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Spin Polarization Conservation during Intramolecular Triplet–Triplet Energy Transfer Studied by Time-Resolved EPR Spectroscopy

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Abstract: Transient triplet EPR spectra of two types of spirans, spiro[9,10-dihydro-9-oxoanthracene-10,2′-benz[*f*]-indan] and spiro[9,10-dihydro-9-oxoanthracene-10,2′-3*H*-phenalene], were measured in a glassy matrix at 77 K. Spin polarization conservation during the intramolecular triplet–triplet energy-transfer process was observed. The results clearly indicate that spin orientation is conserved in the molecular frame in the presence of an external magnetic field and that the high-field approximation cannot explain the spin polarization pattern observed in the X-band EPR spectra. The results contribute to the understanding of the relaxation processes of the excited states.

Introduction

Triplet–triplet (T–T) energy transfer has been extensively studied because of its fundamental and useful roles in photochemistry. Spin dynamics is important to understand the relaxation pathway of the excited states. It is well-known that the exchange interaction is the principal mechanism of T–T energy transfer. As the operator $(1/r_{ij})$ responsible for the energy transfer has no effect on the electron spin, the spin angular momentum is preserved during these pathways. Since the first demonstration of spin conservation during intermolecular energy transfer by El-Sayed et al.,[1] many systems have been examined at zero-field[2] and in an external magnetic field.[3]

There has been little study of the spin dynamics for the case of intramolecular energy transfer, while efficient energy transfer has been reported for many systems. Maki et al.[4] examined a spiran with an anthrone moiety as the donor and a naphthalene as the acceptor with ODMR at very low temperature in the absence of an applied field. They found no spin polarization conservation during intramolecular T–T energy transfer, leading to the conclusion that very fast energy transfer makes the uncertainty width of the donor state comparable to or greater than the zero-field splitting (ZFS).

In the present paper, we studied the spin polarization conservation during intramolecular energy transfer in the presence of an external magnetic field by using time-resolved EPR (TREPR). If the spin angular momentum is conserved during the energy-transfer process, the acceptor triplet state is formed in its three substates with probabilities that are given by the squares of the projections of the donor spin direction on the principal magnetic axes of the acceptor. To confirm the above possibility, we selected the spiran systems spiro[9,10-dihydro-9-oxoanthracene-10,2′-benz[*f*]indan] (**1**) and spiro[9,10-dihydro-9-oxoanthracene-10,2′-3*H*-phenalene] (**2**). Their structures and coordination axes are shown in Figure 1. The two different geometrical arrangements are suitable for examining the conservation of the spin alignment during the excitation energy transfer between the chromophores.

Experimental Section

The rigid spirans, **1** and **2**, were prepared according to the procedure reported previously.[5] The samples were purified by recrystallizations from pyridine–water and from light petroleum ether and sublimation. **1**: mp 223–223.5 °C. Anal. Calcd. for $C_{26}H_{18}O$: C, 90.14; H, 5.24. Found: C, 90.04; H, 5.18. **2**: mp 223–224 °C. Anal. Calcd for $C_{26}H_{18}O$: C, 90.14; H, 5.24. Found: C, 89.84; H, 5.01.

For steady-state and TREPR measurements, a concentration of 1.0×10^{-3} M was used. The samples were degassed by using three freeze–thaw cycles. Luminescence spectra were observed by a Hitachi Model 850 spectrophotometer. Solvent was purified by distillation after dehydration by the methods reported previously.[3] Time-resolved EPR spectra were observed with a Varian E-109E X-band EPR spectrometer without field modulation. In order to excite the anthrone moiety selectively we used a N_2 laser and a Nd-YAG laser (third harmonics, 355 nm) for the pulsed light source. Further details of the instrumentation were reported previously.[6]

Results and Discussion

The energy level of the T_1 state of anthrone is 3100 cm^{-1} higher than that of naphthalene, which is responsible for efficient T–T energy transfer. This fact was confirmed for both samples by measuring the phosphorescence spectra. Excitation of **1** and **2** by light with wavelengths longer than 300 nm gave phosphorescence due to the naphthalene moiety as reported previously.[5] The T–T energy transfer quenches the phosphorescence of the anthrone moiety completely.

The phosphorescence excitation spectrum monitored by the emission at 530 nm due to the acceptor triplet state corresponds closely to the sum of the absorption spectra of the individual chromophores. This indicates that singlet–singlet (S–S) energy transfer from naphthalene to anthrone plays an important role in the relaxation pathway of the S_1 state of the naphthalene moiety, when the photoexcitation is carried out with light of shorter wavelength.

Steady-state EPR measurements confirm the high efficiency of the energy-transfer process. Figure 2a shows the conventional EPR spectrum of $^3\mathbf{1}^*$ generated with N_2 laser (337.1 nm, 10-Hz

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[1] El-Sayed, M. A.; Tinti, D. S.; Yee, E. M. *J. Chem. Phys.* **1969**, *51*, 5721.

[2] Clarke, R. H. *Chem. Phys. Lett.* **1970**, *6*, 413.

[3] Scharnoff, M.; Iturbe, E. B. *Phys. Rev. Lett.* **1971**, *27*, 576. Brenner, H. C. *J. Chem. Phys.* **1973**, *59*, 6362. Kim, S. S.; Weissman, S. I. *Rev. Chem. Intermed.* **1979**, *3*, 107. Weir, D.; Wan, J. K. S. *J. Am. Chem. Soc.* **1984**, *104*, 427. Imamura, T.; Onitsuka, O.; Murai, H.; Obi, K. *J. Phys. Chem.* **1984**, *88*, 4028. Yamamoto, Y.; Murai, H.; I'Haya, Y. J. *Chem. Phys. Lett.* **1985**, *112*, 559. Murai, H.; Mizunuma, Y.; Ashikawa, K.; Yamamoto, Y.; I'Haya, Y. J. *Chem. Phys. Lett.* **1988**, *144*, 417.

[4] Maki, A. H.; Weers, J. G.; Hilinski, E. F.; Milton, S. V.; Rentzepis, P. M. *J. Chem. Phys.* **1984**, *80*, 2288.

[5] Keller, R. A. *J. Am. Chem. Soc.* **1968**, *90*, 1940.

[6] Akiyama, K.; Tero-Kubota, S.; Ikegami, Y. *J. Am. Chem. Soc.* **1984**, *106*, 8322.

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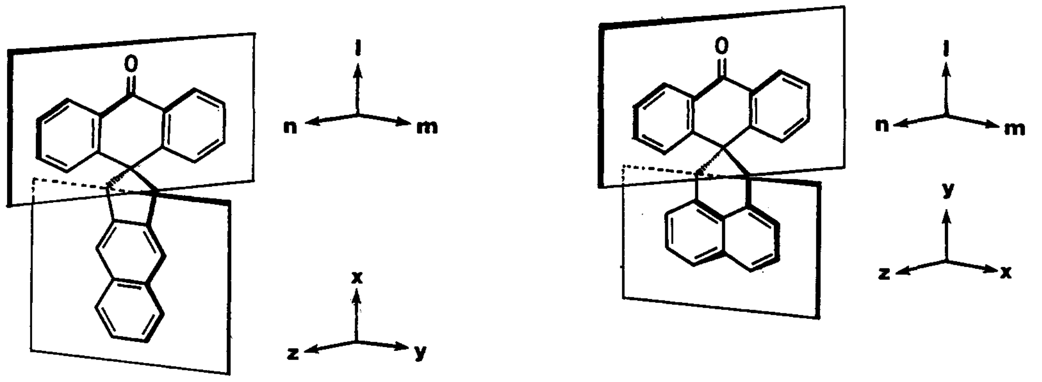

1 **2**

Figure 1. Structure and coordination systems of the rigid spirans (**1** and **2**) studied in this paper.

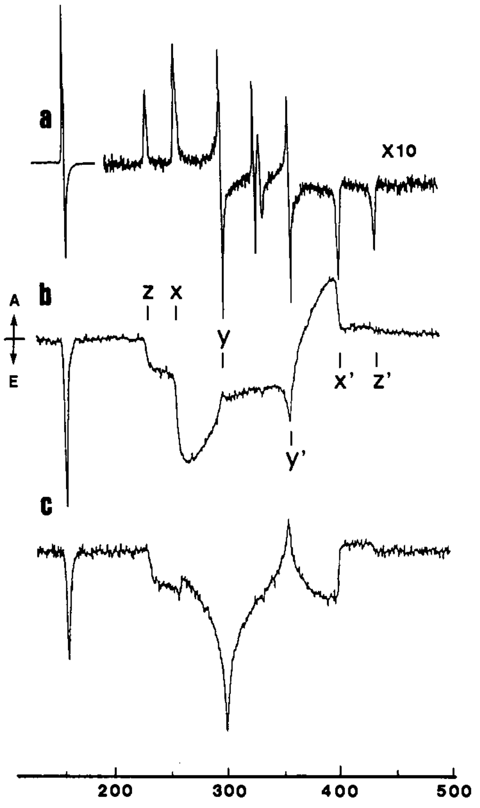

Figure 2. Steady-state (a) and time-resolved EPR spectra for the T_1 states of the spirans **1** (b) and **2** (c) in a toluene glassy matrix at 77 K. TREPR spectra were obtained at 0.5 μs after the laser pulse irradiation.

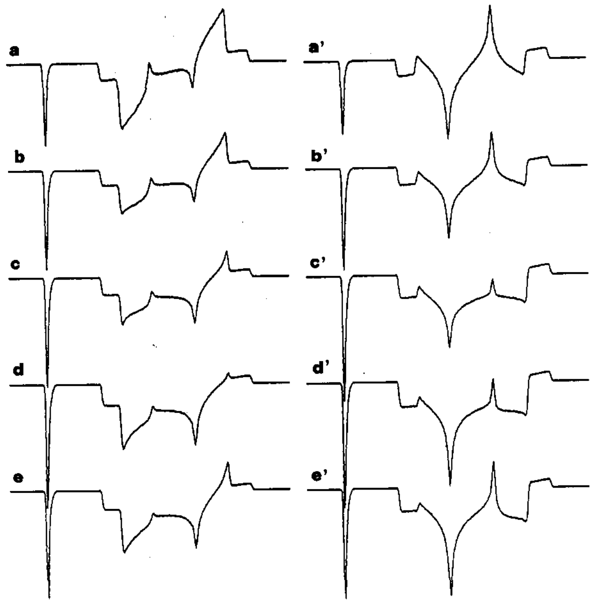

Figure 3. Calculated TREPR spectra for **1** and **2** according to eq 3 by the change of *D* values between −0.1 (a and a′) and −0.5 cm^{-1} (e and e′) with a step of 0.1 cm^{-1}.

repetition rate) excitation, which corresponds to the excitation of the anthrone moiety, in a toluene matrix at 77 K. The spectrum is assigned to the T_1 state of the naphthalene moiety on the basis of the zero-field splitting (ZFS) parameters ($|D| = 0.0952$ and $|E| = 0.0137$ cm^{-1}). These values are nearly identical to those of the T_1 state of naphthalene reported previously.[7] Similar results were also obtained with **2**.

In Figure 2b,c are shown the transient EPR spectra of **1** and **2** in a toluene matrix observed 500 ns after N_2 laser puse irradiation. They show polarization patterns of E EEA/EAA and E EAE/AEA for **1** and **2**, respectively (E denotes emission and A absorption of microwave radiation). The pattern of the spectra was not altered significantly upon excitation by excimer laser light (XeCl, 308 nm). The ZFS parameters determined from the canonical points show good agreement with those of the T_1 state of naphthalene.

When naphthalene in an ether/isopentane/ethyl alcohol (EPA) matrix was excited directly at 77 K,[8] an E EEE/AAA pattern was found, indicating that the relative population rates of the three triplet sublevels are given by P_x:P_y:P_z = 0.5:0.5:0. Since the spectral patterns obtained for both spirans are clearly different from that obtained upon direct excitation of naphthalene, the population distribution in the T_1 state of the acceptor certainly results from spin polarization transfer during intramolecular T–T energy transfer. This conclusion is supported by the observation that the polarization pattern depends on the relative orientation of the donor and acceptor. The original spin alignment created in the donor anthrone is responsible for the different polarization patterns for the T_1 states of the acceptor naphthalene moieties of **1** and **2**.

The high-field approximation cannot explain these spectral patterns because the spectral intensities show a significant asymmetry with respect to the spectral center. Therefore, an attempt was made to fit the data to a general expression for spin polarization transfer in the presence of a finite external magnetic field. The intensity of the TREPR signal, I(θ,ϕ), as a function

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[7] Hutchison, C. A., Jr.; Mangum, B. W. *J. Chem. Phys.* **1961**, *34*, 908.

[8] Yagi, M.; Komura, A.; Higuchi, J. *Chem. Phys. Lett.* **1988**, *148*, 37.

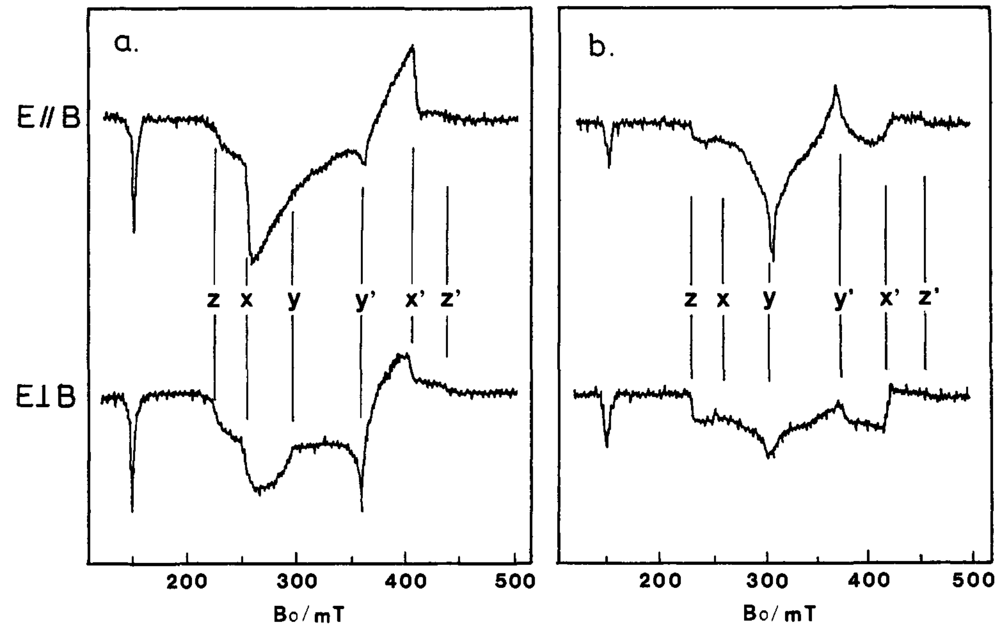

Figure 4. Transient T_1 state EPR spectra of **1** (a) and **2** (b) obtained by the excitation using polarized light in a toluene glassy matrix at 77 K. The directions of the polarized light with the external magnetic field are depicted in the figure.

of the polar angles θ and ϕ of the applied field with respect to the principal molecular axes is given by

$$I(\theta,\phi) = B_{i,j}(P_i^{A} - P_j^{A})G(\theta,\phi)$$

where $B_{i,j}$ is the transition probability between the i and j sublevels in the acceptor, P_i^A and P_j^A are the populating ratios for the corresponding sublevels, and $G(\theta,\phi)$ is the Gaussian function. During the spin selective ISC, each sublevel of the donor moiety is populated with a different rate. The populating probability (P_i^D) for the donor sublevel in an applied field becomes

$$P_i^{D} = \sum_h |C_{ih}^{D}|^2 P_h^{D} \qquad (h = l, m, n)$$

where C_{ih} are the components of the unitary transformation diagonalizing the spin Hamiltonian and P_h^D are the populating ratios for the zero-field donor sublevels in a molecular frame providing $\sum P_h^D = 1$. It can be expected that spin alignment is conserved during T–T energy transfer because the operator responsible for the exchange mechanism is independent of electron spin. Thus, we can assume $\langle \chi_h^D | \chi_k^A \rangle \sim |\cos \Theta_{hk}|$, where Θ_{hk} is the angle between the principal axis h of the donor and k (k = x, y, and z) of the acceptor and $|\chi_h^D\rangle$ and $|\chi_k^A\rangle$ are the zero-field spin functions of the donor and acceptor, respectively. The probability (P_j^A) of acceptor sublevel population is written

$$P_j^{A} = \sum_i \sum_h \sum_k |C_{ih}^{D}|^2 |C_{jk}^{A}|^2 |\langle \chi_h^{D} | \chi_k^{A} \rangle|^2 P_i^{D}$$

It is well-known for the donor anthrone that ISC occurs preferentially to the highest sublevel $|\chi_l^D\rangle$ (l//C=O).[9] For **1**, the direction of l is parallel to that of the x axis of the acceptor naphthalene leading to the relation of $|\cos \Theta_{lx}| = 1.0$. On the other hand, $|\cos \Theta_{ly}|$ is unity for **2** (l//y). The ZFS parameters of the donor anthrone, as well as the acceptor, are required to calculate the line shape because their eigenfunctions depend on the relative magnitudes of the ZFS parameters and the applied field.

Unfortunately, the values of the ZFS parameters of anthrone are uncertain. Therefore, the D and E values of the donor triplet state were treated as adjustable parameters for the simulation. The simulated spectrum was not appreciably altered by a change of E value from 0.05 to 0.01 cm^{-1} but was affected by the D value. The polarizations of the acceptor triplet states were calculated by changing the D value of anthrone from –0.5 to –0.1 cm^{-1} as shown in Figure 3. When the values of $D = -0.5$ and $E = 0.02$ cm^{-1} were used for the simulation, the results well reproduced the observed spectra of both **1** and **2** as shown in Figure 3e,e′.

To get information on the ZFS parameters, a measurement of the triplet TREPR spectrum of 10,10-dimethylanthrone (DMA) was attempted in toluene/ethanol (10/1, v/v) at 77K. However, no TREPR signal was obtained except for a strong emissive signal in the region of $g = 2$ due to free radicals. This indicates that the ZFS values of the T_1 of DMA are too large to observe the triplet EPR spectrum by X-band EPR experiments. Considering the mixing between the $^3n\pi^*$ and $^3\pi\pi^*$ states, which are close in energy, the $|D|$ value of 0.5 cm^{-1} estimated from the present study for the T_1 state of anthrone is within the range expected for aromatic carbonyl compounds. For instance, the reported D value of the T_1 state of acetophenone in durene is –0.54 cm^{-1}.[10]

We also attempted magnetophotoselection experiments in order to confirm the above results. The polarized light selectively excites the molecule when the transition dipole moment of the donor moiety is parallel to the direction of the electric field vector (**E**) of the light. It is expected that the spectral pattern of the acceptor triplet state will reflect the selective excitation of the donor.

Figure 4 shows the magnetophotoselection spectra of the spirans in toluene obtained by excitation with polarized light from a Nd-YAG laser (third harmonics, 355 nm) at 77 K. When **E** of the exciting light was parallel to $\mathbf{B}_0$, the middle and inner most pairs of peaks were intensified for **1** and **2**, respectively. On the other hand, upon photoexcitation with $\mathbf{E} \perp \mathbf{B}_0$, the signals of the other canonical orientations become intense.

As the transition moment of the electronic excitation of anthrone at 355 nm is aligned along the C=O bond axis,[11] irradiation with light polarized parallel to the external magnetic field ($\mathbf{E}$//$\mathbf{B}_0$) preferentially excites molecules aligned with the C=O axis along $\mathbf{B}_0$. With the principal magnetic axes systems defined in Figure 1, the canonical orientation of the C=O bond (l) axis in the donor corresponds to the middle canonical points (x and x') and to the innermost canonical orientations (y and y') of the acceptor for **1** and **2**, respectively. The changes of the signal intensities

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[9] Dym, S.; Hochstrasser, R. M. *J. Chem. Phys.* **1969**, *51*, 2458.

[10] Cheng, T. H.; Hirota, N. *Mol. Phys.* **1974**, *27*, 281.

[11] Shimada, R.; Goodman, L. *J. Chem. Phys.* **1965**, *43*, 2027.

of both spirans at each canonical point observed with photoexcitation with polarized light agreed well with those expected from the mutual orientation between the donor and the acceptor. It was also confirmed from the response of the magnetophotoselection that the spin polarization of the donor is conserved during intramolecular T–T energy transfer, reflecting the geometrical arrangement between the donor and the acceptor.

In contrast to the above results, little change of the spectral pattern was observed by the photoexcitation with polarized light at 337.1 nm. A lack of the dependence of the photoexcitation with polarized light at 337.1 nm is due to the cancellation of the polarization of the transition moments to the excited singlet states as reported previously.[11]

The results clearly indicate that the T_1 state of the donor moiety has a long enough lifetime to align the spin polarization during the T–T energy transfer. According to the uncertainty principle ($\delta E \sim h/\tau$), very fast energy transfer induces broadening of the energy levels, resulting in the nonselective population of the triplet sublevels of the acceptor. The $|D|$ value of 0.5 cm^{-1} estimated for the donor triplet state and the X-band EPR experimental conditions correspond to the widths of broadening lifetime of ~10 and 16 ps, respectively. Maki et al.[4] have reported that the rate constant for T–T energy transfer is very high (1.25×10^{10} s^{-1} at room temperature), deriving no spin conservation during the process at very low temperature. However, the rate could change significantly with temperature because of changes in the fluctuation of the angle between donor and acceptor. The exchange integral depends strongly on the relative orientation of the donor and acceptor groups, that is, the overlap integral between p-orbitals of these chromophores. In a glassy matrix at low temperature, the conformation of the spirans may be fixed in a nearly perpendicular one for the donor–acceptor chromophores, leading to a slower T–T energy-transfer rate than that at room temperature. Thus the negative data for the spin selectivity during the T–T energy transfer in **1** obtained in the ODMR study[4] might be due to the low time resolution of the ODMR method or due to the different relaxation time in the presence and the absence of an external field.

Conclusions

The present results clearly show the spin polarization conservation in the molecular frame during the T–T energy transfer in the presence of an external magnetic field. The spectral patterns of the acceptor triplet states generated by the intramolecular T–T energy transfer depended on the polarization of the donor triplet state, the orientations of the donor and acceptor, the ZFS parameters of the donor and acceptor triplet states, and the magnitude of the external magnetic field. This phenomenon will be useful in clarifying the mutual orientation between the donor and the acceptor as well as the relaxation path of excited states.

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