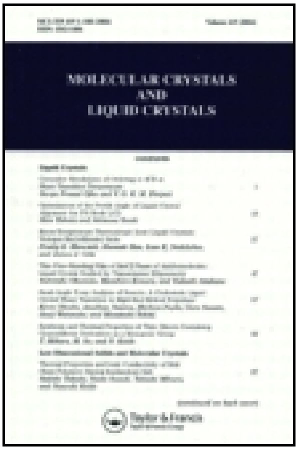

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Optical and Magnetic Resonance Studies of Ground and Excited Spin States on Some Open-Shell Orgnic Radicals

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Optical and Magnetic Resonance Studies of Ground and Excited Spin States on Some Open-Shell Orgnic Radicals

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Study of the electronic excited spin states on open-shell organic radicals are an important research field of organic magnetism. We report the optical and the magnetic resonance study of the electronic excited spin states of naphthalene nitroxide radical (**1**), pyrene nitronyl nitroxide radical (**2**), pyrene thioaminyl radical (**3**). The fluorescence and phosphorescence spectra of **1** and **2** in EPA glass are measured. Both compounds give weak phosphorescence which indicates the existence of metastable excited quartet (S=3/2) state. Doublet like time-resolved ESR signals are observed for these stable radicals. The decay time of the dynamic electron polarization in their excited state is *ms* order. This finding indicates that the observed signals arises from the radical-triplet pair originating the magnetic exchange interaction and the polarization transfer between the triplet excited states of the condensed polynuclear aromatic groups and the dangling stable radicals. The *g* value and the polarization change of the doublet like signal were also observed for **3**, showing a possibility that the signal comes from the middle Kramers doublet of the resulting quartet excited spin state.

Keywords: Excited State; Open-Shell Organic Radical; Time-Resolved ESR Radical-Triplet Pair Mechanism; Quartet Spin State

INTRODUCTION

Study of the electronic ground and excited spin states on open-shell weak charge-transfer organic crystals are an important research field of organic magnetism, since conduction electrons or molecular excitons can be expected to play the key role in the intra- and inter-molecular spin alignment.

For the electronic ground state of the open-shell charge-transfer organic salts, some research groups have already reported their magnetic behaviors [1-5]. However, the electronic excited spin states of their open-shell organic

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molecule or their charge-transfer systems are not enough investigated. In this work, we report the electronic spectra and the time-resolved ESR (TRESR) study of the excited spin states of naphthalene nitroxide radical (**1**), pyrene nitronyl nitroxide radical (**2**) which have the nature of weak organic electron donors with appropriate acceptors such as TCNB. TRESR method [6] has been widely used for the study of the chemical reaction dynamics of the radical pair by detecting the chemically induced dynamic electron polarization (CIDEP). It is well known that CIDEP signal of radicals is generated through the radical pair mechanism (RPM) [7,8] and the triplet mechanism (TM) [9, 10]. Recently, Kawai and Obi have first observed the CIDEP signal using TRESR which has been generated by the radical-triplet pair mechanism (RTPM) [11]. This method is useful for the study of the excited state without any phosphorescence and delayed fluorescence as a result of a strong non-irradiative relaxation process. In this paper, we report the TRESR study of the excited spin states of some π-conjugated aromatic compounds with pendant stable radicals which are interested in the field of the molecular magnetism.

EXPERIMENTAL

The π-conjugated aromatic compounds with pendant stable radicals studied in this work is shown in Figure 1. The naphthalene nitroxide

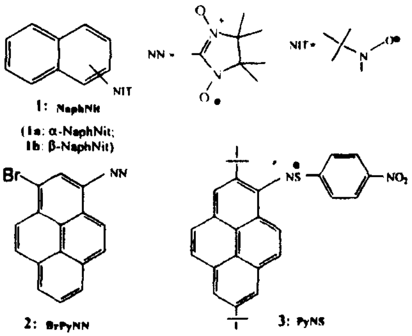
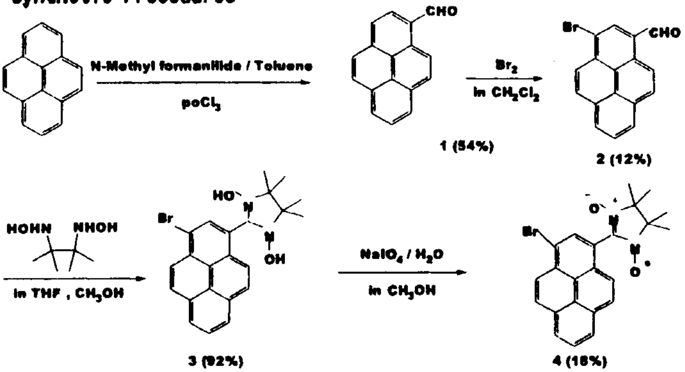


FIGURE 1 Stable Radicals Studied in This Work

was synthesized using usual synthetic procedures and the Br substituted pyrene nitronyl nitroxide was synthesized as follows.

Synthetic Procedures



The synthetic procedures of the pyrene thioaminyl radical was published in our previous paper [12].

UV-vis. Spectra were measured in EPA solution using HITACH U3000 UV-vis. spectrometer. The fluorescence and phosphorescence spectra were obtained with HITACHI F-4500T fluorescence spectrometer in EPA rigid glass matrix at 77 K using Liq. N_2 dewar and with a home made apparatus at 1.5 K using Liq. He optical cryostat. The magnetic properties of the electronic ground states were measured by SQUID magnetometer (Quantum Design MPMS2). The time-resolved electron spin resonance (TRESR) experiments were carried out using a ESR spectrometer (JEOL TE300) with a wide band microwave preamplifier and a high-speed oscilloscope (LeCroy 9350C). Transient ESR signals obtained without field modulation were transferred to the high-speed oscilloscope (LeCroy 9350C). A Nd-YAG pulse laser (Continuum Surelite II) was used for the excitation light source. Temperature was controlled using liq. He transfer cryostat (Oxford ESR910). All apparatus were controlled by a personal computer.

RESULTS AND DISCUSSION

Magnetic Properties of the Electronic Ground State

The powder samples of these stable radicals **1a** and **2** show simple Curie-Weiss behaviors with θ = +0.027 K and θ = -4.1 K, respectively. On the other hand, **3** shows strong antiferromagnetic behavior which is described in terms of the alternating linear chain model with J/k_B = -108.2 K and α = 0.827. $\chi_{mol}T$ vs. T plots of **2** are shown in Figure 2. This large antiferromagnetic interaction is a result of the extensive delocalization of an unpaired π-electron spin and the overlapping between the π-SOMO by stacking between neighboring pyrene groups.

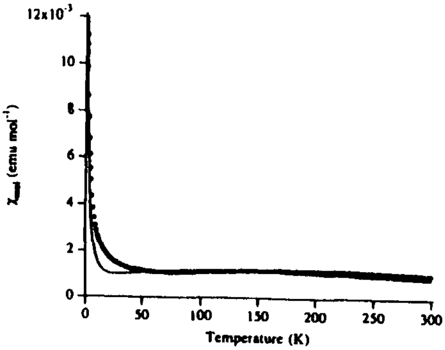


FIGURE 2 χ_{mol} vs. T Plots of 3 in Powder Sample

Results of the Optical Measurements

The fluorescence and phosphorescence spectra of **1a** in EPA glass are shown in Figure 3. **1a** gives weak phosphorescence which indicates the existence of metastable excited quartet (S=3/2) state. The spectral pattern is quite similar to

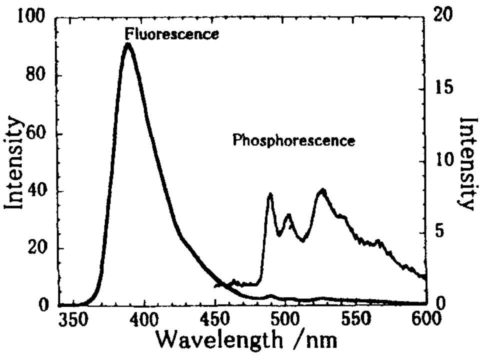


FIGURE 3 Fluorescence and Phosphorescence Spectra of **1a**

that of naphthalene molecule. However, the wavelength shift ca. 20 cm^{-1} longer as well as broader band width. The intensity of the phosphorescence becomes very weak compared with naphthalene itself. This may be the result of the enhancement of a non-irradiative relaxation process from the excited state to the ground state or of a strong spin forbidden of the inter-system crossing between the excited doublet state (S=1/2) and the excited quartet state (S=3/2). The similar phenomena have been found for **2**. Temperature dependence of the emission spectra and the phosphorescence spectra of **2** is shown in Figure 4. This shows that the phosphorescence intensity become lower with decreasing temperature, which indicates the excited quartet spin state of **2** locates higher in energy than that of the first excited doublet spin state. The direct observation and determination of the spin multiplicity using optically detected magnetic resonance experiments (ODMR) are now going in progress for these excited high spin states of **1** and **2**.

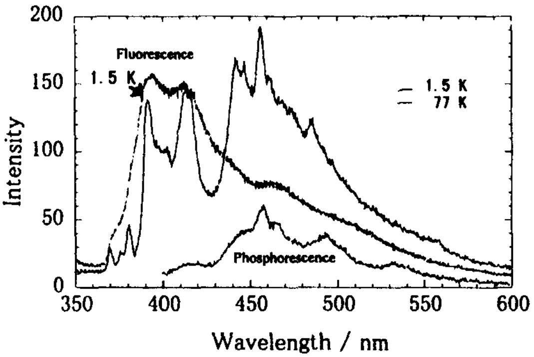


FIGURE 4 Fluorescence and Phosphorescence Spectra of **2**

Results and Discussion of the TRESR experiments

TRESR were measured using powder samples at 3- 20 K. Only doublet-like absorption type TRESR signals were observed for the naphthalene nitroxide radical **1a** and **1b**, and the Br substituted pyrene nitronyl nitroxide **2**. Figure 5 shows EDP (electron dynamic polarization) signals obtained in α-naphthalene nitroxide, β-naphthalene nitroxide, and Br substituted pyrene nitronyl nitroxide. These absorptive DEP signals are observed for a long period (> 1ms). This finding shows that the dynamic electron polarization originating from RTPM between the long-time lived excited triplet states of naphthalene or pyrene groups and the stable doublet radicals. Therefore, we can conclude that the excited doublet (S=1/2) spin states have been detected as a result of the antiferro-magnetic spin alignment between the radical spins and the excited triplet (S=1) spin states of naphthalene or pyrene.

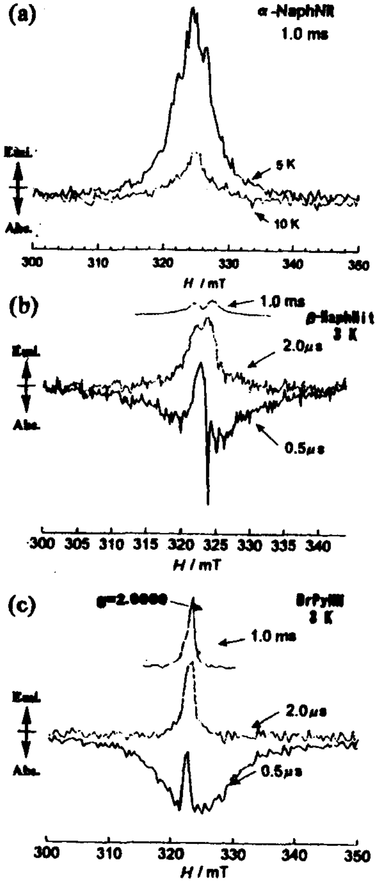


FIGURE 5 Typical TRESR Spectra of **1a**, **1b**, and **2**
(a) **1a**, (b) **1b**, and (c) **2**

For the pyrene thioaminyl radical **3**, the situation is different with those. Figure 6 shows the time profile of the typical TRESR signals of **3**. Two types of signals were observed. The signal is absorptive (A) at earlier times (0.2-1.5 μs) and turned to be emissive (E) at later times (2 μs – 5 ms). These absorptive and emissive signals have g = 2.000 and g = 2.0039, respectively. These g values are expected to those of the weakly coupled doublet-triplet pair. When the magnetic exchange interaction between the radical and the triplet excited state of pyrene group is much larger than the Zeeman interaction and not so strong to brake the nature of each spin state (weak coupling case), the g values of the excited quartet (Q_1) and doublet (D_1) states generated by RTPM are given by [13,14]

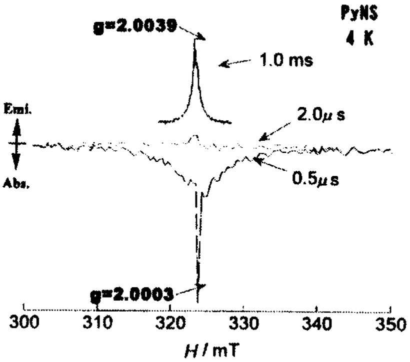


FIGURE 6 Time Profile of the Typical TRESR Spectra of 3

$$g(Q_1) = (1/3)\,g(R) + (2/3)g(T) \qquad (1)$$

and

$$g(D_1) = -(1/3)\,g(R) + (4/3)g(T). \qquad (2)$$

The g values of Q_1 and D_1 states are estimated to be 2.0035 and 2.0010, respectively, using the g values of thioaminyl radical (2.0058) and pyrene (2.0023). The g values of the absorpative (2.0003) and emissive (2.0039) TRESR signals of **3** in Figure 5 are in good agrrement with those of D_1 and Q_1 excited states, respectively. Ishii et al., [14] reported similar g value and polarization changes in the TRESR signals in ZnTPP-nipy system and assign to the D_1 and Q_1 excited states. In the ZnTPP-nipy system, the two sets of outer pair of signals giving (A/E) pattern were observed at earlier times (0.5 μs) and turned to be absorptive (A) at later. However, in our pyrene-thioaminyl radical system, no outer pair of signals could not be observed.

Since in our system the intermolecular exchange interaction exists in the powder sample, the fine-structure may be smear out. The TRESR experiments for the diluted system is now in progress in order to confirm the above discussion by detecting the fine-structure splitting of the excited quartet state of **3**.

ACKNOWLEDGEMENTS

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