

Magnetic field effect on the exciplex luminescence as a probe for estimating the hyperfine interaction in a radical ion pair system

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MS received 18 June 1990; revised 25 October 1990

Abstract. Magnetic field effect on 9-cyanophenanthrene - *trans* anethole exciplex gives the $B_{1/2}$ value, a measure of 'average' hyperfine interaction present in the system. This has been compared with the theoretically computed values of hyperfine coupling constants present in the component radical ions using the INDO-UHF method.

Keywords. Magnetic field effect; exciplex luminescence; radical ion-pair reactions; estimation of hyperfine interaction.

1. Introduction

During the last two decades it has been established that small external magnetic fields affect chemical reactions involving radical pairs (RP) or radical ion pairs (RIP) through hyperfine interaction (HFI) present in the system (Atkins and Lambert 1975; Gould *et al* 1984; Salikhov *et al* 1984; Basu *et al* 1988; Steiner and Ulrich 1989). Charge-transfer between acceptor and donor molecules, either of which may be excited, produces solvent-separated RIP in polar media. After generation, the radical ion pairs start diffusion during which they either geminately recombine resulting in luminescent contact ion pair (i.e. exciplex) if they are in the singlet state or may diffuse apart resulting in the loss of spin correlation between two partner radicals. Beyond a certain inter-radical distance when exchange interaction becomes negligible, the intersystem crossing (ISC) process between the degenerate S and $T_{0, \pm 1}$ states gets facilitated by HFI between the unpaired electron and nuclear spins in each radical. On application of an external magnetic field the ISC process between S and $T_{\pm 1}$ states decreases as the latter states are now energetically non-degenerate with the S state. The external magnetic field effect (MFE) saturates when Zeeman splitting exceeds the HFI (Atkins and Lambert 1975; Gould *et al* 1984; Salikhov *et al* 1984).

The field at which half the saturation is reached is called $B_{1/2}$ which is a measure of 'average' HFI present in the system. The average magnitude of the HFI (B_i) in an individual radical ion can be written as (Schulten and Wolynes 1978)

$$B_i = \left(\sum_N a_{iN}^2 I_N(I_N + 1) \right)^{1/2}, \quad (1)$$

where, I_N is the nuclear spin and a_{iN} is the isotropic hyperfine coupling constant between the unpaired electrons and the N th nucleus of the i th radical. The a_{iN} values

might be obtained either from EPR spectra or by theoretical calculations using the INDO-UHF method (Pople *et al* 1968; Pople and Beveridge 1970). The expression for the isotropic hyperfine coupling constant is (Pople and Beveridge 1970)

$$\begin{aligned} a_N &= [(4\pi/3)g\beta\gamma_N h \langle S_z \rangle^{-1} |\phi_{s_N}(R_N)|^2] \rho_{s_N s_N}^{\text{spin}}(\text{INDO}) \\ &= Q_N \rho_{s_N s_N}^{\text{spin}}(\text{INDO}), \end{aligned} \quad (2)$$

where, g is the electronic g -factor, β is the Bohr magneton, γ_N is the gyromagnetic ratio of nucleus N , R_N is the position vector of nucleus N , $|\phi_{s_N}(R_N)|^2$ is the magnitude of the density of the valence s -electron on the atom N at its nucleus and $\rho_{s_N s_N}^{\text{spin}}(\text{INDO})$ is the INDO – unpaired electronic population in the valence s -orbital of atom N . The quantity Q_N in (2) is constant for every type of magnetic nucleus (Pople *et al* 1968). However, at the INDO level of approximation, Q_N values are parametrized by calibration of a_{iN} s against a set of experimentally known a_N values in a wide variety of systems and assumed to be transferable. The observed $B_{1/2}$ value has been shown to be related to the B_i values of two radicals in the following way (Weller *et al* 1983):

$$B_{1/2}(\text{HFI}) = 2(B_1^2 + B_2^2)/(B_1 + B_2), \quad (3)$$

where, B_1 and B_2 are the hyperfine interactions given by (1) for each of the individual radical ions in the RIP.

Weller *et al* (1983) compared experimentally obtained $B_{1/2}$ values for some exciplex systems with their theoretical counterparts given by (3). The a_{iN} values required for computing B_1 and B_2 were extracted from the EPR spectrum of the relevant radical ions (Weller *et al* 1983). However, these MFE-HFI correlation studies have so far been limited to only one type of donor, namely dimethylamino derivatives of aromatic systems. There could be several reasons for this limitation, the important one being the necessity of having a large HFI in component molecules. We have recently extended the studies to exciplex systems involving other types of donors, such as one formed between 9-cyanophenanthrene (CNP) and *trans*-anethole (AN) (Basu *et al* 1987), where the degree of charge transfer was found to be substantially less than in the pyrene–dimethylaniline (Py-DMA) system (Basu *et al* 1987). The objective of the present investigation was to study the $B_{1/2}$ of this system as a function of concentration and correlate the limited $B_{1/2}$ with the average HFI present in the constituent radical ions. Since EPR data on our radical ions could not be resolved adequately for extracting reliable values of hyperfine coupling constants needed for this purpose, we have explored the possibility of calculating a_{iN} values theoretically by computing the net spin densities at the nuclei.

2. Experimental

The change in exciplex luminescence ($\Delta\phi$, where ϕ is the relative emission quantum yield in the absence of a magnetic field) with an externally applied magnetic field B has been measured with the help of an improved phase-sensitive detector system, details of which can be obtained from an earlier publication from this laboratory (Nath and Chowdhury 1984b). CNP and AN (Aldrich, 99% pure) have been used without further purification. Spectroscopic grade and redistilled acetone and acetonitrile

were used as solvents. Concentration of CNP was taken as 10^{-3} M in each sample, whereas, that of AN was varied from 0.2×10^{-2} M to 8×10^{-2} M. Each sample was degassed for 45 minutes to remove oxygen from the system, as O_2 severely quenches exciplex emission, and to prevent degradation of the sample during the experiment.

A nanosecond fluorimeter (Applied Photophysics) with single-photon-counting technique was used to determine the lifetime of the samples.

3. Results and discussion

The dependence of $B_{1/2}$ on donor concentration was studied at wavelength $\lambda = 500$ nm. The lowest limiting value of $B_{1/2}$ has been obtained as 3.47 mT with the very low donor concentration. The observations, that the $B_{1/2}$ value increases and the lifetime of the exciplex (τ) decreases (i.e. τ^{-1} increases) with donor (here AN) concentration, are depicted in figure 1. The decrease in lifetime of the exciplex with increasing donor concentration is presumably due to the inelastic deactivating collision between the exciplex and the donor; a non-emitting or shorter-lifetime triplex could serve as an intermediate in this deactivating process. As regards the variation of $B_{1/2}$ with

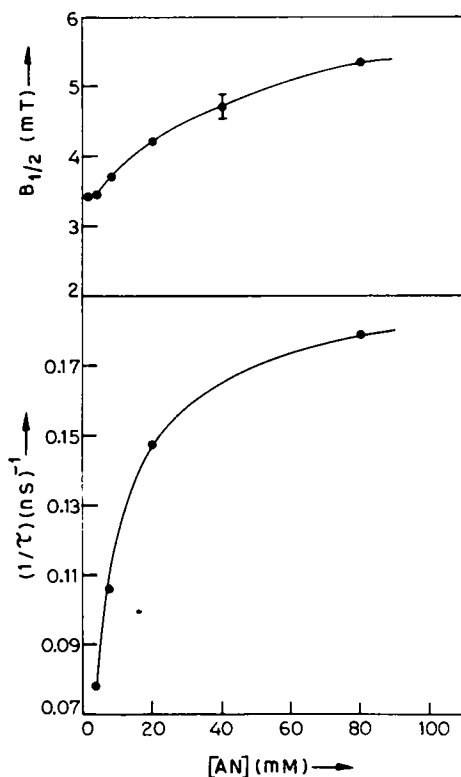
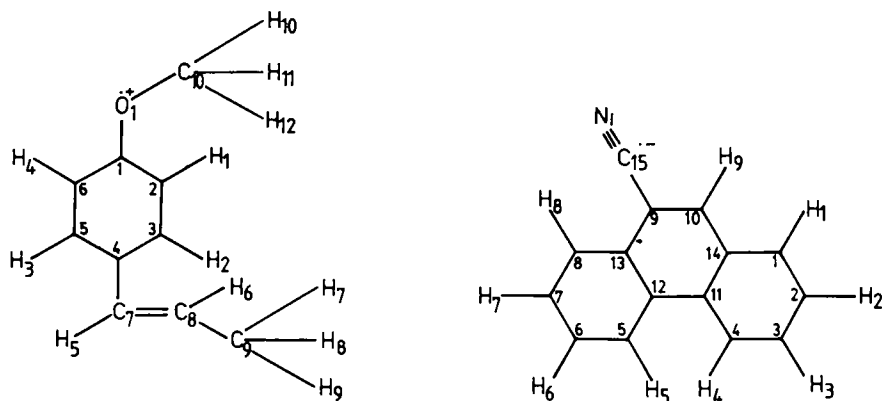


Figure 1. Dependence of $B_{1/2}$ and inverse of lifetime (τ^{-1}) on *trans*-anethole (donor) concentration in acetonitrile at $\lambda = 500$ nm, $[\text{CNP}] = 10^{-3}$ M.

concentration, the phenomenon has been observed earlier and several interpretations have been offered: (i) uncertainty broadening of the energy levels of radical ion pairs either due to fast electron hopping between ionic and excess neutral donors (Knapp and Schulten 1979; Nolting *et al* 1982; Staerk *et al* 1983), (ii) shortening of the lifetime of the exciplex due to quenching by excess donor (Nath and Chowdhury 1984), and (iii) environmental perturbation of excess donor molecules on solvent caged RIP (Nath and Chowdhury 1984; Nath *et al* 1986). In the case of Py-DMA complex, the first explanation was negated by comparison of the $B_{1/2}$ of a two-component system with that of a chosen three-component (two donors with identical B_i and one acceptor) system having overall donor concentration same as that of the two-component system (Nath and Chowdhury 1984a). In the present case similar experiments could not be carried out as we failed to find a second donor having B_i identical to *trans*-anethole. Further, in the Py-DMA case the correlation with lifetime was poor and therefore, the third alternative was preferred (Nath and Chowdhury 1984a; Nath *et al* 1986). In the present case, however, the correlation of $B_{1/2}$ with lifetime is comparatively strong as two curves of figure 1 have more or less the same nature though they do not exactly match with each other and so the second explanation could very well be the reason for the increase of $B_{1/2}$ with donor concentration. However, our experimental data in the present case do not allow us to make a definitive choice between explanations (i), (ii) and (iii). Whatever be the cause of change of $B_{1/2}$ with donor concentration, we choose the $B_{1/2}$ at extrapolated zero concentration as the true $B_{1/2}$ (3.47 mT) for comparison with the theoretical value.

One way to estimate $B_{1/2}$ is to obtain a_{in} values of (3) from EPR spectra. However, the EPR spectrum of $AN^{\cdot+}$ was not well-resolved. We have, therefore, calculated the relevant a_{iN} values by (2) using standard INDO computer program (Pople and Beveridge 1970). The values of Q_N for some nuclei which would be required are given in Pople *et al* (1968). The bond-lengths and bond-angles (figure 2) have been taken from *Tables of interatomic distances and configuration* (1965) and the computed $\rho_{S_n S_n}^{spin}$ and a_{iN} values for $CNP^{\cdot-}$ and $AN^{\cdot+}$ radical ions are reported in tables 1 and 2 respectively.

The calculated $B_{1/2}$ value is found to be 3.41 mT (milli tesla) which is almost the same as the experimental value obtained with a very low donor concentration



trans-Anethole radical cation ($AN^{\cdot+}$) 9-cyanophenanthrene radical anion ($CNP^{\cdot-}$)

Figure 2. Structure of *trans*-anethole radical cation and 9-cyanophenanthrene radical anion.

Table 1. Calculation of values of a_{iN} and for B_1^2 for CNP^- radical anion.

Nucleus	Atom no.	Calculated $\rho_{S_N S_N}^{\text{spin}}$	a_i (mT)	$a_{iN}^2 I_N(I_N + 1)$ (mT ²)	B_1^2 (mT ²)
¹ H	H ₁	0.0024	0.13	0.0126	
¹ H	H ₂	-0.006	-0.324	0.0787	
¹ H	H ₃	-0.0044	-0.238	0.0423	
¹ H	H ₄	0.0005	0.027	0.0005	
¹ H	H ₅	-0.0023	0.124	0.0116	0.755
¹ H	H ₆	-0.0082	-0.443	0.147	
¹ H	H ₇	-0.0071	-0.383	0.110	
¹ H	H ₈	0.004	0.216	0.035	
¹ H	H ₉	-0.0118	-0.637	0.3044	
¹⁴ N	N ₁	0.0034	0.129	0.0125	

Table 2. Calculation of values of a_{iN} and B_2^2 for AN^+ radical cation.

Nucleus	Atom No.	Calculated $\rho_{S_N S_N}^{\text{spin}}$	a_{iN} (mT)	$a_{iN}^2 I_N(I_N + 1)$ (mT ²)	B_2^2 (mT ²)
¹ H	H ₁	-0.0052	-0.28	0.0588	
¹ H	H ₂	0.0009	0.049	0.0018	
¹ H	H ₃	0.0014	0.076	0.0043	
¹ H	H ₄	-0.0048	-0.259	0.0503	
¹ H	H ₅	0.0027	0.146	0.0127	
¹ H	H ₆	-0.0076	-0.41	0.1260	4.23
¹ H	H ₇	0.0208	1.123	0.9408	
¹ H	H ₈	0.0008	0.043	0.0014	
¹ H	H ₉	0.0208	1.123	0.9408	
¹ H	H ₁₀	0.0219	1.18	1.0443	
¹ H	H ₁₁	0.0001	0.005	0.0000	
¹ H	H ₁₂	0.0219	1.18	1.0443	

(3.47 mT). The exact agreement is probably fortuitous. Nevertheless, it gives credence to our contention that the observed MFE on CNP-AN exciplex system is predominantly mediated by hyperfine interactions. The other two major mechanisms of spin-rephasing which have been suggested to explain MFE on RIP reactions – Δg -mechanism and electronic spin-lattice relaxation mechanism – would have led to a $B_{1/2}$ value much higher than that observed. The Δg -mechanism requires a high field and can be recognised by its linear dependence on a magnetic field. This is not what is observed in the present case. In the case of relaxation mechanisms between T_{\pm} and T_0 states anisotropic components of hyperfine and Zeeman interactions induce the S - T ISC process in a microsecond time scale and the rate increases with the magnetic field. The fact that saturation is reached at a fairly low value of field indicates that the relaxation mechanism plays an insignificant role for these radical pairs with nanosecond lifetimes.

Acknowledgements

The author wishes to thank Prof M Chowdhury for his valuable guidance, Dr S P Bhattacharyya for helping in theoretical calculations and Dr D N Nath for instrumental assistance. This work has been supported by an Indo-US project (CE-2) sponsored by the Department of Science and Technology, Government of India, and the National Institute of Standards and Technology, USA, and by the Council of Scientific and Industrial Research, India.

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