

Ferromagnetic Spin Coupling of *tert*-Butylnitroxide Diradicals through a Conjugated Oligo(1,2-phenylenevinylene)-Coupler

Takashi Kaneko, Shuichi Toriu, Eishun Tsuchida, Hiroyuki Nishide,* Daisuke Yamaki,† Goro Maruta,† and Kizashi Yamaguchi†
 Department of Polymer Chemistry, Waseda University, Tokyo 169
 † Department of Chemistry, Osaka University, Toyonaka, Osaka 560

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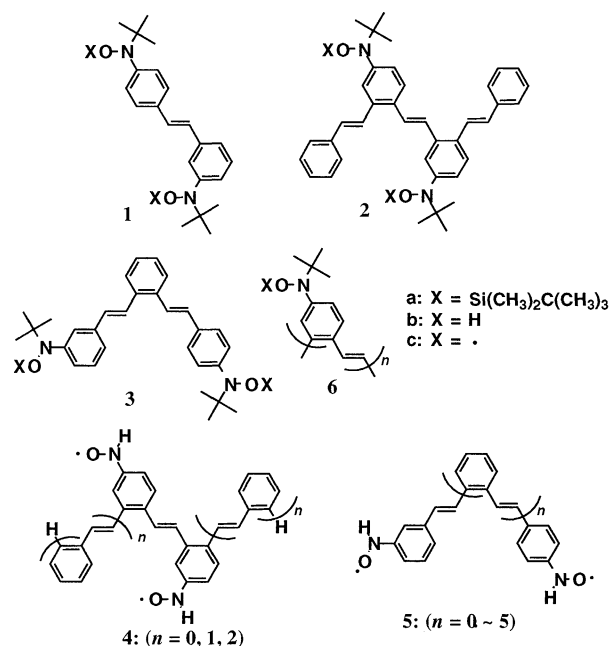
Ferromagnetic spin coupling of the *tert*-butylnitroxide diradicals connected to the oligo(1,2-phenylenevinylene)-skeleton was studied to relate with their π -conjugated electronic structure. The spin coupling constant (J) determined from their magnetic susceptibility increased with the degree of oligomerization in the conjugated skeleton and was reduced in response to the conjugated but spacing phenylenevinylene unit. These $2J$ values qualitatively agreed with the semiempirically calculated ones.

Molecular magnetic materials are recently of great interest. Polymeric high-spin organic molecules with through-bond ferromagnetic coupling have been expected¹⁻⁴ as one of the best possible candidates for magnetic materials; such molecules have been synthesized⁵⁻¹¹ and also studied using semiempirical calculations.^{12,13} A number of organic diradicals with various π -conjugated magnetic couplers such as phenylene,¹⁴⁻¹⁷ diphenylethylene,¹⁸⁻²² diphenyldiacetylene,^{18,23} and benzophenone²¹ have been synthesized, and their spin couplings have been characterized to verify the theoretical prediction for the connecting networks of the radical centers to the magnetic couplers. One of the typical examples is a stilbene-diradical (**1c**); the *m,p'*-isomer displayed a ferromagnetic interaction as theoretically predicted.²² However, the effects of the electronic states such as due to π -conjugation length or distance of the magnetic couplers on the spin coupling energy have not been studied for diradicals with similar ferromagnetic connecting networks. This communication describes the π -conjugation effects of the magnetic coupler for *tert*-butylnitroxide diradicals having an oligo(1,2-phenylenevinylene)-skeleton.

2,2'-Distyryl-5,4'-bis(*N-tert*-butyl-*N*-oxyamino)stilbene (**2c**) was synthesized *via* the Heck reaction from a mixture of 2-bromo-4-(*N-tert*-butyl-*N-tert*-butyldimethylsiloxy)aminostyrene with bromobenzene and styrene. 1-[3-(*N-tert*-Butyl-*N*-oxyamino)styryl]-2-[4-(*N-tert*-butyl-*N*-oxyamino)styryl]benzene (**3c**) was also synthesized *via* the coupling reaction of 3-bromo-2'-(4-bromostyryl)stilbene with 2-methyl-2-nitrosopropane.¹⁰ The absorption maximum or shoulder of their UV/vis spectra increased in the order **1b**(324 nm) < **3b**(338 nm) < **2a**(350 nm), suggesting a π -conjugation developing with the degree of oligomerization in the phenylenevinylene skeleton.

The experimental magnetization data of **2c** and **3c** in a 0.5 - 7 T magnetic field located between the Brillouin curves for $S=1/2$ and $S=1$ at 2-10 K revealed the triplet ground state of **2c** and **3c**. The curve fitting of the μ_{eff}/μ_B data (μ_{eff} and μ_B are the effective magnetic moment and Bohr magneton, respectively) for **2c** to Eq.1²² gave $2J = 67 \pm 11 \text{ cm}^{-1}$, $\theta = -0.16 \pm 0.01 \text{ K}$ and $x = 0.71 \pm 0.06$, and that for **3c** gave $2J = 3 \pm 2 \text{ cm}^{-1}$,¹⁰ $\theta = -0.06 \pm 0.16 \text{ K}$ and $x = 0.61 \pm 0.42$.²⁴

$$\mu_{eff}/\mu_B = \left[\frac{6g^2T}{(T-\theta)(3+\exp(-2J/kT))} (1-x) + \frac{3g^2T}{2(T-\theta)} x \right]^{1/2} \quad (1),$$



where J , θ and x are the spin coupling constant, the Weiss constant for the intermolecular magnetic interaction and the fraction of the doublet species in each sample, respectively, and $2J$ is equal to the triplet-singlet energy gap. The positive $2J$ value indicated a through-bond intramolecular ferromagnetic spin coupling in **2c** and **3c**.

The $2J$ of **2c** is *ca.* 1.5 times larger than that of **1c** ($2J = 41 \pm 1 \text{ cm}^{-1}$ ²²). It is suggested that the triplet state of **2c** is stabilized with the decrease in the potential energy gap between two NBMOs, due to the developed π -conjugation of the phenylenevinylene skeleton, as indicated by the transition energy (Δ) in Figure 1. This consideration agrees with the semiempirical INDO calculation of the model compounds **4** as also shown in Figure 1. The original INDO parameters were used for the semiempirical calculation of the oligomers. The reliability of the calculation has already been discussed in the lit.²⁵

The $2J$ of **3c** is reduced to *ca.* 1/10 (from **1c** to **3c**) in response to the conjugated but spacing phenylenevinylene unit, while the $2J$ value of the oligo(1,3-phenylenemethylene) has been reported to be decreased by about two orders of magnitude with one unit of spacing.²⁶ The semiempirical calculation data of the model compounds **5** (Figure 2) supports the experimental results.

The conjugation effects observed for the

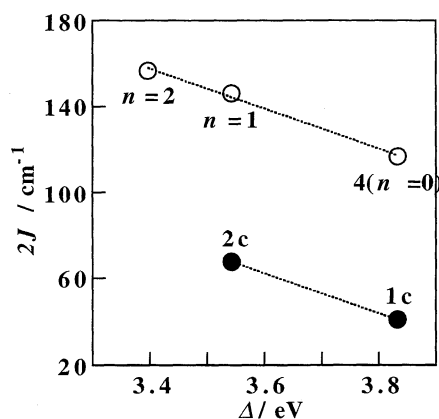


Figure 1. Spin coupling constant ($2J$) determined with a SQUID magnetometer measurement vs transition energy (Δ) estimated from UV/vis absorption spectroscopy for (●) **1c**, **2c**, and (○) INDO calculation for oligo(1,2-phenylenevinylene) **4**.

oligo(phenylenevinylene)-based diradicals suggest that a π -conjugated macromolecule bearing pendant radicals such as **6c** is the most possible candidate of the high-spin macromolecules, because its spin coupling energy is expected to increase with the degree of polymerization, and a long-distance but strong ferromagnetic interaction will be established through the conjugated skeleton even in the presence of a spin defect along the skeleton.

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- μ_{eff}/μ_B of **2c** and **3c** showed intermediate values between $\mu_{eff}/\mu_B = 2.45$ and 2.83 for $S = 1/2$ and 1 , respectively. These μ_{eff}/μ_B values of **2c** and **3c** were corrected by the spin concentration of 1.00 and 1.22 spin/molecule, respectively, which were determined by careful integration of the ESR signals in comparison to those of the TEMPO solution as the standard and by the saturated magnetization at 2K.
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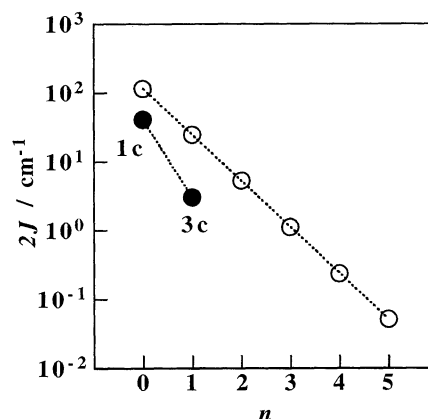


Figure 2. Spin coupling constant ($2J$) vs phenylenevinylene spacing for **1c**, **3c** (●), and INDO calculation for oligo(1,2-phenylenevinylene) **5** (○).