excited volume along the line of focus. Synchronization of the two lasers is such that the time delay amounts to 200 ns. In the presence of an adjusted external magnetic field, 10 probing laser pulses each with and without excitation are provided so as to determine and compute the absorbance difference caused by the excitation, at a repetition rate of 5 Hz. Thereafter, a new value of the magnetic field is selected, and the excitation and absorbance measurements are repeated. In this manner, a predetermined range of magnetic field strengths is covered. In order to ensure stability of the sample and of the measuring technique, the first measurement progresses from low to high magnetic fields, followed by a second measurement in the reverse direction. In the absence of drift, both results would coincide.

In ACN, the MFE of the triplet absorption is quite evident, as shown in Figure 5. It is the most pronounced level-crossing characteristic (*J*-resonance) observed to date in triplet absorption. A relatively high maximum at a field strength of 85 G is noted,



Figure 6. Normalized triplet absorbance of Py3(C6)3DMA in DEG as a function of an applied external magnetic field.

followed by a decrease of the triplet yield (Φ_T) to a level of about one-half of the initial value: compared to the normalized absorbance of 1.0 at B = 0, the peak at B = 85 G is 1.48; in saturation at $B \gg 1000$ G, Φ_T has decreased to 0.58. The halfwidth of the maximum is $B_{HW} = 66$ G, and the half-width of the subsequent decay portion is $62 \text{ G}.^{24}$ Compared to the more flexible alkane-linked molecules, we observe a significantly narrower maximum and a more enhanced decrease toward the saturation value, i.e., $Q_{max} = \Phi(85)/\Phi(0)$ and $Q_{sat} = \Phi(1200)/\Phi(0)$ are large: 1.48 and 0.58, respectively. Similar results were obtained with N,N-dimethylformamide as solvent, which has comparable polarity and only slightly lower viscosity than ACN.

In contrast, the MFE in the higher viscosity diethylene glycol (DEG) is different, as indicated in Figure 6. DEG has a viscosity of 38 mPa·s at 20 °C compared to 0.36 mPa·s for ACN. The initial rise toward the maximum at B = 70 G is weaker, and the half-width of the decay toward the saturation value is comparable to that observed with ACN; we obtain $Q_{max} = 1.08$ and $Q_{sat} = 0.85$ for DEG. The spread of data points is considerably larger because of reduced transient absorbance changes, despite stronger excitation. Reasons for that are reduced ET quenching due to the high solvent viscosity and lower Py3(C6)3DMA concentration due to weaker solubility.

B. MFE of the Delayed Fluorescence (DF) and Exciplex Fluorescence. The exciplex fluorescence intensity of 3(C6)3 is so weak in ACN that with the detectivity of our measuring system an MFE in exciplex emission was not discernible because the signal of the delayed excimer emission was dominant throughout the total spectral range during non-time-selective signal detection.

The experimental arrangement for measuring the MFE of the luminescence comprises a chopper-modulated Xenon short arc source and a suitable filter (Schott UG 11) for extraction of the UV component for the excitation. The fluorescence signal emanating from the cuvette is directed to a remote photomultiplier by quartz fibers from the cuvette location between the magnet pole pieces. The photomultiplier is part of a lock-in amplifier system operating at 35 Hz, thereby achieving the desired signal/ noise improvement and elimination of the effect of undesired stray light. The MFE of delayed excimer emission was detected through interference filters.¹⁹ The MFE of delayed emission at different fixed wavelengths exhibits a similar functional trend as the triplet absorbance: a peak rising from B = 0 at about 85 G, followed by a decay toward a saturation value at high magnetic field strength. The maximum of the delayed excimer fluorescence MFE is also observed at B = 85 G, and the magnitude of the effect is smaller than that of the triplet yield, probably due to a superposition with the complementary function of the (weak) exciplex emission.

The delayed-fluorescence MFE throughout the *entire spectral* range was determined with a fluorescence spectrometer (PELS50) whose output signal in the phosphoroscope mode can be gated during the excitation period so that the measured spectra of delayed fluorescence and prompt fluorescence can be separated. That separation was not always complete, but the fraction of the prompt emission could be determined and subtracted. The corrected DF spectrum in Figure 4 is shown as a solid line for B = 0. Incorporating an adjustable permanent magnet yielded the more intense spectrum for $B \approx 90$ G (dashed trace) and the lowest-intensity saturation spectrum for $B \approx 1000$ G (dotted trace). It is worth emphasizing that the magnetic field effect has the same behavior throughout the entire spectral range from about 360 to 560 nm. This means that the external magnetic field affects both the excimer fluorescence and the delayed monomer fluorescence in the same manner. We define the ratio Q' of emission intensities in eq 4. Quantitatively, the effects are

$$Q'_{\rm DF}^{\rm max} = \frac{I_{\rm DF}(B=85{\rm G})}{I_{\rm DF}(B=0{\rm G})} = 2.13$$
$$Q'_{\rm DF}^{\rm sat} = \frac{I_{\rm DF}(B=1000{\rm G})}{I_{\rm DF}(B=0{\rm G})} = 0.312$$
(4)

Due to the influence of the triplet concentration squared terms in the rate equations, we have to take the square roots, yielding

$$\sqrt{Q'_{\rm DF}^{\rm max}} = 1.46$$

$$\sqrt{Q'_{\rm DF}^{\rm sat}} = 0.56$$
(5)

thus providing a substantial agreement with the Q values derived for the triplet absorbance. In the magnetic field range 85-500 G, the delayed fluorescence intensity decreases by a factor of 7! The fact that the spectra have a similar shape throughout the total spectral range indicates that the delayed monomer fluorescence as well as the excimer fluorescence derive from T-T annihilation, with an equal lifetime of 305 μ s and a square dependence on excitation intensity.

The investigations of the exciplex fluorescence have been performed with 3(C6)3 in a 1:1 mixture of ACN and ethyl acetate at low excitation intensity in order to enhance the relative yield of the exciplex emission compared to the delayed excimer emission.¹⁹ While the viscosity of this mixture is comparable to that of ACN alone, the dielectric constant (DK) is about 22. We have observed an MFE curve having an inverse relationship to the triplet MFE with a *minimum* in the range $B \approx 70-90$ G. The relative intensity at this minimum is about 0.95 of the initial value at B = 0, while at B = 500 G the intensity is higher by a factor of 1.16. From that, we conclude that the small fraction of exciplexes formed is not derived just from the cis-isomer, to which we would attribute negligible magnetic field dependence. The *inverse dependence* of exciplex MFE¹¹ is due to competitive processes in steps (3) \rightarrow (5) and (3) \rightarrow (4), cf. Figure 2a.

In order to explain the appearance of the small exciplex remnant, particularly in THF, we have carried out a Monte-Carlo simulation of the distance distribution of RIPs.¹⁷ In addition to the usual unaltered conformation energy, we have included the Coulomb energy

$$U_{\rm c} = {\rm e}^2/\epsilon r_{\rm cc} \tag{6}$$

With $\epsilon = 7.4 \times \epsilon_0$ as the DK of THF, we obtain the relationship shown in Figure 7 (dotted trace). There, a fraction of conformations with small pyrene–DMA distances is favored by the energy decrease brought about by the Coulomb term. The fraction of conformations with an edge-to-edge (ee) spacing smaller than 5 Å is found to be 0.4% for the uncharged molecule, 0.5% for the RIP in ACN, and 6.4% for the RIP in THF. It is these



Figure 7. Result of Monto-Carlo calculations (cf. ref 17) of edge-to-edge distance distributions $p(r_{ee})$ for Py3(C6)3DMA in THF (DK = 7.4): uncharged A–D molecule (solid line); radical ion pair ²A⁻–²D⁺ (dotted line).



Figure 8. Low-energy conformation of the radical ion pair $Py-3(C6)3-DMA^+$ in THF. The edge-to-edge distance is 2.2 Å. The atoms are pictured with their CPK radii (see ref 21); van der Waals radii are smaller by a factor of 0.65. The scale mark (lower left) represents 1 Å.

conformations which give rise to emission within the exciplex bands, thus leading to the fluorescence spectrum shown in Figure 3.

The molecular model of Figure 8 suggests that for a few conformations in THF (because of the additional Coulomb energy term) the end groups can be very close together and yet not be sandwich exciplexes. The conformation shown is one of the lowestenergy simulated RIP conformations in THF, with an ee spacing of 2.2 Å. A significant overlap of the electron wave functions of pyrene and DMA must be present with that conformation leading to that distance. The interesting topic of electronic coupling in contact ion pairs and solvent-separated ion pairs of bimolecular systems has been addressed recently by Farid and co-workers.²⁵ Spectral shifts related to such phenomena are under study in this laboratory with selected chain-linked A–D compounds utilizing picosecond transient absorption spectroscopy²⁶ and spectro-streak-camera methods leading to informative time-resolved emission spectra.²⁷

Discussion

The following discussion is based on the framework of the stochastic Liouville equation and the static ensemble approximation, the essentials of which have been described in the literature.^{3a-c,11,14a,b,28} Key features are as follows:

1. With an assumed fixed exchange interaction J, a theoretical triplet yield curve $\varphi_T(B)$ as a function of the magnetic field strength



Figure 9. Theoretical triplet yields $\varphi_T(B)$ as a function of the magnetic field strength at fixed exchange interactions J between 0 and 80 G. RIP recombination rates are taken to be 0.1 ns⁻¹ and are assumed equal in this model calculation for singlet and triplet RIPs.²⁸

B is obtained; Figure 9 depicts examples. The maximum of such a curve is associated with the degeneracy of the S and T_{-1} levels where $g\mu B = 2J$. Its width is determined by the hyperfine coupling energy $\Delta E_{\rm hfc}$ and by the lifetime of the RIPs. For long lifetimes, the MFE curve narrows until its minimal half-width approaches the value of $\Delta E_{\rm hfc}$.

2. In the course of chain motion, the exchange interaction J is modulated stochastically. The resulting final MFE curve is obtained from the summation of the product of the fixed J-curves and the probability distribution function w(J).¹¹

3. The function w(J) does not directly correspond to the equilibrium end-to-end distance distribution, p(r), of the molecule. Rather, it is influenced significantly by the dynamics of the chain motion, where J(r) has a very strong exponential dependence on the distance r (cf. eq 11) with a large exponential coefficient and therefore decidedly impacts the w(J) function. The faster the distance modulation, the more strongly w(J) is narrowed and shifted with respect to the slow-motion distribution $w_0(J)$.¹¹ Rapid distance modulation leads to a steep and narrow w(J) distribution with a maximum probability for J between J_0 , corresponding to the most probable *static* exchange interaction, and J_{∞} , which would be obtained at *infinitely rapid* chain motion. The above behavior has been termed motional narrowing and motional shifting.¹¹

The rigid *trans*-cyclohexane part in the chain leads to a reduced intramolecular mobility and to a missing portion in the p(r) distribution at short distances. The latter effect was the outcome of a Monte-Carlo simulation of the distance distribution.¹⁷ It is confirmed by the measured fluorescence decay time and by the absence of a significant exciplex emission within the fluorescence spectral range.

The partially rigid chain also leads to a reduced recombination rate of RIPs with the consequence of a longer RIP lifetime (56 ns). This long lifetime has the following consequences for the MFE:

1. The MFE curves at fixed J turn so narrow that in the limit the width is mainly determined by ΔE_{hfc} ;^{14,28} for the pyrene/ DMA system, ΔE_{hfc} is about 57 G, as obtained from theoretical considerations and from the $B_{1/2}$ value of the unlinked system.^{3f,g}

2. The spin system in the RIP has sufficient time to reach its respective equilibrium. According to calculations,^{3b,29} the equilibrium is established in about 10 ns in the Py/DMA system at J = 0. Thereby, the MFE can evolve to its highest possible value.

As a consequence of eliminating conformations at short distances, which would yield large J values, the remaining conformations at long distances restrict the w(J) distribution to smaller J values, and the motional shifting process is reduced.

 TABLE I:
 Absorbance and Fluorescence Lifetimes in Eq 10

	solvent	
	DEG	ACN
τ_0	169 ns	180 ns
τ	131 ns	36 ns
E ^{exp}	0.09 ± 0.01	0.18 ± 0.01
E_{T}^{0}	0.08 🏚 0.01	0.085 ± 0.01
$\dot{E_{T}^{RIP}}/E_{T}^{Py}$	0.4 ± 0.3	11 ± 2

When fitting calculated curves to measured data, it is important for one to remember that the RIP reaction path $(2) \rightarrow (3) \rightarrow (5)$ $\rightarrow (6)$, cf. Figure 2, does not provide the only triplet generation process (e.g., in Figure 2 the direct path $(2) \rightarrow (6)$ with k_{isc} also contributes). Thus, the experimental triplet absorbance is

$$E_{\rm T}^{\rm exp} = E_{\rm T}^{\rm Py} + E_{\rm T}^{\rm RIP} \tag{7}$$

The absorbance (extinction) at 415 nm is proportional to the triplet yield Φ_T and

$$\Phi_{\rm T}^{\rm exp} = \Phi_{\rm T}^{\rm Py} + \Phi_{\rm T}^{\rm RIP} \tag{8}$$

Assuming that the intersystem crossing rate constant k_{isc} of the linked pyrene (index Py) is equal to that of 1-methylpyrene (index 0) in the same solvent, we calculate

$$\frac{\Phi_{\rm T}^{\rm Py}}{\Phi_{\rm T}^{\rm 0}} = \frac{\tau}{\tau_0} \quad \text{and thus} \quad \frac{E_{\rm T}^{\rm Py}}{E_{\rm T}^{\rm 0}} = \frac{\tau}{\tau_0} \tag{9}$$

where Φ_T^0 and E_T^0 are the triplet yield and triplet absorbance in methylpyrene, respectively; τ is the fluorescence lifetime of the linked compound; and τ_0 is the lifetime of the methylpyrene. Equations 7 and 9 yield

$$\frac{E_{\rm T}^{\rm RIP}}{E_{\rm T}^{\rm Py}} = \frac{E_{\rm T}^{\rm exp}}{E_{\rm T}^{\rm 0}} \frac{\tau}{\tau_0} - 1$$
(10)

To determine the ratio of triplets generated via the two different channels, measurements of the absorbance and of the fluorescence lifetimes of methylpyrene and Py3(C6)3DMA under identical conditions are required (see Table I). In the last line of Table I, the results according to eq 10 are listed. In ACN, roughly 9% of the triplets are due to direct intersystem crossing, whereas in DEG this fraction amounts to about 70% (with some uncertainty for this value).

A fit of the theoretical curve based on the Liouville formalism is shown in Figure 5 for Py3(C6)3DMA in ACN. The corresponding w(J) distribution, chosen such that an optimal fit is obtained, is depicted in Figure 10. Examples of individual triplet yield functions $\varphi_T(B)$ for fixed J are shown in Figure 9. Integration of the products $\varphi(B)$ times w(J) yields the fitted curve in Figure 5.¹¹ The fit programs were the same as those in ref 28. The agreement between the measured curve and the calculated one is excellent. How appropriate the assumed function w(J) is, however, remains to be discussed. A distinctly broader w(J)distribution would result, if calculated on the basis of quasistatic (i.e., slow motion) conditions, where the distance distribution p(r) is converted to a $w_0(J)$ distribution using

$$J(r) = \exp(-\alpha r) \tag{11}$$

with the parameters $J_0 = 9.46 \times 10^9$ G and $\alpha = 2.136$ Å^{-1.30} It is clear, of course, that under such conditions the fraction of conformations leading to small J's is larger than the fraction in that distribution yielding the best fit to the experimental data. One cannot expect that the w(J) distribution found in the procedure described above corresponds to the static $w_0(J)$ distribution (see also refs 14 and 28) since in the range of energetically favorable conformations, between 11 and 18 Å, rapid conformational changes are unrestrained. Therefore, the w(J)found is a dynamically narrowed distribution in the range of



Figure 10. The w(J) distributions as used for the calculated fitted curves for Py3(C6)3DMA in ACN (Figure 5), solid lines, and in DEG (Figure 6), dashed lines.



Figure 11. Magnetic field dependent triplet absorbance in ACN of Py3-(C6)3DMA compared with that of Py9DMA and Py10DMA.¹³

largest J's, governed by the chain. An indication of an MFE curve, altered by reduced intramolecular motion, is found in the case of 3(C6)3 in the viscous solvent DEG (Figure 6). The MFE, overall, is much smaller, since at B = 0 already 70% of the triplets are formed directly and therefore do not show a magnetic field sensitivity. Furthermore, the curve is broadened and shifted to smaller field strengths. The fitted curve drawn in Figure 6 includes this 70% of directly generated triplets. It is based on the w(J)distribution shown in Figure 10 as the dashed trace. It does not exhibit such a distinct narrow maximum as in ACN, since a larger range of J-values now contributes to the MFE curve. Both effects, namely, the shift to smaller field strengths and the broadening, are a consequence of the larger viscosity of DEG and have been derived from the intramolecular motional behavior.14,28 These effects are explained by the deceleration of conformation changes.

In summary, we conclude that the magnetic field effect observed in the compound Py3(C6)3DMA (with its partially rigid chain) confirms the theoretical and numerical predictions. Figure 11 compares magnetic field dependent relative triplet absorbance curves in acetonitrile of Py3(C6)3DMA with those of Py9DMA and Py10DMA. The half-width of the "J-resonance" maximum obtained with 3(C6)3 is relatively sharp: 66 G, corresponding to 7.7×10^{-7} eV or 6.2×10^{-3} cm⁻¹. The extraordinary large and distinct MFE results from the narrow pair distribution function of this molecule with its partly rigid chain; only conformations with distances between about 12 and 19 Å (the half-width of the center-to-center distance distribution is ≈ 4 Å) contribute to the probability distribution of intramolecular center-to-center distances of the radical ion pair moieties A⁻ and D⁺. The results provide perspectives for measuring the exchange interaction related to the maximum of the MFE curves.

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