

# Evaluation of the $\beta$ Value of the Phenylene Unit by Probing Exchange Interaction between Two Nitroxides

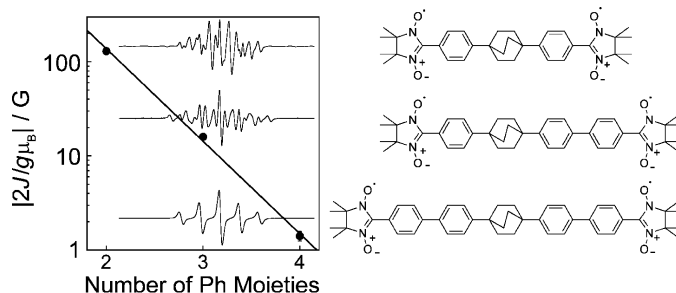
Kenji Higashiguchi, Koji Yumoto, and Kenji Matsuda\*

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

kmatsuda@sbchem.kyoto-u.ac.jp

Received September 28, 2010

## ABSTRACT



Oligophenylene molecular rods with bicyclo[2.2.2]octane having two nitronyl nitroxide radicals were synthesized to investigate the decay constant of *p*-phenylene. By the measurement and simulation of the ESR spectra of the biradicals with different rod length, it was found that the exchange interaction was decreased with the decay constant  $\beta$  of  $0.51 \pm 0.01 \text{ \AA}^{-1}$ . This result indicates that the spin–spin exchange interaction between neutral radicals has a decay constant similar to the molecular conductance.

The relationship between molecular conductance and molecular structure in organic molecules is attracting interest in the field of molecular electronics.<sup>1–5</sup> Electron tunneling through molecular wire is described by the Landauer formula using transmission probability which decays exponentially with molecular length. The conductive property of the molecular wire is characterized by the decay constant  $\beta$  according to the following equation

$$G = G_0 \exp(-\beta l)$$

where  $l$  is the molecular length and  $G_0$  is the contact conductance.

Among many organic molecules, oligo(*p*-phenylene) has a rigid  $\pi$ -conjugated structure, and therefore it is a representative molecule to discuss molecular conductance. The decay constant has been obtained not only from the direct measurement of molecular conductance<sup>6,7</sup> but also from the rate of electron transfer<sup>8</sup> or the magnitude of exchange interaction,<sup>9,10</sup> all of which decay exponentially with molecular length. Theoretical studies have also been performed to evaluate the relationship among the rate of electron transfer, the molecular conductance, and the decay constant.<sup>11–15</sup>

(1) Moth-Poulsen, K.; Bjørnholm, T. *Nat. Nanotechnol.* **2009**, *4*, 551–556.

(2) Weiss, P. S. *Acc. Chem. Res.* **2008**, *41*, 1772–1781.

(3) Tao, N. J. *Nat. Nanotechnol.* **2006**, *1*, 173–181.

(4) Joachim, C.; Ratner, M. A. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 8801–8802.

(5) Nitzan, A.; Ratner, M. A. *Science* **2003**, *300*, 1384–1389.

(6) Wold, D. J.; Haag, R.; Rampi, M. A.; Frisbie, C. D. *J. Phys. Chem. B* **2002**, *106*, 2813–2816.

(7) Ishida, T.; Mizutani, W.; Aya, Y.; Ogiso, H.; Sasaki, S.; Tokumoto, H. *J. Phys. Chem. B* **2002**, *106*, 5886–5892.

(8) Schlicke, B.; Belser, P.; De Cola, L.; Sabbioni, E.; Balzani, V. *J. Am. Chem. Soc.* **1999**, *121*, 4207–4214.

(9) Weiss, E. A.; Ahrens, M. J.; Sinks, L. E.; Gusev, A. V.; Ratner, M. A.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2004**, *126*, 5577–5584.

(10) Wang, W.; Wang, S.; Li, X.; Collin, J.-P.; Liu, J.; Liu, P. N.; Lin, N. *J. Am. Chem. Soc.* **2010**, *132*, 8774–8778.

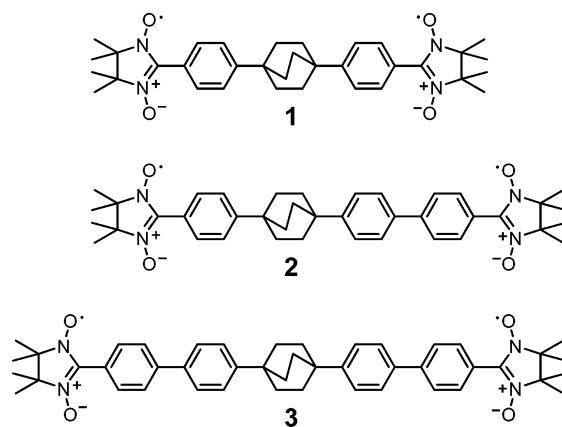
The decay constant of the exchange interaction has been measured by means of the effect of the magnetic field on the electron transfer<sup>9</sup> and the splitting of the molecular orbital.<sup>10</sup> The exchange interaction between spins of unpaired electron, which is the origin of the magnetism, can be directly measured by the temperature dependence of magnetic susceptibility<sup>16</sup> or the simulation of the ESR spectrum.<sup>17</sup> Herein, we describe the evaluation of decay constant  $\beta$  of oligo-*p*-phenylene molecular rods by the measurement of exchange interaction between two nitronyl nitroxide radicals. The analysis of the splitting pattern of the ESR spectrum provides the information on the spin–spin exchange interaction between the nitroxide radicals.

The nitronyl nitroxide radical was used as a spin source because of the stability under air. Nitronyl nitroxide itself has two identical nitrogen atoms to give a 5-line ESR spectrum, with a 7.5 G spacing and  $g = 2.006$ . When two nitronyl nitroxides are magnetically coupled with an exchange interaction, the diradical gives a 9-line ESR spectrum with a 3.7 G spacing. If the exchange interaction is smaller than the hyperfine coupling in the diradical, two nitronyl nitroxide radicals are magnetically independent and give the spectrum that is identical to the monoradical. In intermediate situations, the spectrum shows further splitting.<sup>18</sup>

In the midst of the *p*-phenylene rod, a bicyclo[2.2.2]octane unit was introduced as a regulator because an exchange interaction through two or three phenylene units is too large to be evaluated by the analysis of the ESR splitting pattern. When two nitronyl nitroxides are attached directly to the terphenylene spacer, the obtained ESR signal was clear 9 lines, so that the analysis of the splitting pattern was impossible (see Supporting Information). The synthesized molecules are shown in Figure 1.

The synthesis of diradicals **1–3** was performed using 1,4-dibromobicyclo[2.2.2]octane as an intermediate (see Supporting Information).<sup>19</sup> Several steps of reactions afforded diformyl derivatives. These formyl derivatives were refluxed in appropriate solvent with 2,3-bis(hydroxyamino)-2,3-dimethylbutane sulfate in the presence of potassium carbonate. The cyclodehydrated derivatives were oxidized with sodium periodate in dichloromethane/water to give nitronyl nitroxide derivatives **1–3**. The structures of the synthesized compounds were confirmed by NMR/ESR spectroscopy and mass spectrometry.

The change of the ESR spectra with the increase of phenylene moieties was examined. Figure 2 shows the ESR spectra of biradicals **1**, **2**, and **3** measured in N<sub>2</sub>-bubbled dichloromethane solution at room temperature. The ESR spectrum of **1** shows distorted 9 lines. This suggests that the central bicyclo[2.2.2]octane



**Figure 1.** Synthesized bis(nitronyl nitroxide) radicals with a *p*-phenylene molecular rod.

unit plays a role of a regulator because the terphenylene derivative showed clear 9 lines. The ESR spectrum of **2** shows 15 lines. The exchange interaction between the two spins in **2** decreased with the introduction of one phenylene moiety compared with **1**. The biradical **3** shows a 5-line ESR spectrum, and it means that the exchange interaction in **3** is smaller than the hyperfine coupling constant.

To estimate the exchange interaction of the biradicals, the obtained spectra were simulated using several exchange interactions using the BIRADG program.<sup>20</sup> From the simulation, the exchange interactions in **1** and **2** were determined to be  $|2J/g\mu_B| = 1.2 \times 10^2$  G ( $|2J/k_B| = 1.6 \times 10^{-2}$  K) and 16 G ( $|2J/k_B| = 2.2 \times 10^{-3}$  K), respectively. Biradical **3** showed a 5-line spectrum, which generally indicates  $|2J/g\mu_B| < 2$  G. However, by close examination of  $\Delta H_{pp}$  of the peaks, which gets larger by the increase of the exchange interaction, the  $|2J/g\mu_B|$  value was determined as  $1.4 \pm 0.2$  G ( $|2J/k_B| = (1.9 \pm 0.2) \times 10^{-4}$  K) for **3** (see Supporting Information).<sup>21</sup>

From these exchange interaction values, the decay constant of the phenylene moiety was calculated (Figure 3). The exchange interaction was decreased by the factor of 0.10 per one phenylene unit, and the  $\beta$  value was obtained as  $\beta = 0.51 \pm 0.01$  Å<sup>-1</sup> by assuming the length of one phenylene unit as 4.4 Å. The reported decay constant determined by the molecular conductance<sup>6</sup> was 0.42 Å<sup>-1</sup>, and the value determined by electron transfer<sup>8</sup> was 0.32 Å<sup>-1</sup>. The similar values are reported by the theoretical studies.<sup>11–14</sup>

Concerning the decay constant of the exchange interaction, Wasielewski et al. studied the decay of the spin–spin exchange interaction by the effect of the magnetic field on the electron transfer and determined the value as  $\beta = 0.37$  Å<sup>-1</sup>.<sup>9</sup> Lin et al. studied the decay constant of superexchange coupling of the orbitals by STM measurement and reported  $\beta$  as 0.10 Å<sup>-1</sup>.<sup>10</sup> In the surface of the substrate, the dihedral angle between phenylene units is considered to be reduced to give a smaller decay constant. Additionally, because the

(11) Magoga, M.; Joachim, C. *Phys. Rev. B* **1997**, *56*, 4722–4729.

(12) Kaun, C.-C.; Larade, B.; Guo, H. *Phys. Rev. B* **2003**, *67*, 121411.

(13) Kondo, M.; Tada, T.; Yoshizawa, K. *J. Phys. Chem. A* **2004**, *108*, 9143–9149.

(14) Liu, H.; Wang, N.; Zhao, J.; Guo, Y.; Yin, X.; Boey, F. Y. C.; Zhang, H. *ChemPhysChem* **2008**, *9*, 1416–1424.

(15) Nitzan, A. *J. Phys. Chem. A* **2001**, *105*, 2677–2679.

(16) Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346–351.

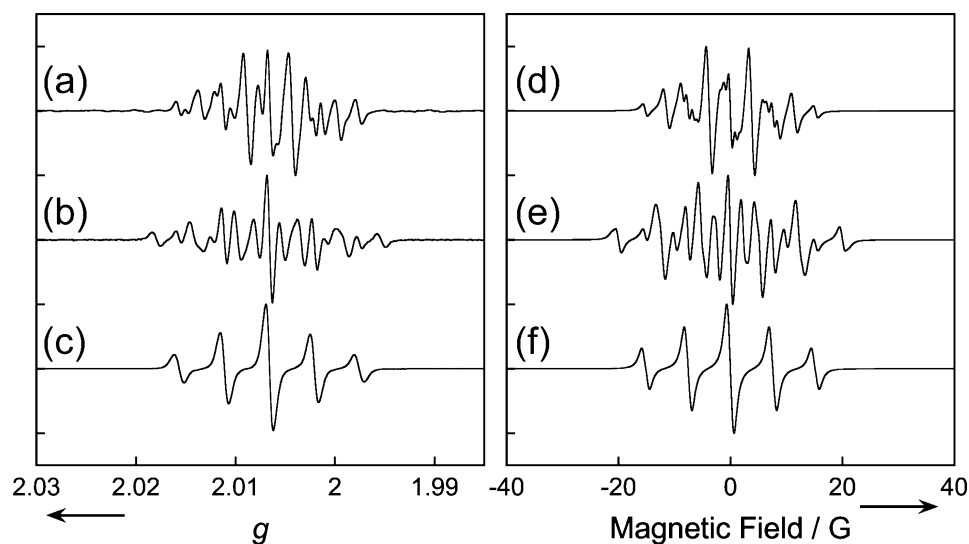
(17) Glarum, S. H.; Marshall, J. H. *J. Chem. Phys.* **1967**, *47*, 1374–1378.

(18) Matsuda, K.; Irie, M. *Chem.—Eur. J.* **2001**, *7*, 3466–3473.

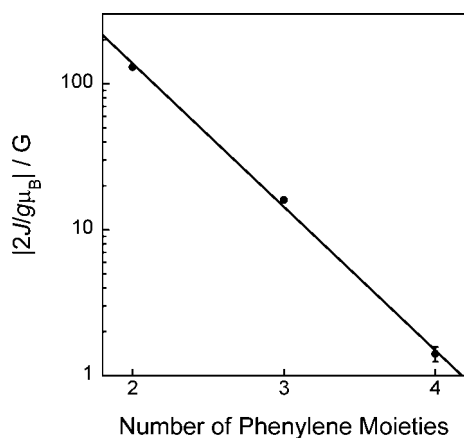
(19) Dewar, M. J. S.; Goldberg, R. S. *J. Am. Chem. Soc.* **1970**, *92*, 1582–1586.

(20) Kirste, B. *Anal. Chim. Acta* **1992**, *265*, 191–200.

(21) By simply changing the linewidth, the simulation could not reproduce the observed spectrum (see Supporting Information).



**Figure 2.** X-band ESR spectra measured at room temperature of (a) biradical **1** ( $g = 2.0061$ ), (b) biradical **2** ( $g = 2.0064$ ), and (c) biradical **3** ( $g = 2.0066$ ). Simulated spectra of (d)  $|2J/g\mu_B| = 1.2 \times 10^2$  G, (e) 16 G, and (f) 1.4 G.



**Figure 3.** Correlation of the exchange interaction with the number of phenylene moieties.

rate constant is formulated to be proportional to the square of the exchange coupling, the decay constant of the exchange coupling is predicted to be half of the decay constant of the rate of the electron transfer.<sup>15,22</sup>

The obtained decay constant of the *p*-phenylene unit,  $\beta = 0.51 \pm 0.01 \text{ \AA}^{-1}$ , is very similar to the reported experimental and theoretical values of the decay constant of the molecular conductance and the rate of electron transfer. This value is the first example of the decay constant determined by the spin–spin exchange interaction between neutral radicals. In the molecular conductance and the rate of electron transfer, in addition to the coherent tunneling, incoherent hopping becomes important as the molecule gets longer.<sup>23</sup> In this study of exchange interaction, the participation of the hopping mechanism was not

observed. Further theoretical and experimental investigation provides the deeper understanding of the transport phenomena through molecules.

In conclusion, oligophenylene molecular rods with bicyclo[2.2.2]octane having two nitronyl nitroxide radicals were synthesized to investigate the decay constant of *p*-phenylene. By the measurement and simulation of the ESR spectra of the biradicals with different rod lengths, it was found that the exchange interaction was decreased with the decay constant  $\beta$  of  $0.51 \pm 0.01 \text{ \AA}^{-1}$ . This result indicates that the spin–spin exchange interaction between neutral radicals has a decay constant similar to the molecular conductance and the rate of electron transfer.

**Acknowledgment.** We thank Professor Yasujiro Murata (Kyoto Univ., Japan) for the measurement of ESR spectra. We thank Professor Paul M. Lahti (Univ. of Massachusetts, USA) and Professor B. Kirste (Free Univ. of Berlin, Germany) for providing the program BIRADG. This work was supported by CREST, JST, and a Grant-in-Aid for Young Scientists (A) (No. 19685013) from the MEXT, Japan.

**Supporting Information Available:** Experimental methods, <sup>1</sup>H NMR spectra of synthesized compounds, ESR spectrum of reference compound, and details of the spectrum simulation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OL102339M

(22) In ref 10, the decay constant of the molecular conductance and the rate of electron transfer was divided by 2 for comparison. The value taken from ref 9, which is the exchange interaction, was also divided by 2.

(23) (a) Giese, B.; Amaudrut, J.; Köhler, A.-K.; Spormann, M.; Wessely, S. *Nature* **2001**, 412, 318–320. (b) Berlin, Y. A.; Burin, A. L.; Ratner, M. A. *Chem. Phys.* **2002**, 275, 61–74. (c) Choi, S. H.; Kim, B.; Frisbie, C. D. *Science* **2008**, 320, 1482–1486.