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ESR Study of Intramolecular Magnetic Interactions in Bis(nitrenophenyl) Sulfides

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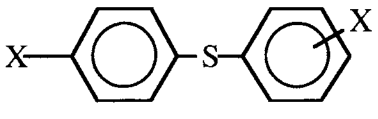
In photolysis of 4,4'-diazidodiphenyl sulfide quintet ESR peaks were observed and the plots of these signal intensities vs. temperature obeyed the Curie law, although no quintet signals were observed in the photolysis of 4,4'-diazidodiphenyl ether. The ESR spectrum upon the irradiation of 3,4'-diazidodiphenyl sulfide showed quintet resonances of 3,4'-dinitrenodiphenyl sulfide. Both Curie analysis and PM3-CI calculations indicated that the quintet state is a ground-state.

In order to achieve superhigh-spin ground state, the magnetic intramolecular interactions between open-shell units have been studied by a number of groups.1,2,4-7,10,12) In previous studies on the photolysis of diazidodiphenyl ethers by Lahti et al.1) and by our group,2) while no ESR signals characteristic of quintet state were observed in the case of the 4,4'-isomer, the photolysis of the 3,4'-isomer gave rise to quintet ESR peaks that obeyed the Curie law. We now report the intramolecular magnetic interactions between two phenylnitrenes that are linked by a sulfur atom in the isomeric compounds; 4,4'- and 3,4'- dinitrenodiphenyl sulfides (**1n** and **2n**).



4,4'- ; **1** $X = N_3$; **a**
3,4'- ; **2** $= N:$; **n**

The dinitrene precursors **1a** and **2a** were synthesized by diazotization of the corresponding diamine followed by addition of sodium azide.3) The precursors **1a** and **2a** were dissolved in 2-methyltetrahydrofuran (MTHF) and these solutions were degassed by freeze-pump-thaw cycles. The dinitrenes were generated upon the irradiation of the dilute frozen solutions (ca. 10^{-3} mol dm^{-3}) with a xenon lamp through cut-off filters (270 nm < λ < 400 nm). The ESR spectra were taken on an ESR spectrometer (JEOL JES-RE3X) equipped with a liquid helium transfer system (Air Products Model LTR-3).

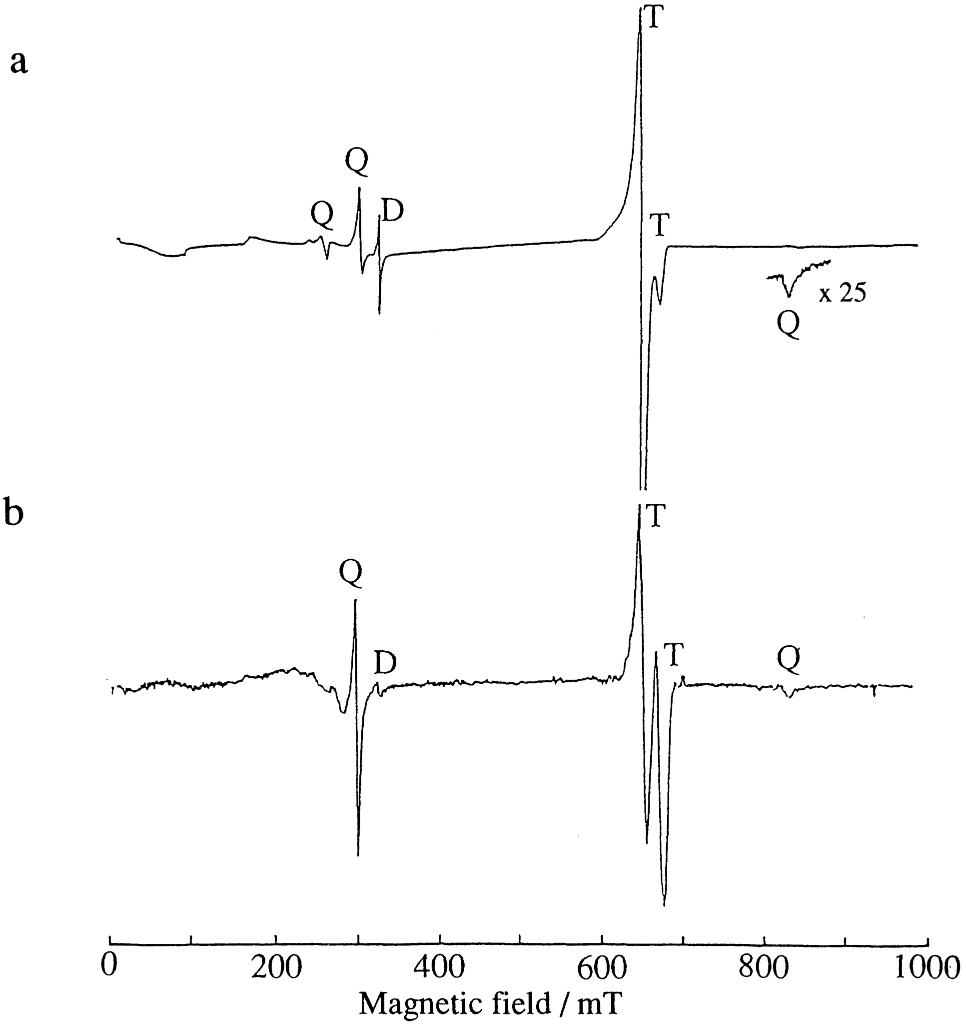


Fig. 1. ESR spectra (ν = 9.08 GHz) from the irradiation of (a) **1a** at 6 K and (b) **2a** at 64 K in MTHF. Symbols Q, T, and D denote the quintet dinitrene, triplet mononitrene, and doublet radicals, respectively.

Figure 1a shows the ESR spectrum from the photolysis of **1a** at 6 K. The resonance signals at about 655 and 675 mT are assigned to transitions of triplet mononitrene and the peak at 328 mT can be assigned to doublet radicals.[8)] Other observed resonances are characteristic signals of the quintet dinitrene species. If we assume that the highest field transition is the resonance at 845 mT and the next highest is hidden under the intense mononitrene resonance at 655 mT, the zero field splitting (zfs) parameters are estimated to be D = 0.163 cm^{-1} and E = 0.02 cm^{-1} on the basis of a third-order perturbation theory with a high-field approximation.[9-11)] The plots of the signal intensity vs. reciprocal temperature followed the Curie law in the temperature range of 4-40 K, no resonances of thermally excited states were observed over the temperature range of 4-77 K. The Curie analysis suggests either that the quintet state is a ground state or that the spin states are nearly degenerate. The dinitrene **1n** is expected to be a singlet ground-state by the superexchange mechanism that has applied to explain the singlet ground-state of 4,4'-bis(phenylmethylene)diphenyl ether.[12)] Our experimental result is inconsistent with that expectation.

Semiempirical PM3-CI calculations [13)] were carried out to understand the effect of conformation on the singlet-quintet energy gap in **1n**. A five-orbital and six-electron active space was used for the CI calculations. The energy gaps ($\Delta E = E_{quintet} - E_{singlet}$) between the quintet and singlet state were calculated by changing the twist angle of two phenyl rings, assuming C_2 symmetry, as shown in Fig.2. The energy gap decreases with the increase of twist angle. In the region of larger torsinal angle than 50 degrees the value of the energy gap becomes negative, suggesting the presence of ferromagnetic coupling between two nitrenes. The torsion greatly affects the electronic nature in **1n** by decreasing the π-conjugation through the sulfur. It is likely that the effect of the twist on **1n** leads to either the quintet ground-state or the very small singlet - quintet energy gap.

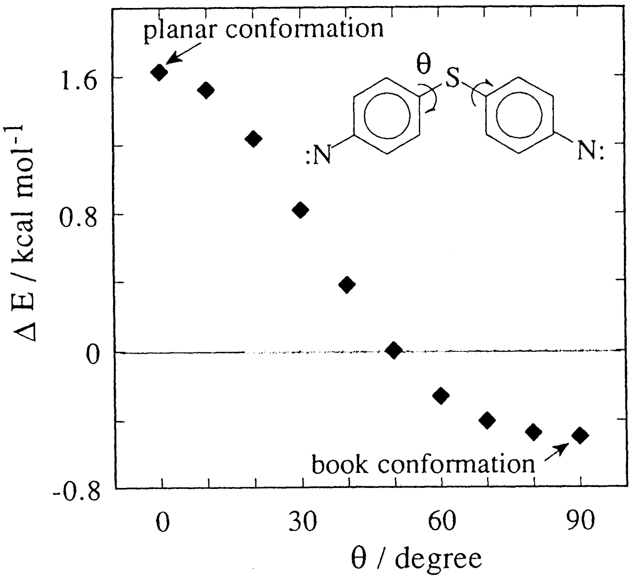


Fig. 2. Torsional angle dependence of the singlet-quintet energy gap in **1n**. The positive value of ΔE denotes the singlet ground state.

The ESR spectrum from the photolysis of **2a** in Fig.1b shows typical quintet resonances at 835 mT and 300 mT, and broad resonance lower than 250 mT, besides doublet radicals and two mononitrene signals. On similar assumptions as was used in the analysis of the ESR spectrum of **1n**, the zfs parameters of **2n** are estimated to be $D = 0.161\ cm^{-1}$ and $E = 0.02\ cm^{-1}$. The temperature dependence of the quintet peak intensity obeys the Curie law in the temperature range of 4-40 K. Our PM3-CI calculation indicates that, although the energy gap decreases, ΔE in **2n** remains negative even if the torsional angle of the two phenyl rings becomes 90 degrees. These results imply that **2n** has a quintet ground-state and the two nitrene units are ferromagnetically coupled.

PM3-CI computations show that the singlet - quintet energy gap of **1n** is more sensitive to the twisting of the two phenyl rings than that of **2n**, probably because π-conjugation is a more important factor for the energy gap in **1n**. Our results indicate that the conformational effects on the electronic nature are crucial to achieve superhigh-spin ground state by through-bond coupling. Studies on photolysis of 3,3'-diazidodiphenyl sulfide are now in progress.

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References

1) M. Minato and P. M. Lahti, *J. Phys. Org. Chem.*, in press.
2) M. Kaise, T. Ohana, A. Yabe, S. Nimura, and O. Kikuchi, 64th National Meeting of the Chemical Society of Japan, September 1992, Abstr., No. 3-A2-13.
3) 4,4'-Diaminodiphenyl sulfide is obtained as a commercial product. 3,4'-Diaminodiphenyl sulfide was given by a nucleophilic condensation of 4-chloronitrobenzene with 3-aminothiophenol in refluxing alkaline ethanol followed by catalytic reduction (Fe / HOAc).
4) T. Ohana, M. Kaise, S. Nimura, O. Kikuchi, and A. Yabe, *Chem. Lett.*, **1993**, 765.
5) S. Nimura, O. Kikuchi, T. Ohana, A. Yabe, and M. Kaise, *Chem. Lett.*, **1993**, 837.
6) P. M. Lahti, C. Ling, N. Yoshioka, F. C. Rossitto, and H. van Willigen, *Mol. Cryst. Liq. Cryst.*, **233**, 17 (1993).
7) T. Doi, A. S. Ichimura, N. Koga, and H. Iwamura, *J. Am. Chem. Soc.*, **115,** 8928 (1993).
8) We also observed similar two triplet peaks due to two mononitrenes in the photolysis of 4-azidophenyl phenyl sulfide; Unpublished results.
9) K. Itoh. 6th ESR Symposium of the Chemical Society of Japan, October 1967, Abstr., p. 117.
10) E. Wasserman, R. W. Murray, W. A. Yager, A. M. Trozzolo, and G. Smolinsky, *J. Am. Chem. Soc.*, **89**, 5076 (1967); H. Iwamura and S. Murata, *Mol. Cryst. Liq. Cryst.*, **176**, 33 (1989).
11) Sato et al. have recently suggested that the D values of this type of the quintet dinitrene are larger than one from this analysis; K. Sato, A. S. Ichimura, T. Takui, T. Kinoshita, K. Itoh, and P. M. Lahti, 67th National Meeting of the Chemical Society of Japan, March 1994, Abstr., No. 4-A6-15.
12) K. Itoh, T. Takui, Y. Teki, and T. Kinoshita, *Mol. Cryst. Liq. Cryst.*, **176**, 49 (1989).
13) J. J. P. Stewart, *J. Comput. Chem.*, **10**, 209, 221 (1989); The PM3-CI calculations were carried out with Version 6.00 of the MOPAC program package.

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