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COLLEGE ON ATOMIC AND MOLECULAR PHYSICS: PHOTON ASSISTED COLLISIONS IN ATOMS AND MOLECULES

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MAGNETIC FIELD EFFECTS ON PHOTOINDUCED ELECTRON TRANSFER

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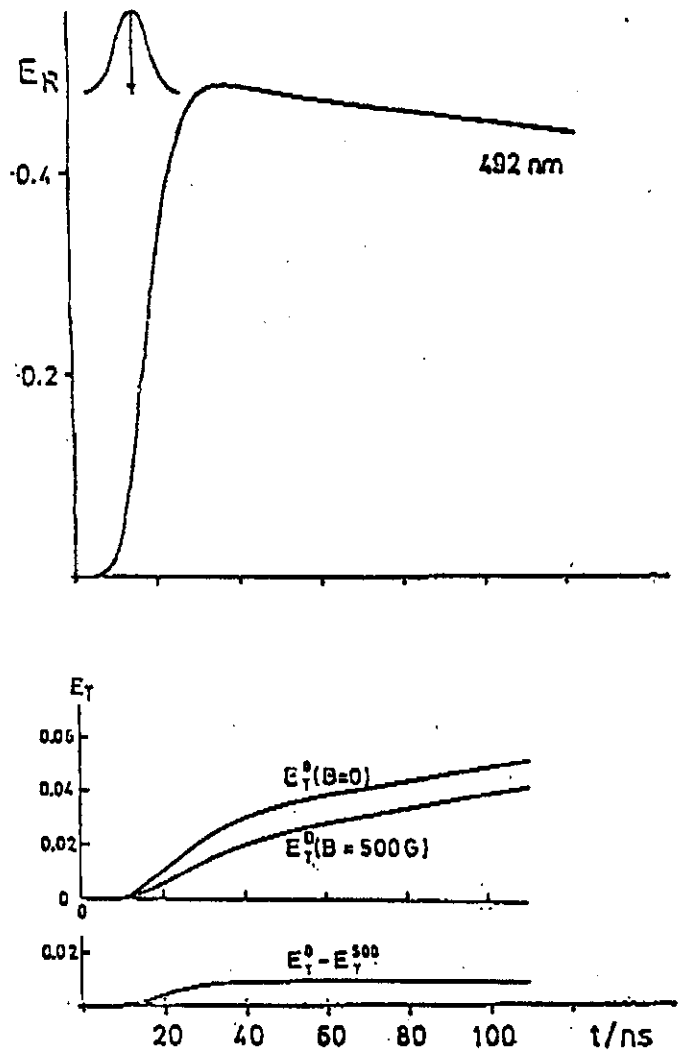
MAGNETIC FIELD EFFECT ON GEMINATE RADICAL PAIR RECOMBINATION. NUCLEAR HYPERFINE VERSUS SPIN EXCHANGE INTERACTION

I

Pairs of radical ions, $^2A^- + {}^2D^+$ generated in polar solvents by nanosecond laser flashes have been investigated in the presence of external magnetic fields. The pairs are produced in the overall singlet state, via photoinduced electron-transfer between electron donor (D) and acceptor molecules (A) and recombine geminately by back electron-transfer to form the molecular triplet state;

$$^1(^2A^- + {}^2D^+) \xrightarrow{k_{S\to T}(B)} {}^3(^2A^- + {}^2D^+) \longrightarrow {}^3A^* \text{ or } {}^3D^*$$

The magnetic field effect can be interpreted quantitatively by assuming that the spin realignment in the radical ion pair leading from the initially produced overall singlet state to the molecular triplet state is governed by the hyperfine interaction in each radical, the exchange interaction of the radical spins in the pair (which increases with decreasing n), and by the Zeeman splitting of the T_{+1}, T_0, T_{-1} energy levels of the radical pair triplet state.



Transient absorption of the system pyrene/dimethylaniline in acetonitrile at room temperature.
Top: time evolution of the radical ion extinction
Bottom: time evolution of the pyrene triplet extinction

III 2

$$100 \text{ Gauss} \triangleq 1.16 \times 10^{-6} \text{ eV} \approx 0.01 \text{ cm}^{-1}$$

The magnetic field effect on $k_{S\to T}(B)$ is based on the following interactions:

The HYPERFINE INTERACTION in each radical between the nuclear spins (I_k) and the unpaired electron spin is governed by the hyperfine coupling constant, a_{ik}, and can be expressed by

$$\boxed{B_i = \sqrt{\sum_k a_{ik}^2 I_k(I_k+1)}}\,.$$

This root-mean-square value, B_i, (2-40 Gauss) is a measure of the nuclear magnetic field acting on the electron spin in the radical, i, and causing its realignment.

With the values B_1 and B_2 for the two radicals and their arithmetic mean $\bar{B} = \frac{1}{2}(B_1 + B_2)$ one obtains for the hyperfine interaction in the geminate radical pair

$$\boxed{\Delta E_{hfi} = \frac{B_1}{\bar{B}} B_1 + \frac{B_2}{\bar{B}} B_2 = 2\,\frac{B_1^2 + B_2^2}{B_1 + B_2} = B_{1/2}}$$

The EXCHANGE INTERACTION between the two radicals in the pair splits the singlet and triplet levels of the pair by the amount

$$\boxed{2J(r) = 1.9 \times 10^{10} \text{ Gauss } \exp\left(-\frac{r}{0.468\,\text{Å}}\right)}$$

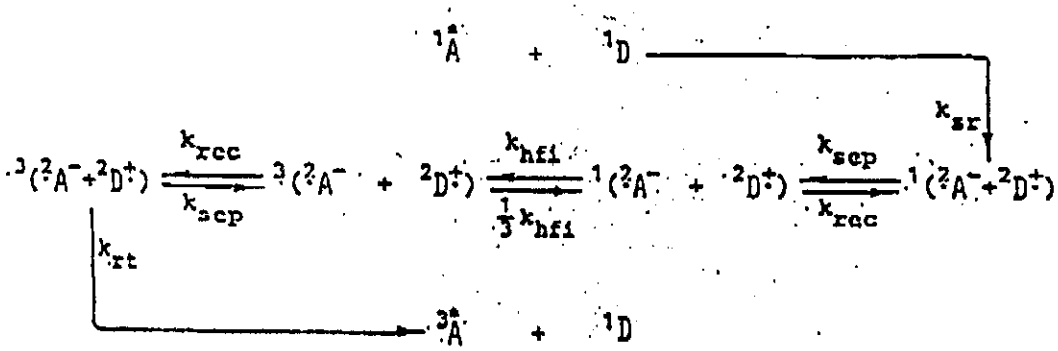
which decreases exponentially with increasing distance, r, so that

$$2J(13\text{Å}) \approx 0.016 \text{ Gauss}$$
$$2J(10\text{Å}) \approx 10 \text{ Gauss}$$
$$2J(7\text{Å}) \approx 6000 \text{ Gauss}$$

ZEEMAN SPLITTING of the triplet radical pair into T_+, T_0, T_- by $\boxed{\Delta E_Z} = g\,\mu_B B$.

III 3

MOLECULAR TRIPLET FORMATION IN GEMINATE RADICAL PAIR RECOMBINATION

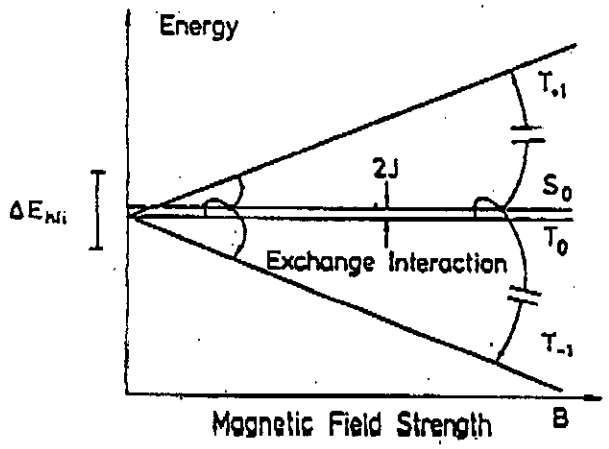


Spin Realignment can only occur when

$\Delta E_{hfi} > 2J(r)$

i.e. at Radical Pair Distances $r > 1$ nm

T_{+1}, T_0, T_{-1} ZEEMAN SPLITTING OF $^3(^2A^- + ^2B^+)$ and SINGLET-TRIPLET SPLITTING DUE TO EXCHANGE INTERACTION, J



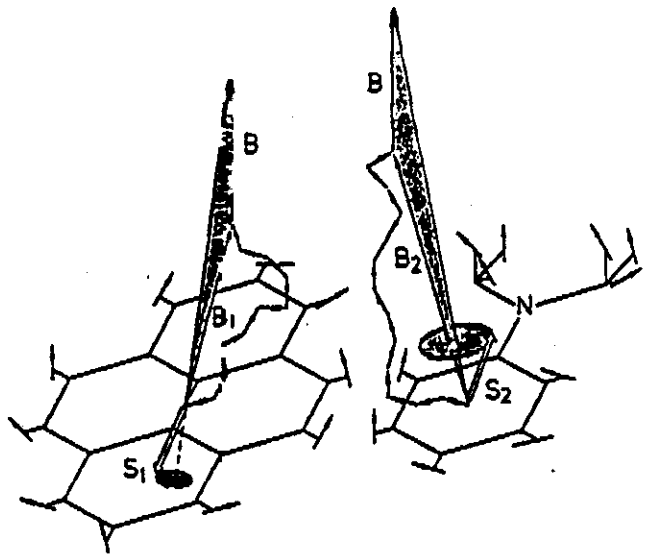
HYPERFINE-INDUCED SINGLET-TRIPLET TRANSITION

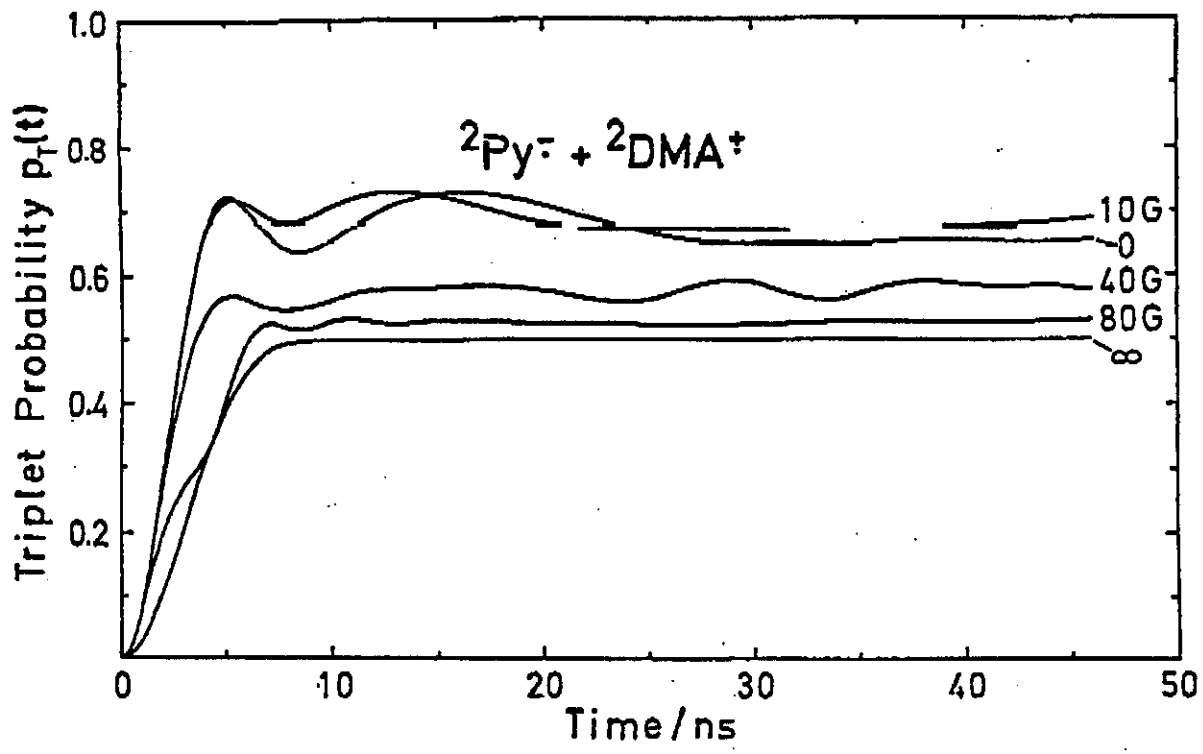
$$^1(^2A^- + ^2D^+) \xrightarrow{k_{st}} ^3(^2A^- + ^2D^+)$$

	S_0 $(\uparrow+\downarrow)$	T_{+1} $(\uparrow+\uparrow)$	T_0 $(\uparrow+\downarrow)$	T_{-1} $(\downarrow+\downarrow)$	
at B = 0	100% $\xrightarrow{k_{st}}$ 25%	0 25%	0 25%	0 25%	75%
at B ≫ ∞	100% $\xrightarrow{k_{st}}$ 50%	0 0	0 50%	0 0	50%

III 4

ELECTRON SPIN PRECESSION
Induced by the Hyperfine Interaction
in each of the Radicals $^2Py^-$ and $^2DMA^+$
LEADING TO SPIN REALIGNMENT IN THE PAIR
$^1(^2A^- + ^2D^+) \rightarrow ^3(^2A^- + ^2D^+)$

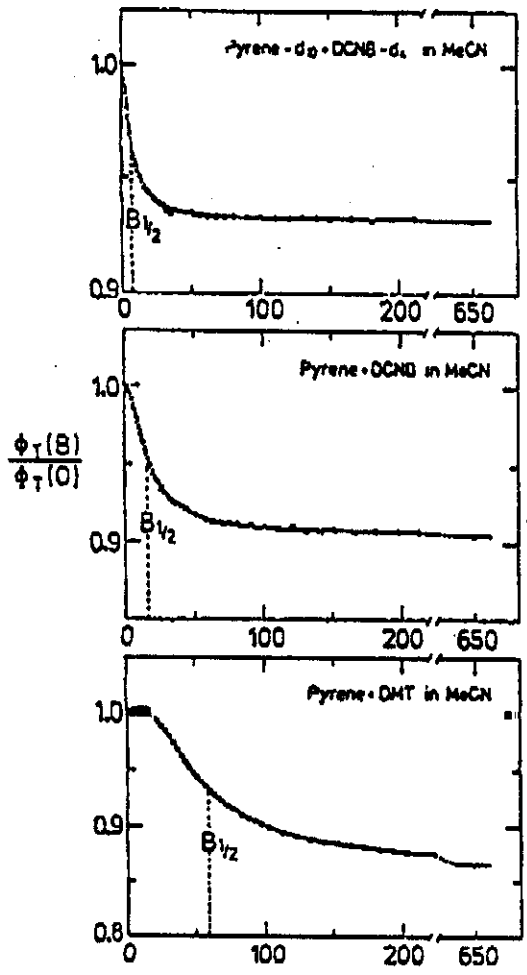




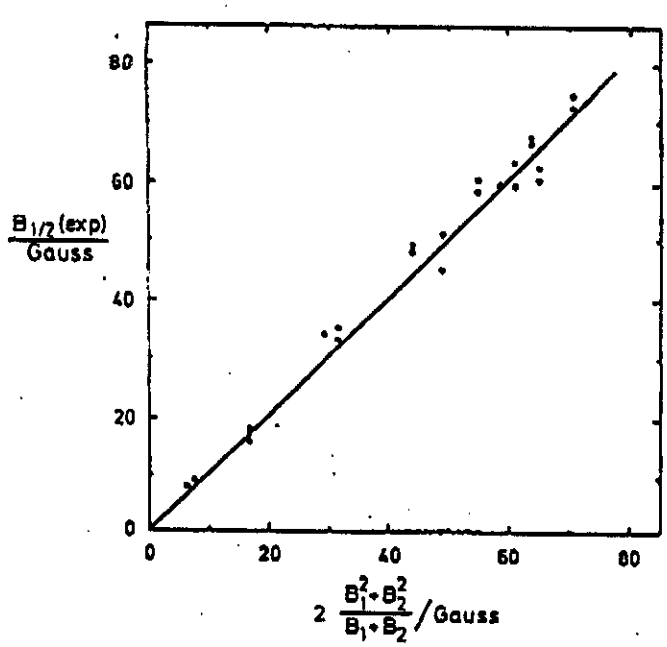
II.5

MAGNETIC FIELD DEPENDENCE OF THE PYRENE TRIPLET YIELD

root-mean-square value $B_i = \sqrt{\sum_k a_{ik}^2 I_k (I_k+1)}$ (Gauss) due to hyperfine coupling



B_1	B_2	$2\frac{B_1^2+B_2^2}{B_1+B_2}$
2.5	3.7	6.4
10.0	4.6	16.8
9.1	34.5	58.4



III 6

Model compounds of the type A–$(CH_2)_n$–D (with A = pyrene, D = dimethylaniline and n = 4 - 16) have been used to investigate the effect of the polymethylene chain on the intramolecular electron transfer processes, and also the influence of external magnetic fields on the spin dynamics in the radical ion pair $^2A^-$–$(CH_2)_n$–$^2D^+$ from which the molecular triplet state ^3A–$(CH_2)_n$–D is formed. This was done using the fluorescence lifetime and transient absorption measurements with the aid of nanosecond laser flashes.

The results show that the most frequently occurring (equilibrium) end-to-end distance of the polymethylene chain increases with $\sqrt{n}$ and that the chain dynamics are governed by an effective diffusion coefficient, D_{eff}. Although the latter increases with n^2, it is several orders of magnitude smaller than the relative diffusion coefficient of the unlinked A and D molecules.

The magnetic field effect can be interpreted quantitatively by assuming that the spin realignment in the radical ion pair leading from the initially produced overall singlet state to the molecular triplet state is governed by the hyperfine interaction in each radical, the exchange interaction of the radical spins in the pair (which increases with decreasing n), and by the Zeeman splitting of the T_{+1}, T_0, T_{-1} energy levels of the radical pair triplet state.

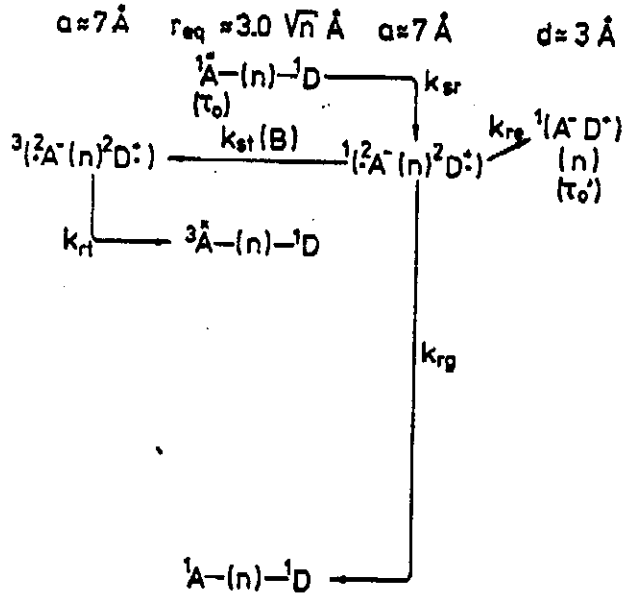
The differences in behaviour with respect to molecular triplet formation of the linked compounds with long ($n \geq 12$), medium ($6 < n < 12$) and short ($n \leq 6$) polymethylene chains are discussed.

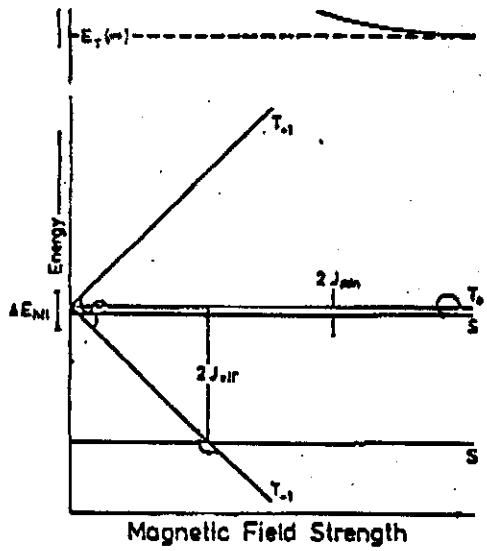
General Reaction Scheme
for Polymethylene-Linked A–$(CH_2)_n$–D Systems

r_{eq} : most frequently occurring (equilibrium) A,D distance

a : A,D encounter distance

d : *interplanar* separation in the exciplex





systems A—$(CH_2)_n$—D with n = 7-11.
Bottom: general energy level diagram for the geminate doublet pair. The splitting of the T_{+1}, T_0, T_{-1} energy levels of the triplet pair state is due to Zeeman interaction. Also indicated is the singlet-triplet splitting due to weak ($2J_{min}$) and strong ($2J_{eff}$) exchange interaction relative to the nuclear hyperfine interaction (ΔE_{hfi}). The bent arrows indicate the hyperfine-coupling-induced singlet-triplet transitions.

In the linked compounds:

$$A—(CH_2)_n—D \quad (n = 1\text{-}16)$$

The polymethylene chain is continually undergoing conformational changes leading to a distribution of end-to-end distances, r, and hence of the singlet-triplet splittings, $2J(r)$, over the lifetime of the linked radical pair.

III 7

MAGNETIC FIELD EFFECT

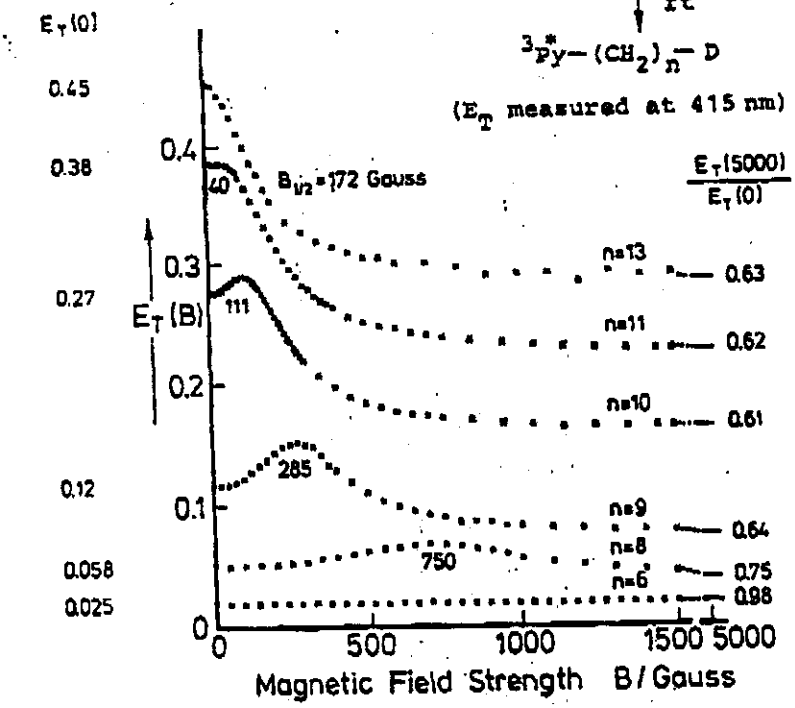
on the geminate recombination of polymethylene-linked radical pairs

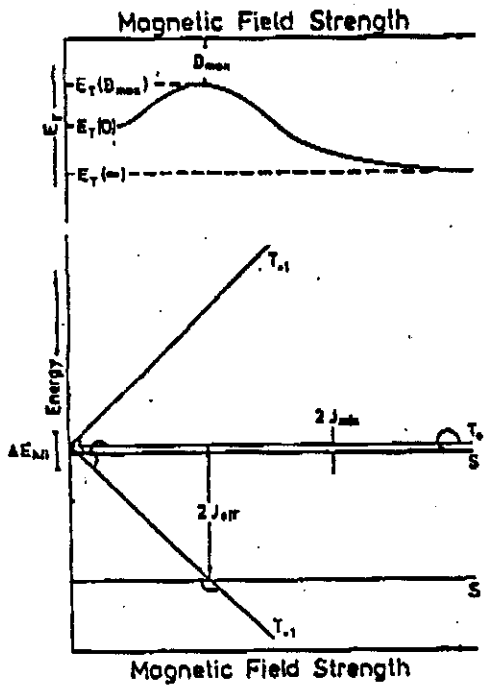
$$^1(^2Py^- - (CH_2)_n - ^2D^+) \xrightleftharpoons{k_{S\rightarrow T}} {}^3(^2Py^- - (CH_2)_n - ^2D^+)$$

$$\downarrow k_{rt}$$

$$^3Py^* - (CH_2)_n - D$$

(E_T measured at 415 nm)





Top: relative pyrene triplet extinctions, E_T, as function of the magnetic field strength obtained for the linked systems $A-(CH_2)_n-D$ with $n = 7-11$.
Bottom: general energy level diagram for the geminate doublet pair. The splitting of the T_{+1}, T_0, T_{-1} energy levels of the triplet pair state is due to Zeeman interaction. Also indicated is the singlet-triplet splitting due to weak ($2J_{min}$) and strong ($2J_{eff}$) exchange interaction relative to the nuclear hyperfine interaction (ΔE_{hfi}). The bent arrows indicate the hyperfine-coupling-induced singlet-triplet transitions.

In the linked compounds:

$$A-(CH_2)_n-D \quad (n = 1-16)$$

the polymethylene chain is constantly undergoing conformational changes leading to a distribution of end-to-end distances, r, and hence of the singlet-triplet splittings, $2J(r)$, over the lifetime of the linked radical pair.

II 8

The Through-Space Spin-Exchange Interaction of Polymethylene-Linked Pairs $^2A^*-(CH_2)_n-^2D^*$

n	$2J_{eff}$ (B_{max}) (Gauss)	r_{eff} (Å)	$\frac{r_{eff}}{\sqrt{n}}$ (Å)	$2J_{min}$ (Gauss)	r_{min} (Å)
13	(7.3)			10^{-6}	17.6
12	(17)			10^{-5}	16.4
11	40	9.35	2.820	0.0002	15.1
10	111	8.87	2.806	0.003	13.9
9	285	8.43	2.811	0.038	12.6
8	750	7.98	2.821	0.57	11.3
7	2300	7.45	2.818	8.4	10.1
6	(7600)			125	8.8

$r_{eff} = 2.815\sqrt{n}$ Å $\qquad r_{min} = 1.26\ (n+1)$ Å

MAGNETIC FIELD DEPENDENCE OF INTRAMOLECULAR EXCIPLEX FORMATION IN POLYMETHYLENE-LINKED A–D SYSTEMS

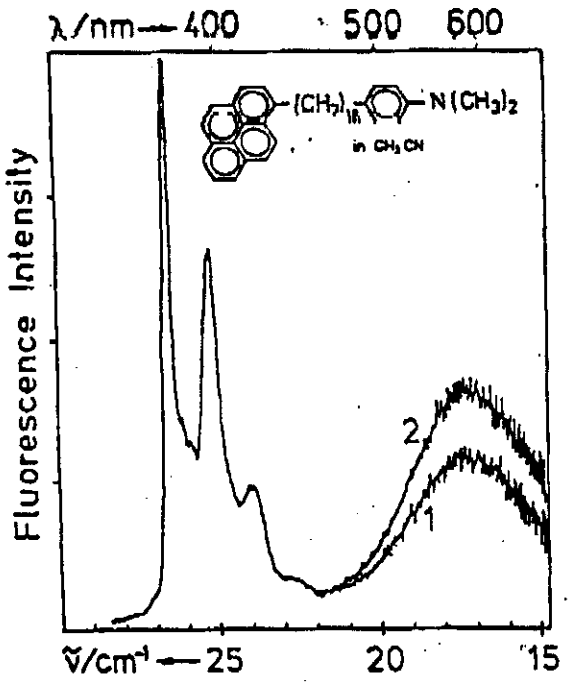


Fig. 1. Fluorescence spectra (corrected) of Py(16)DMA in CH_3CN (1) without, (2) with external magnetic field B = 50 G. The pyrene moiety was excited at 337 nm.

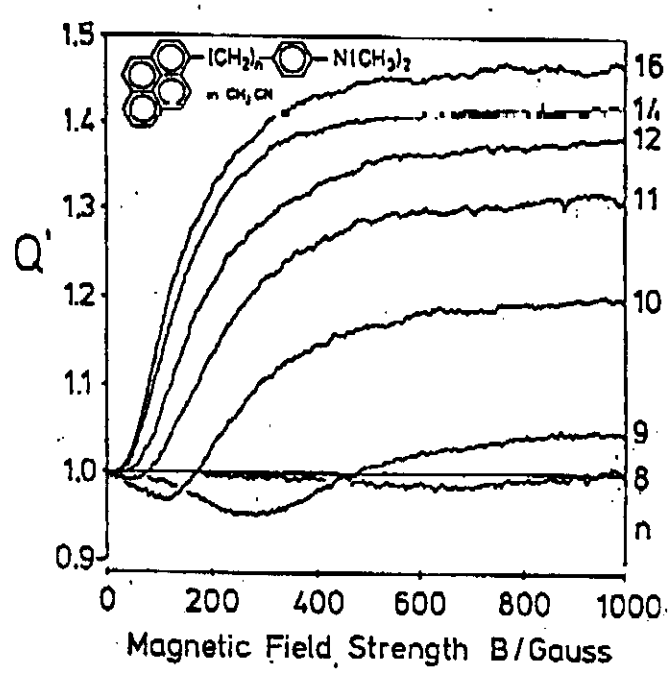


Fig. 3. Magnetic field dependence of the relative exciplex fluorescence intensity $Q' = I'(B)/I'(0)$ of compounds $Py(CH_2)_nDMA$, n = 8–16, in CH_3CN, detected at 595 nm and at room temperature.