

**TIME-RESOLVED ESR STUDIES
OF TRIPLET ENERGY TRANSFER AND TRIPLET PROPERTIES
OF SOME MODEL BROMO-SUBSTITUTED NAPHTHALENE COMPOUNDS AT 77 K**

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The technique of time-resolved ESR together with the photosensitization method was applied to obtain information on the triplet lifetimes and spin-depolarization rates of some model bromo-substituted naphthalene compounds. In the triplet excitation transfer process at high field the magnetic quantum number of the donor is conserved in the acceptor.

1. Introduction

The classic studies of photoexcited organic triplets in single crystals by Hutchison and Magnum [1], and in glassy matrices by van der Waals and de Groot [2] established the milestones for many exciting ESR developments which followed. Then and now the properties, the dynamics, and the chemistry of excited organic triplet states have continued to capture the attention of spectroscopists, optical and magnetic resonance alike, photophysicists, and photochemists.

A decade ago we proposed that organic free radicals formed in some triplet-state photochemical reactions are spin polarized, deriving their non-Boltzmann population from the initial polarization generated in the triplet-state precursor via the spin-selective intersystem crossing (ISC) mechanism [3]. This concept provided the basis for the subsequent establishment of the "triplet mechanism" in the chemically induced dynamic electron polarization phenomenon [4-8]. In addition to the spin-polarization features, an excited organic triplet state often has a rather long radiative lifetime compared to an excited singlet state. This property makes it feasible to follow experimentally the energy transfer process

between an excited donor and a ground-state acceptor.

Energy transfer processes are of fundamental importance. In electronic-electronic energy transfer, most of the early studies involved excitation exchange between atoms in the gas phase [9] and the first triplet-triplet energy transfer between organic molecules in glassy matrices was observed by Terenin and Ermolaev [10]. While flash techniques with optical detection were mainly used in the earlier triplet energy transfer studies [11,12], it was McDowell and his co-workers [13], who first demonstrated the potential of ESR spectroscopy for organic triplet energy transfer investigations in solids. The general theory of electronic-electronic energy transfer involving short-range exchange interactions was developed by Dexter [14], who was mainly concerned with sensitized luminescence in solids, while Stepp and Andersen [15] treated the aspects of conservation of electronic angular momentum accompanying energy transfer in the gas phase.

In our laboratories we have been developing applications of time-resolved ESR techniques to photochemical and photophysical studies of excited organic triplet states. In recent years significant improve-

ments in the time-resolved ESR techniques have afforded unique opportunities for many authors [16–23] to probe directly the spin-selective intersystem crossing processes of phosphorescent and non-phosphorescent organic triplet states. The possibility of spin-polarization conservation in the triplet energy transfer processes was first demonstrated in single crystals where the excitation transfer was from the host molecules to specifically aligned guest molecules of equal symmetry [16,24–26]. Using McDowell's [13] classic system of benzophenone and naphthalene in glassy matrices, we were able to extend the general phenomenon of conservation of spin memory in triplet energy transfer processes to systems with randomly oriented donors and acceptors of different symmetry [23,27]. In this paper we wish to apply the time-resolved energy transfer technique to the glassy-matrix study of the lowest triplet properties of some model bromo-substituted naphthalenes which show significant intramolecular heavy atom effect. The high-field energy transfer processes further confirm the conservation of the magnetic quantum numbers, thus eliminating the role of the zero-field states (and parameters) in the excitation transfer.

2. Experimental

The custom syntheses of the bromonaphthonorbornenes have been reported previously [28]. In a typical experiment an ethanol solution containing ≈ 0.2 M of a photosensitizer (either benzophenone or pyruvic acid) and the bromonaphthonorbornenes was frozen into a glass at 77 K in a quartz dewar within the ESR cavity.

The time-resolved ESR spectrometer was modified for simultaneous observations of thermalized (steady-state) and polarized ESR signals, as previ-

ously described [29]. The excitation source used was either a Molecron 1 MW nitrogen laser or a Lambda Physik EMG 101 MSC XeCl laser at 150 mJ. The procedure for analysis of the depolarization rate has been given elsewhere [30].

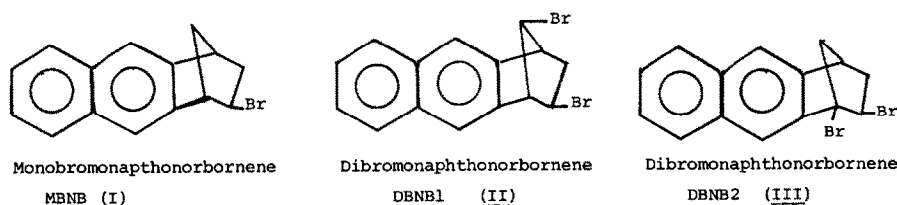
Phosphorescence lifetimes at 77 K were measured using a Varian SF330 spectrofluorimeter, interfaced to Zenith personal computer.

3. Results and discussion

Table I summarizes the data obtained for the zero-field splitting parameters, triplet lifetimes (phosphorescence and ESR), and the spin-depolarization characteristic times of naphthalene and its bromo-substituted analogs: MBNB(I), DBNB1(II), and DBNB2(III) (see scheme 1).

The similarity of the zero-field splitting parameters among all four triplets suggests that the symmetry and the triplet wavefunctions are mainly associated with the naphthalene moiety. On the other hand, the triplet lifetimes as measured by both phosphorescence and ESR decays are drastically shortened from naphthalene to its bromo-substituted analogs. This is well understood in terms of the intramolecular external heavy-atom (Br) effect [28] on the radiative rate constant of phosphorescence.

However, there is no corresponding variation of the characteristic spin-depolarization times monitored at both B_{\min} and high-field lines for all the four triplets. When benzophenone was used as a sensitizer, a typical spectrum (fig. 1) of naphthalene and MBNB triplets exhibited total emission on all observed transitions. With the pyruvic acid sensitizer, the naphthalene and MBNB triplets were in the absorptive mode, as expected [27]. In the analysis of the spin-depolarization rate at a fixed magnetic field, we have followed the approach given by Kim and



Scheme 1.

Table 1

The spectroscopic and dynamic properties of some model bromonorborene-substituted naphthalene triplets in alcohol glasses at 77 K generated by photosensitization

Triplet	D^* (cm^{-1})	D (cm^{-1})	E (cm^{-1})	$t_{1/2}^{a)}$ (s)	Sensitizer	${}^3T_1^{b)}$ (10^{-6} s)
naphthalene	0.1058	0.0994	-0.0149	2.2 ± 0.1	Ph ₂ CO CH ₃ COCOOH	1.7 ± 0.6 1.6 ± 0.5
MBNB (I)	0.1047	0.0997	-0.0150	0.4 ± 0.03	Ph ₂ CO CH ₃ COCOOH	2.0 ± 0.4 1.8 ± 0.3
DBNB1 (II)	0.1030	-	-	0.08 ± 0.02	Ph ₂ CO CH ₃ COCOOH	1.6 ± 0.4 1.7 ± 0.3
DBNB2 (III)	0.1028	-	-	0.11 ± 0.01	Ph ₂ CO CH ₃ COCOOH	1.7 ± 0.3 1.6 ± 0.2

^{a)} The lifetimes, $t_{1/2}$, were measured by both phosphorescence decay and ESR decay and were in excellent agreement.

^{b)} The estimated triplet spin-lattice relaxation times were the average of all transitions observed.

Weissman [16] for using a less complex two-level description when only one of the triplet transitions is close to resonance. The simple fact that these organic triplets in glassy matrices are strongly polarized in the experimental observations defines the

upper bound for the spin-lattice relaxation rates in these systems. It follows that the same intramolecular external heavy-atom effect operative on the triplet lifetimes, does not play any significant role in the relaxation process and the model of modulated

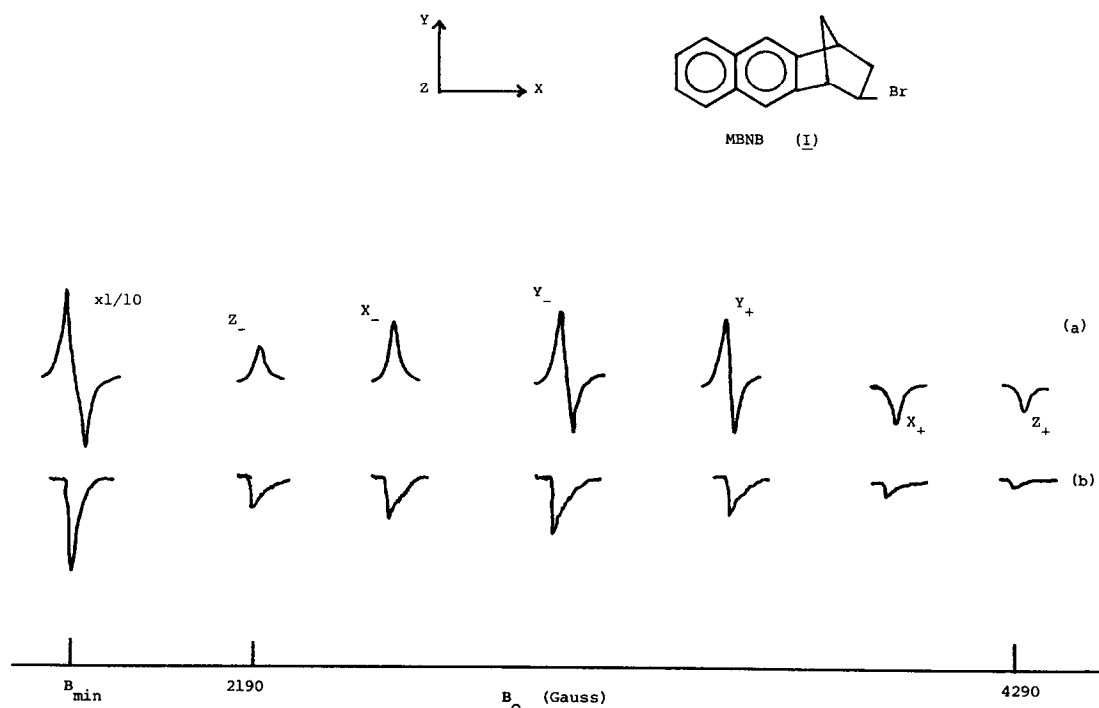


Fig. 1. ESR spectrum of the triplet state of monobromonaphthonorborene photosensitized by benzophenone in an ethanol glass at 77 K. (a) The 100 kHz modulated spectrum. (b) The time-resolved spectrum.

spin-rotational interaction in the slow motion region is adequate in explaining the triplet relaxation phenomenon in glassy matrices, as evidenced by the temperature-dependence study [23]. It is our belief that in the photoexcitation experiments (in which a high-power laser is always employed), the higher transient density of the excited triplet states could well lead to local softening of the rigid medium to allow some degree of molecular rotation. In other words, the whole matrix is not uniformly at thermal equilibrium, having pockets of excited triplets possessing much higher energy than that available at equilibrium.

With the confirmation that spin memory is conserved during a triplet-triplet excitation transfer process in solids, it is now obvious that the rate of the polarization transfer must compete with the spin-lattice relaxation rates and is therefore an additional probe to the understanding of the triplet-triplet energy transfer processes. As in Dexter's [14] exchange mechanism for triplet-triplet energy transfer, the rate constant (not the rate) is dependent on the spin functions and the specific orbital overlaps between the donor and the acceptor molecules. In rigid matrices, translational diffusion of acceptor molecules and donor triplets are severely restricted and energy transfer may become a "localized" phenomenon. A question then arises whether in such localized phenomenon the triplet excitation transfer is initially between the zero-field states of the donor and acceptor before they evolve into the high-field states. The experimental observation on the conservation of the high-field magnetic quantum numbers clearly eliminates the zero-field states as playing a role in the transfer process, because should that be the case, the observed time-resolved spectrum of the acceptor triplet would exhibit an E/A pattern on the high-field transition. Our experimental results are also in agreement with those reported by Obi [31] in the acetophenone-naphthalene system in EPA glass. The results on conservation of magnetic quantum numbers confirm the operation of the exchange mechanism in the triplet excitation transfer at a high external magnetic field.

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