Theoretical Investigation of the β Value of the Phenylene and Phenylene Ethynylene Units by Evaluating Exchange Interaction between Organic Radicals

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Abstract: The nature of π-conjugated wire is characterized by the decay constant β of electron tunneling. To evaluate the decay constant, intramolecular magnetic exchange interaction was calculated by density functional theory for organic biradicals: nitronyl nitroxide and verdazyl were chosen for the radical substituent and oligophenylene and oligo(phenylene ethynylene) were chosen for the wire. For phenylene and phenylene ethynylene units, β was calculated to be 0.42 $Å^{-1}$ and 0.24 $Å^{-1}$, respectively, and the β value was independent of radical species. The obtained β values are in good agreement with the experimental value of the molecular tunneling conductance.

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1. Introduction

π-Conjugated wire-like molecules are attracting interests in the field of molecular electronics because of the potential application as a conductive wire [1,2]. The property of a molecular wire is characterized according to the decay constant β of the electron tunneling, which is defined according to the following equation:

$$G = G_0 \exp(-\beta l) \qquad (1)$$

where G is the conductance of the molecule, l is the molecular length, and G_0 is the contact conductance. Among many π-conjugated wire-like molecules, oligo(*p*-phenylene) and oligo(phenylene ethynylene) have a rigid π-conjugated structure, and therefore they are representative molecules to discuss molecular conductance. The decay constant β has been determined not only for the conductance [3-6] but also for the rate constant of electron transfer [7], and for the exchange interaction [8-11]. They all indicate the exponential decay with molecular length. As for *p*-phenylene unit, Frisbie et al. determined β as 0.41 $Å^{-1}$ using conductive atomic force microscopy (AFM) technique [3] and Balzani et al. reported β of the same unit as 0.32 $Å^{-1}$ by measuring the rate constant of electron transfer [7]. Higashiguchi and co-workers have shown that β of the *p*-phenylene unit is 0.51$Å^{-1}$ by probing exchange interaction between two nitroxides [8]. The reported β values determined from different experiments are similar each other and also matches with the theoretical value determined for the molecular conductance [12-16]. Theoretical studies have been carried out to evaluate the relationship among the rate constant of electron transfer, the molecular conductance, and the decay constant [17,18]. All the properties are related to electron tunneling through the π-conjugated molecule, so the similar behavior is expected.

Yamaguchi and co-workers have developed the method of evaluating J using energy splitting between triplet and broken-symmetry (BS) state [19]. Yamaguchi's methodology is widely used to evaluate J value in the field of molecular magnetism and is successful to estimate J value of organic and inorganic magnetic materials [20-22]. In this work, we have used this methodology to evaluate β of molecular wire by calculating the exchange integral J for organic biradicals in which radical substituent bridged by different π-conjugated wire. We have studied two types of organic biradicals and two types of molecular wires as shown in Figure 1. Nitronyl nitroxide (NN) and

verdazyl (VER) were chosen for the radical substituent and oligophenylene (PP) and oligo(phenylene ethynylene) (PE) were chosen for the π-conjugated wire.

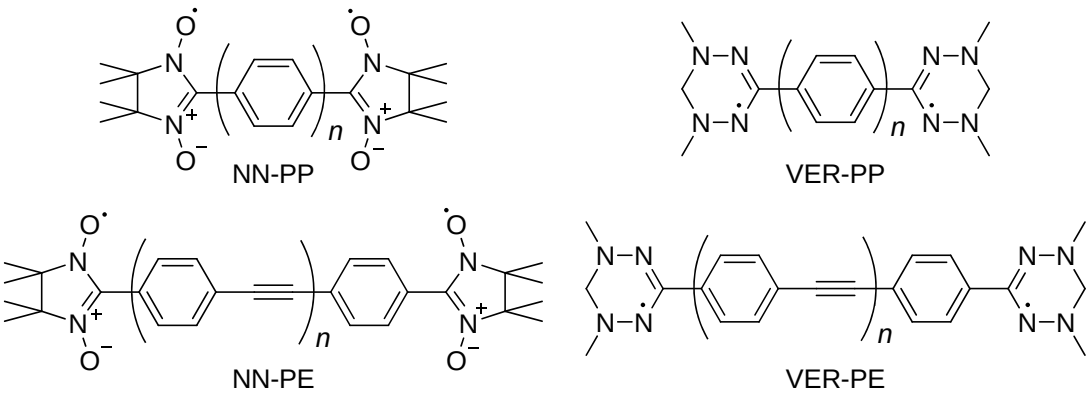

Figure 1. Biradicals used in this work.

2. Theoretical background and computational details

The magnetic interaction in a biradical can be described by the Heisenberg effective spin Hamiltonian H_{ex} as follows:

$$H_{ex} = -2JS_1 \cdot S_2 \qquad (2)$$

From this Hamiltonian, singlet-triplet energy gap is described by the exchange interaction J as follows:

$$E(S=1) - E(S=0) = -2J \qquad (3)$$

The biradical triplet state can be described as a single determinant, but the biradical singlet must use two determinants to express the state. However, the BS solution is described by a single determinant. Despite using the unrestricted formalism, we cannot describe the single determinant wave function of a pure singlet state of biradical due to the spin contamination problem. To circumvent this problem, we have adopted Yamaguchi's method in which the exchange integral J for a biradical can be given by

$$J = \frac{E^{BS} - E^{T}}{\langle S_T^2 \rangle - \langle S_{BS}^2 \rangle} \qquad (4)$$

where E^{BS}, E^{T}, $\langle S_{BS}^2 \rangle$, $\langle S_T^2 \rangle$ are the energies and average spin square values for corresponding BS and triplet states.

Density functional theory (DFT) was used for geometry optimization and energy calculation. All the calculations were carried out using a suit of Gaussian 09 programs [23]. Geometry optimizations were performed using DFT, UB3LYP/6-311G(d,p) level. To signify the basis set effect on β value, geometry optimizations were also carried out using 6-31G(d) basis set. The "ultrafine" grid points were employed for numerical integration of the exchange correlation functional. Firstly, the geometries of the triplet systems were optimized and then the BS wave function was calculated on those geometries. All the molecules have been fully optimized and frequency calculations have been performed to confirm the minima on the potential energy surfaces.

3. Results and discussion

The geometries of four types of biradical system, NN-PP, NN-PE, VER-PP, and VER-PE were all optimized with triplet state using 6-311G(d,p) basis set. We have carried out the single point calculations with triplet and BS states using those geometries. Figure 2 shows the representative optimized structures of four types of molecular wire. The dihedral angle between two phenyl rings in PP system is around 37.6°, which is similar to the reported calculation of related structure [24]. Because the initial geometry was chosen at random, there is no regularity in the relative helicity, *P* or *M*, between two adjacent phenyl rings. The dihedral angle between two phenyl rings in PE system is around 0°, which is in agreement with the reported crystal structural data [25].

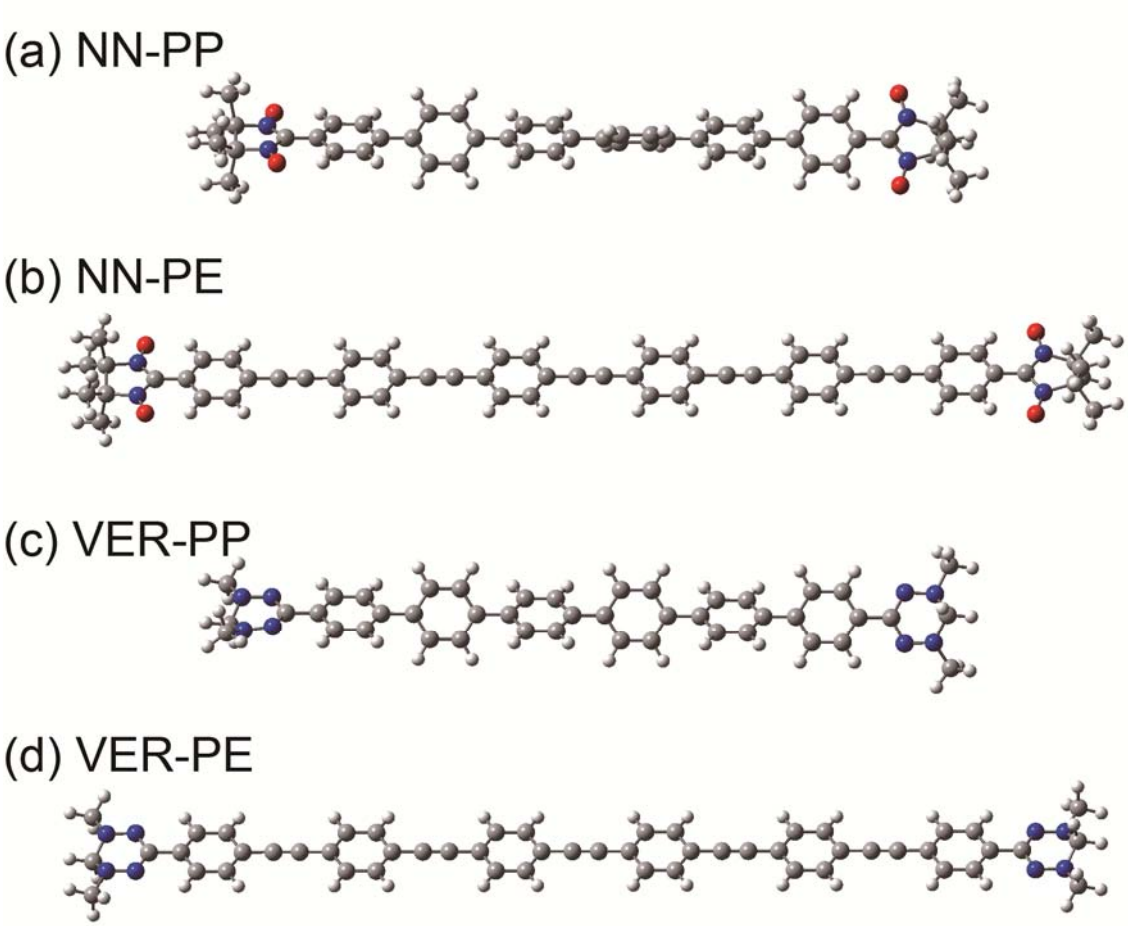

Figure 2. The optimized structures of four types of biradicals in which radical substituents are bridged by molecular wires. (a) NN-PP, (b) NN-PE, (c) VER-PP, (d) VER-PE.

We calculated the energies of triplet and BS states and average of S^2 values of triplet and BS states and then determined the exchange interaction $2J$ by Yamaguchi's method. For instance, for NN-PP(n = 1), the energies and S^2 values are calculated as E(triplet) = −1299.00690664 hartrees, E(BS) = −1299.00797758 hartrees, $\langle S_T^2 \rangle$ = 2.1075, and $\langle S_{BS}^2 \rangle$ = 1.1469. Therefore, the value of $2J$ was calculated to be −489.4 cm^{-1}. The calculated data using 6-311G(d,p) basis set are shown in Tables 1–4.

To investigate the effect of helicity on $2J$ value, we have calculated NN-PP(n = 4) molecule which has only P helicity between two adjacent phenyl rings. Starting with the initial structure with only P helicity, the obtained optimized structure had only P helicity (see supplementary material). The optimized energy for triplet state was about 6.0×10^{-5} hartrees higher than that of random structure when using 6-311G(d,p) basis set. We have calculated the $2J$ value to be −2.332 cm^{-1}

while $2J$ value is −1.905 cm^{-1} in the random structure. Although the calculation with the structure with *P* helicity has given little larger $2J$ value, this little difference does not affect the β value that will be discussed later.

Table 1. Enegies, average S^2 values, and $2J$ values for NN-PP series using 6-311G(d,p) basis set.

n	*E*(triplet) / hartrees	*E*(BS) / hartrees	$\langle S_T^2 \rangle$	$\langle S_{BS}^2 \rangle$	$2J$ / cm^{-1}
1	−1299.00690664	−1299.00797758	2.1075	1.1469	−489.4
2	−1530.11822556	−1530.11840939	2.1211	1.1303	−81.4
3	−1761.22807141	−1761.22810372	2.1250	1.1270	−14.2
4	−1992.33789537	−1992.33789971	2.1258	1.1262	−1.91
5	−2223.44766609	−2223.44766683	2.1258	1.1259	−0.33
6	−2454.55741215	−2454.55741229	2.1259	1.1259	−0.06

Table 2. Enegies, average S^2 values, and $2J$ values for NN-PE series using 6-311G(d,p) basis set.

n	*E*(triplet) / hartrees	*E*(BS) / hartrees	$\langle S_T^2 \rangle$	$\langle S_{BS}^2 \rangle$	$2J$ / cm^{-1}
1	−1606.29365269	−1606.29384161	2.1268	1.1380	−83.9
2	−1913.57930442	−1913.57933664	2.1313	1.1339	−15.3
3	−2220.86482615	−2220.86483176	2.1325	1.1330	−2.46
4	−2528.15032574	−2528.15032672	2.1327	1.1329	−0.43
5	−2835.43581944	−2835.43581962	2.1328	1.1329	−0.08

Table 3. Enegies, average S^2 values, and $2J$ values for VER-PP series using 6-311G(d,p) basis set.

n	*E*(triplet) / hartrees	*E*(BS) / hartrees	$\langle S_T^2 \rangle$	$\langle S_{BS}^2 \rangle$	$2J$ / cm^{-1}
1	−983.612400707	−983.612757835	2.0463	1.0596	−158.9
2	−1214.72294561	−1214.72300169	2.0518	1.0547	−24.7
3	−1445.83302263	−1445.83303144	2.0531	1.0537	−3.87
4	−1676.94291678	−1676.94291810	2.0534	1.0535	−0.58
5	−1908.05278614	−1908.05278635	2.0535	1.0535	−0.09
6	−2139.16256944	−2139.16256947	2.0535	1.0535	−0.01

Table 4. Enegies, average S^2 values, and $2J$ values for VER-PE series using 6-311G(d,p) basis set.

n	E(triplet) / hartrees	E(BS) / hartrees	$\langle S_T^2 \rangle$	$\langle S_{BS}^2 \rangle$	$2J$ / cm^{-1}
1	−1290.90558522	−1290.90565477	2.0568	1.0609	−30.7
2	−1598.19161946	−1598.19163155	2.0587	1.0596	−5.31
3	−1905.47732838	−1905.47733052	2.0591	1.0594	−0.94
4	−2212.76291631	−2212.76291669	2.0593	1.0593	−0.17
5	−2520.04845320	−2520.04845326	2.0593	1.0593	−0.03

In each case the singlet calculation led to BS state, which is confirmed by S^2 value around 1. The calculations showed that BS state is more stable than triplet state and provided the negative value of $2J$. Negative sign of $2J$ means antiferromagnetic interaction between two radical centers. The sign of exchange interaction in π-conjugated biradicals has been discussed by Ovchinnikov's topology rule [26] and recently also by the rule of spin alternation in unrestricted SCF methodologies [27,28]. In our structures, the number of carbon atoms between two NN or VER is always even, so that the antiferromagnetic interaction is expected.

As the molecular unit becomes longer by one *p*-phenylene unit, the value of $2J$ in NN-PP and VER-PP series decreases to 16% in average. In the NN-PE and VER-PE series, the value of $2J$ decreases to 17% in average as the molecular unit becomes longer by one phenylene ethynylene unit. This numerical behavior implies exponential decay of $2J$ and can be expressed using decay constant β as follows.

$$J = J_0 \exp(-\beta l) \qquad (5)$$

The slope in the plot of $\log|2J|$ as the function of molecular length corresponds to the decay constant β. We have calculated the molecules up to n = 6 for PP series and n = 5 for PE series and the magnitude of $2J$ was in the range of 10^2–10^{-2} cm^{-1}. For the longer molecules the energy difference got too small to estimate accurate $2J$ value.

When we compare $2J$ values between NN and VER biradicals which have the same length of linker units, the value of $2J$ of NN biradical is about three times as large as that of VER biradical

for both PP and PE series. Datta et al. calculated the magnetic exchange interaction of azobenzene biradical and reported that NN biradical has stronger interaction than VER biradical [29]. These results indicate that exchange interaction between two NN is stronger than that between two VER.

To check the effect of the basis set, we have also calculated the exchange interaction 2*J* using 6-31G(d) basis set (see supplementary material). The numerical result of 2*J* is similar to that based on 6-311G(d,p) basis set. Basis set has little effect on the calculation of 2*J*. The effect of functional is also checked. Calculation was performed using UCAM-B3LYP/6-31G(d)//UB3LYP/6-31G(d) for the NN-PP series to check the effect of HF exchange on β value (see supplementary material). The obtained β value was 0.41 $Å^{-1}$ while β = 0.42 $Å^{-1}$ for UB3LYP methodology. There is no dependence of functional for the calculation of β.

We have estimated the singlet biradical character using CASSCF(2,2)/6-31G(d)//RB3LYP/6-31G(d) method for the shortest biradical, NN-PP(n = 1). The biradical character was calculated to be 99.21% [30]. In general, biradical character gets larger as molecular bridge gets longer, so all the calculated molecules are completely biradical, therefore, the effect of closed-shell structure does not need to be considered.

The calculated exchange integral values are plotted against the molecular lengths of wires (Figure 3). The molecular lengths are determined as the distance between the carbon atoms of NN or VER at which the π-conjugated wires are connected. From this plot, the decay constants of PP and PE were determined by the least-square analysis. For PP series, the decay constant β was determined to be 0.42 $Å^{-1}$ and 0.44 $Å^{-1}$ for NN and VER radicals, respectively. This value is similar to that reported by the experiment of the conductance that is 0.42 $Å^{-1}$ [3]. Meanwhile, for PE series, β value is 0.24 $Å^{-1}$ and 0.25 $Å^{-1}$ for NN and VER radicals, respectively. This value is also similar to that reported by the experiment of the conductance that is 0.20 $Å^{-1}$ [4]. This result indicates that the β value is only dependent on the type of molecular unit and independent of the type of radical. The similarity between the reported experimental value and our result supports the validity of the method we have performed. The β value reflects the overall efficiency of electron tunneling through the π-conjugated units. The difference clearly shows that oligo(phenylene ethynylene) is more conductive than oligo(phenylene). This difference may be attributed to the planarity of the units, but more detailed study on the origin of the different β value is awaited.

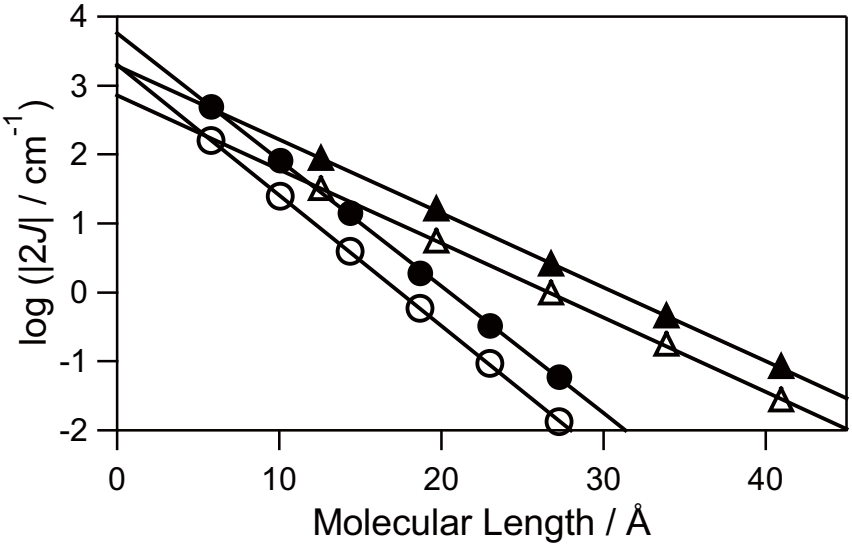

Figure 3. Dependence of the molecular length on the exchange interaction 2*J*: (○) VER-PP; (●) NN-PP; (Δ) VER-PE; (▲) NN-PE. The line is the least-square fitting to determine the decay constant β.

The extrapolated lines of PE series lie over the point of PP(n =1). The overlapping is reasonable because PE(n = 0) and PP(n = 1) are the same molecule from the definition, but the overlapping ensures the validity of our treatment. Exponential decay of the exchange interaction with different decay constants is clearly visualized.

4. Conclusions

In conclusion, we have investigated the decay constant of intramolecular exchange interaction by DFT calculation for organic biradicals with different length of π conjugated wire. For phenylene and phenylene ethynylene units, β was calculated to be 0.42 Å^{-1} and 0.24 Å^{-1}, respectively, and the same β value was obtained for nitronyl nitroxides and verdazyls. The obtained β values are in good agreement with the experimental value of the decay constant of the molecular tunneling conductance. The result suggests that the fundamental character of π-conjugated wire can be obtained by this method.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2012.10.092.

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