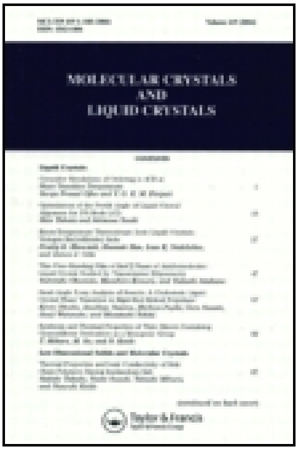

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Magnetic Interaction Between the Photochemically Generated Triplet Centers Through the π-Conjugated Skeleton of PPV

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MAGNETIC INTERACTION BETWEEN THE PHOTOCHEMICALLY GENERATED TRIPLET CENTERS THROUGH THE π-CONJUGATED SKELETON OF PPV

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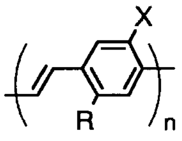
Abstract PPV **1** is considered to be a high-spin polymer by theories on its topological symmetry and expected to have interesting magnetic properties. Dinitrenes **2n** and **3n** would serve as prototypes for evaluating the sign and magnitude of the intramolecular coupling in **1**. **2n** and **3n** were photochemically generated from **2a** and **3a** , respectively, and found to have ground triplet states by means of ESR spectroscopy.

Keywords: poly-(phenylenevinylene), conjugated polymers, dinitrenes, high-spin, open-shell, paramagnetic

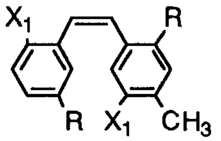
MOLECULAR DESIGN

One of the promising structures leading to organic molecules with superhigh-spin ground states is a π-conjugated polymer having open shell centers as pendants in the side chains.[1] PPV (Poly-(phenylenevinylene))[2] has been taken into account in this study as a versatile polymer main chain for making potentially high-spin organic polymers.[3] While PPV **1** is predicted to be superhigh-spin by theories on its topological symmetry, it is necessary to know the sign and magnitude of the intramolecular coupling between the two neighboring open-shell centers in PPV **1**, experimentally. For this purpose, we prepared prototype dimers **2** and **3** and studied how the two nitrene centers would couple through the π-conjugated chromophores. Nitrenes have been chosen as triplet centers because paramagnetic samples are phtochemically generated from the corresponding diamagnetic azides.

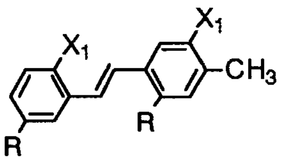


X : spin source

1



(cis)
2n X1 : N:



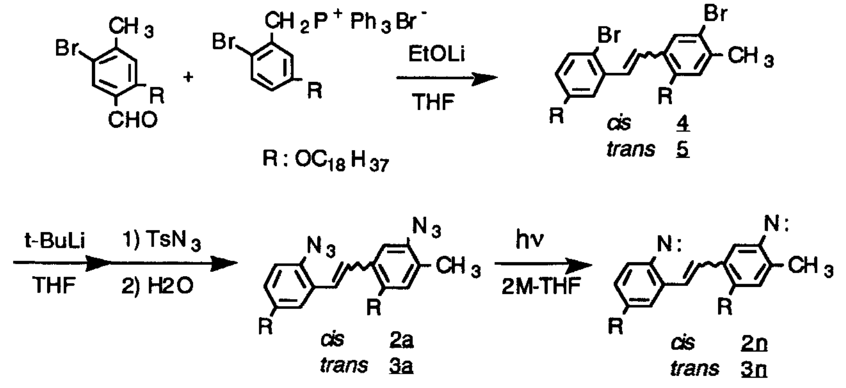
(trans)
3n X1 : N:

R : $OC_{18}H_{37}$

SYNTHESES

Preparation of *cis* and *trans* isomers of diazides 2a and 3a as precursors of nitrenes is summarized in Scheme I. Isomeric stilbene dibromides 4 and 5 were prepared by the Wittig reaction to give a *cis*-rich mixture (*cis* : *trans* = 7 : 3) from which *cis* and *trans* isomers were separated and purified by fractional recrystallization from hexane. The stearyloxy substituent was introduced to increase the solubilities of these compounds and the higher homologs. Each dibromide was lithiated with *t*-butyllithium, followed by the reaction with *p*-tosyl azide to afford diazides 2a and 3a in 55 and 60 % yields, respectively. Photolysis ($\lambda > 420$ nm) of 2a and 3a in 2-methyltetrahydrofuran (MTHF) matrices at cryogenic temperature was carried out in an EPR cavity and followed by EPR measurement.

SCHEME I



ESR SPECTROSCOPIC STUDIES OF THE PHOTOCHEMICALLY GENERATED ISOMERIC DINITRENES

X-band EPR spectra of **3n** and **2n** in MTHF matrix at 10 K are reproduced in Figures 1a and 1b, respectively .

When diazide **3a** was irradiated, signals[4] characteristic of quintet dinitrene appeared at 849, 817, and 618 mT in pairs together with those due to isolated mononitrenes ($X = Y$ transition) carrying *o*-and *m*-vinyl substituents at 659 and 677 mT, respectively. Zero field splitting (zfs) parameters for the quintet states were determined to be $|D_1/hc| = 0.150$, $|E_1/hc| = 0.012$ cm^{-1} ; $|D_2/hc| = 0.159$, $|E_2/hc| = 0.008$ cm^{-1} by applying a third-order perturbational method to the highest-field Z transition ($m_S = -2 \rightarrow -1$) and next highest-field Y transition ($m_S = 1 \rightarrow 2$).[5] These vales are quite similar to those of *m,p'* and *m,m' trans* isomers.[8,9]

Temperature dependence of the signals of **3n** due to the quintet states is reproduced in Figure 2a. The observed plots obeyed a Curie law in the temperature range 13-85 K, indicating that the quintet species are either ground states or degenerate with singlet states. Since any additional signal due possibly to an excited triplet state was not detected, the latter possibility was regarded to be remote.

In the case of **2n**, characteristic signals of quintet dinitrenes[4] were observed, too; peaks are at 1186 and 259 mT. But only one peak characteristic of a triplet mononitrene was observed at 676 mT that are attributed to m-vinyl substituted nitrene and it was rather strong , compared with the quintet signals. It is likely that the nitrenyl center ortho to the double bond is very reactive against it and the spectrum is dominated by m-mononitrene. The zfs parameters of **2n** were computed to be $|D/hc| = 0.265$ cm^{-1}. The $|E/hc|$ value could not be determined because Y transition was not observed.

Temperature dependence of the signals of **2n** due to the quintet state is reproduced in Figure 2b. The observed plots obeyed a Curie law in the temperature range 13-85 K. The quintet state is therefore a ground state.

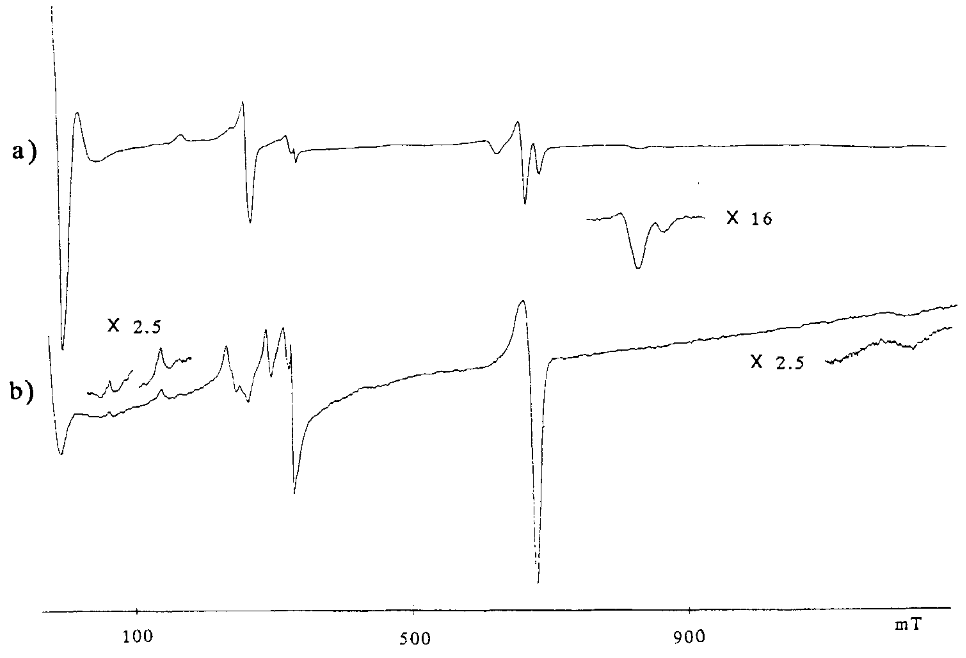


FIGURE 1. X-band EPR spectra in MTHF matrix at 10K of a) **3** (ν = 9.4148 GHz) and b) **2** (ν =9.4188 GHz)

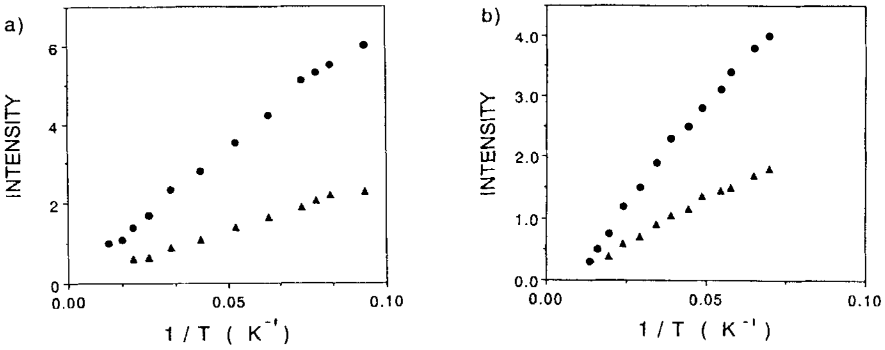


FIGURE 2. Temperature dependence of the quintet signals a) at 19 (•) and 265 (▲) mT for **3** and b) at 19 (•) and 246 (▲) mT for **2** in EPR spectra

DISCUSSION

The zfs parameters of the quintet states formed from weakly interacting triplet species depend more on the relative orientation of the two triplets rather than the distance separating them. This is explained in terms of the spin Hamiltonian for the system consisting of weakly interacting units a and b as written in eq 1:

$$H = H_a(1) + H_b(2) + H_{ab}(1,2) \qquad (1)$$

The dipolar coupling tensor D^Q of the quintet is then given by eq 2:[5,6]

$$D^Q = (D_a^T + D_b^T) / 6 + D_{ab}^T /3 \qquad (2)$$

When the component triplets a and b have strong one-center interaction as in nitrenes, their dipolar coupling tensors, D_a^T and D_b^T, are much larger than D_{ab}^T. When the last term in eq 2 thus drops out, D^Q becomes independent of the distance between the two triplets a and b but depends only on their relative orientation.[5,6] Therefore the zfs parameters can be estimated for given structures of the dinitrenes by the sum of the dipolar coupling tensors D^T of each triplet species.

The orientation can be defined by the angle θ made by the two carbon-nitrogen bonds. With the zfs parameters of the mononitrene triplet observed in the spectra for the calculation of D^T, we could estimate the parameters of the quintet with the structure $\theta = 0°$, 120° (cis 2) ; $\theta = 0°$, 120° (trans 3)(Table 1).

		θ	$\lvert D/hc \rvert$	$\lvert E/hc \rvert$
trans **3n**	obs		0.150 0.159	0.012 0.008
	calc	0 120	0.303 0.265	0.000 0.000
cis **2n**	obs		0.265	——
	calc	0 120	0.265 0.303	0.000 0.000

(cm^{-1})

TABLE 1. Observed and calculated zfs values for **2n** and **3n**

In the case of **2n**, the observed zfs parameter corresponds nicely to that of the $\theta = 0°$ structure. But in the case of **3n**, the observed zfs parameters are not close to the calculated values. This suggests that the last term of eq 2 may not be neglected in **3n** in which the two nitrene units might interact strongly.

When two nitrene centers are placed at the *m,p'* positions of a *trans*-stilbene skeleton, they couple strongly in a ferromagnetic fashion, too.[7] In the corresponding *m,m'* isomer, a quintet state is found as an excited state higher in energy by $6J = -84.6\ \mathrm{cm}^{-1}$ than a singlet.[8] These results together with those of the present studies on the *o,m'* isomers demonstrate that topology of the π-conjugated polyradicals is the most important factor in determining the sign of the magnetic coupling. Geometrical isomerism is less important in this respect.

CONCLUSION

Two isomeric dinitrenes of *cis*-stilbene **2n** and *trans*-stilbene **3n** have been generated and studied by X-band ESR spectroscopy. The interaction of the two remote triplet nitrene units connected through the stilbene skeleton is sufficiently strong to form the quintet states. These high-spin states are apt to be ground states. Thus we have obtained experimental evidence for the correct molecular design; head-to-tail homopolymer **1** should be a super-high-spin PPV. The *trans*-form is preferable because of its stability.

REFERENCES

1. K. Inoue, N. Koga and H. Iwamura, J. Am. Chem. Soc , 113, 9803 (1991). H. Nishide, N. Yoshioka, K. Inagaki and E. Tsuchida, Macromolecules, 21, 3119 (1988). A. .Fujii, T. Ishida, N. Koga and H. Iwamura, Macromolecules, 24, 1077 (1991).
2 M. Kanbe, M. Okawara, J. Polym. Sci. A-1, 6, 1058 (1968). T. Kaino, K. I. Kubodera, S. Tomaru, T. Kurihara, S. Saito, T. Tsutsui, S. Tokito, Electron.Lett., 23, 1905 (1987)
3. H. Nishide, T. Kaneko, Y. Kuzumaki, N. Yoshioka and E. Tsuchida, Mol. Cryst. Liq. Cryst , 232, 143 (1993).

4 H. Iwamura and S. Murata, Mol. Cryst. Liq. Cryst., 176, 33 (1989). S. Murata and H. Iwamura, J. Am. Chem. Soc , 113, 5547 (1992). E. Wasswrman, R. W. Murray, W. A. Yager, A. M. Trozzolo, G. Smolinsky, J. Am. Chem. Soc , 89, 5076 (1967). T. Matsumoto, T. Ishida, N. Koga, H. Iwamura, J. Am. Chem. Soc 114 , 9954 (1992).

5 K. Itoh, Pure Appl. Chem. , 50, 1251, (1978)

6 A. Izuoka, S. Murata, T. Sugawara and H. Iwamura, J. Am. Chem. Soc , 107, 1786, (1987). , A. Izuoka, S. Murata, T. Sugawara and H.Iwamura, J. Am. Chem. Soc, 109, 2631, (1987).

7 C. Ling, M. Minato, P. M. Lahti and H. van Willigen , J. Am. Chem. Soc , 114, 9959, (1992).

8 Unpublished results from these laboratories.