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Polyhedron 22 (2003) 1829–1836

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Molecular design toward spin-polarized nano-wire: oligomer model study

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Received 6 October 2002; accepted 27 December 2002

Abstract

In order to investigate the possibility of spin-polarized conducting polymers, quantum chemical calculations were performed for oligomer model compounds of some promising polymers carrying spin-containing units. Upon one-electron oxidation, it was confirmed that the high-spin-correlation takes place for 2-site model compounds. For 3-site and 4-site model compounds, the spin-correlation was found to be strongly dependent on the oxidation number and the molecular structure.

Keywords: Double-exchange mechanism; High-spin organic polymer; Spin-polarized nano-wire; Quantum chemical calculations

1. Introduction

In recent years, there has been much interest in attempts to control the electrical conductivity through modulation of the magnetic state (or spin state) in a single system [1]. In this emerging field, “spintronics”, one of the most fascinating materials is “half-metal” in which only one of the two spin directions is metallic [2]. Although a large number of studies have been carried out for the transition metal oxides, little is known about organic materials. The purpose of this study is to investigate the possibility of spin-polarized conducting polymers. In order to embody the idea, we focus on the double-exchange mechanism [3]. In the case of two orbitals per site (A and B), as in Fig. 1, where the localized B orbital on all the sites is singly occupied and moreover the Hund coupling is assumed between two electrons on A and B. The moving electron on A can easily hop due to the high-spin-correlation among the electrons on B (top figure), while it can hardly move when the electrons on B align antiferromagnetically (bottom figure). This mechanism is expected to work on the positively doped model polymers shown in Fig. 2. Poly(p-phenylenecarbene) is a simple example (Fig. 2(a)). Polyaniline-based polyradicals are more realistic polymers (Fig. 2(b)). In particular, it is well known that polyaniline shows a high electrical conductivity when it is partially oxidized [4]. However, the spin-correlation strongly depends on the number of delocalized electron, the molecular structure, and so forth. A detailed discussion on the possibility of spin-polarized nano-wire is made on oligomer model of these candidate polymers on the basis of the ab initio quantum chemical calculations.

2. Method of calculation

The calculations of cationic species of p-phenylenebismethylene were performed with complete active space SCF (CASSCF(5,6)) wave functions [5] using 6-31G* basis set [6]. The molecular geometry of the other oligomer model compounds was optimized utilizing density functional theory (DFT) approach [7] and the 6-31G* basis set [6]. We used Becke’s three-parameter [8] together with the correlation functional of Lee, Yang, Parr, abbreviated as B3LYP [9]. All calculations were carried out using Gaussian 98 package of ab initio molecular orbital (MO) programs [10].

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doi:10.1016/S0277-5387(03)00165-7

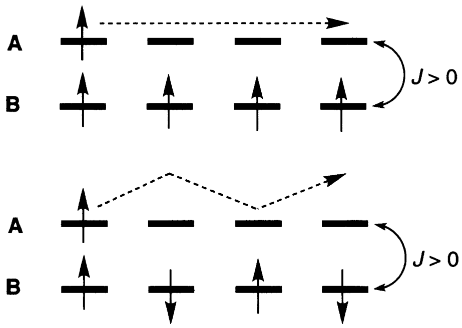
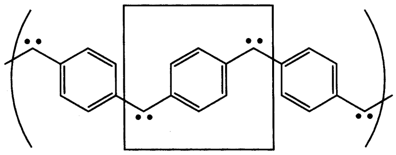
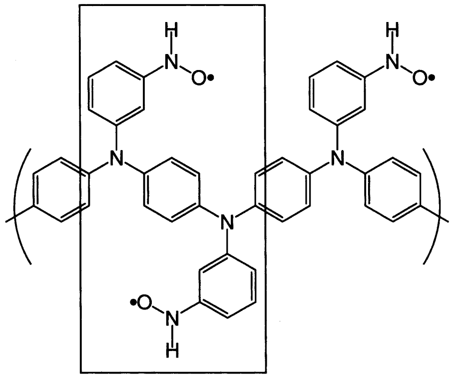


Fig. 1. Schematic drawings of double-exchange mechanism.



(a) **1**



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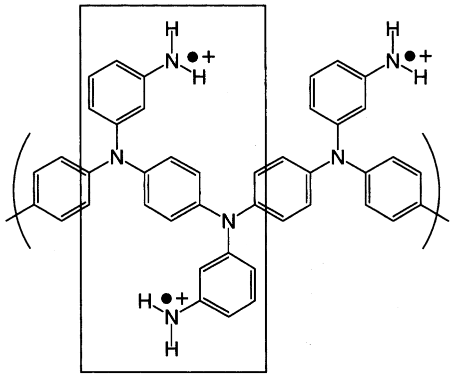

(b) $\mathbf{3}^{2+}$

Fig. 2. Model polymers for spin-polarized nano-wire.

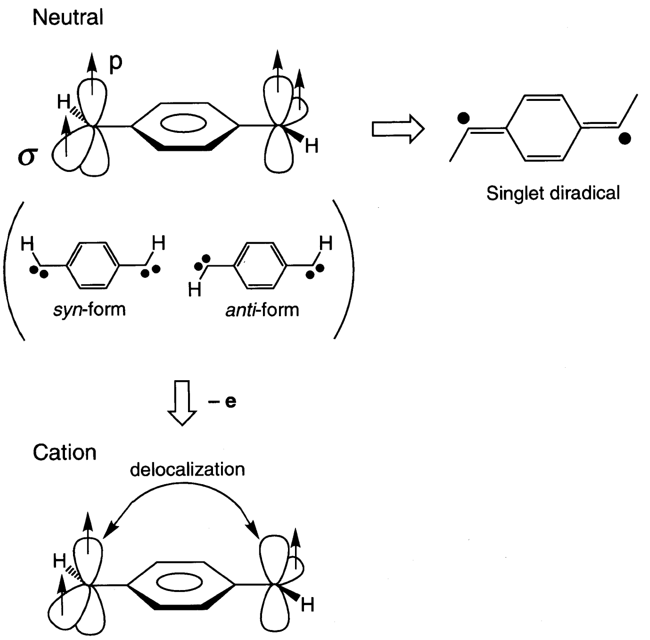

Fig. 3. p-Phenylenebismethylene (**1**) and its cation ($\mathbf{1}^{+}$) as 2-site model.

3. Results and discussion

3.1. 2-site model

The molecules enclosed in Fig. 2 are considered to be a minimal model in order to examine the double-exchange interaction when the candidate polymers are positively doped (or oxidized). In particular, p-phenylenebismethylene (**1**) is a simple model in that the spin-containing site consists of one divalent carbon atom, i.e., carbene. In diphenylcarbene, the divalent carbon has two nearly degenerate orbitals which two electrons occupy. One is a nearly sp^2-hybridized orbital in the molecular plane (we call it σ). The remaining 2p-orbital perpendicular to the molecular plane can conjugate to the π-electron system (we call it p). Moreover, diphenylcarbene is known to have a ground triplet state due to strong one-center exchange interaction between two spins [11]. In the neutral form of **1**, the spin-correlation between the triplet carbene units leads to lower spin multiplicity simply because of the quinonoid deformation. In fact, the CASSCF(6,6)/6-31G* calculation on *anti*-**1** showed that the quintet biscarbene is 29.3 kcal mol^{-1} higher in energy than singlet diradical with quinonoid geometry (Fig. 3, Table 1). Hence, in the numerous studies of high-spin molecules [12], **1** has not attract attention as compared with m-phenylenebiscarbene [13]. However, upon oxidation, the remaining electron on the p-orbital can delocalize from one site to the other. Consequently, we can expect that the orthogonal σ-spins align ferromagnetically and, finally, the delocalized π-spin is also ferromagnetically coupled

Table 1
Relative energies and $\langle S^2 \rangle$ values of **1**, $\mathbf{1}^+$, $\mathbf{2}^+$, and $\mathbf{3}^{3+}$

State	Calculation	E (Hartree)	$E_{\rm rel}$ (kcal mol^{-1})[a]	$\langle S^2 \rangle$
anti-**1**				
^1A_g	CAS(6,6)/6-31G*	−306.3056	−29.3	0
^5A_g	CAS(6,6)/6-31G*	−306.2589	0	6
anti-$\mathbf{1}^+$				
^2B_g	CAS(5,6)/6-31G*	−306.0149	6.1	0.75
^4B_g	CAS(5,6)/6-31G*	−306.0247	0	3.75
syn-$\mathbf{1}^+$				
$^2B_2$	CAS(5,6)/6-31G*	−306.0194	5.7	0.75
$^4B_2$	CAS(5,6)/6-31G*	−306.0285	0	3.75
$\mathbf{2}^+$				
^2A_u	B3LYP/6-31G*	−1064.6370	0.8	1.66
^4A_u	B3LYP/6-31G*	−1064.6382	0	3.80
$\mathbf{3}^{3+}$				
^2A_u	B3LYP/6-31G*	−914.7642	−0.2	1.57
^4A_u	B3LYP/6-31G*	−914.7639	0	3.82

[a] Energy relative to the high-spin state.

to the σ-spins, as shown in Fig. 3. Here, hole density, x, is defined as oxidation number per site: $x = 0$ for neutral; $x = 1/2$ for cation.

This was verified from the CASSCF(5,6)/6-31G* calculations. In both *syn*- and *anti*-$\mathbf{1}^+$, the geometry for the doublet state resembles that for the quartet state and, more importantly, the quinonoid deformation was not seen in both states (Fig. 4). Indeed, the calculated fractional occupation numbers of the active orbitals (Fig. 5) clearly shows that both the doublet and quartet states take a triradical electronic structure. Our CASSCF calculations place the doublet states 5.7 and 6.1 kcal mol^{-1} above the quartet states of *syn*- and *anti*-$\mathbf{1}^+$, respectively. This indicates that the double-exchange interaction works on $\mathbf{1}^+$. Although the quartet *anti*-$\mathbf{1}^+$ lies 2.4 kcal mol^{-1} above the quartet *syn*-$\mathbf{1}^+$,

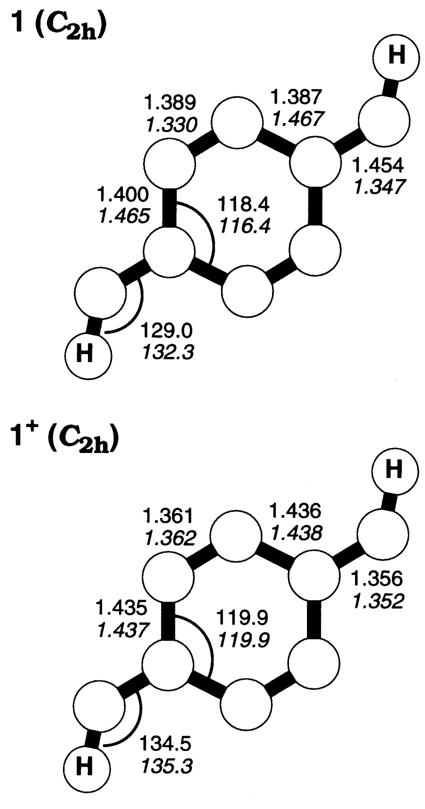

Fig. 4. Optimized bond lengths (Å) and angles (°) for the singlet (italics) and quintet states of **1** at the CAS(6,6)/6-31G* level and for the doublet (italics) and quartet states of $\mathbf{1}^+$ at the CAS(5,6)/6-31G* level. Both pictures show the *anti*-type.

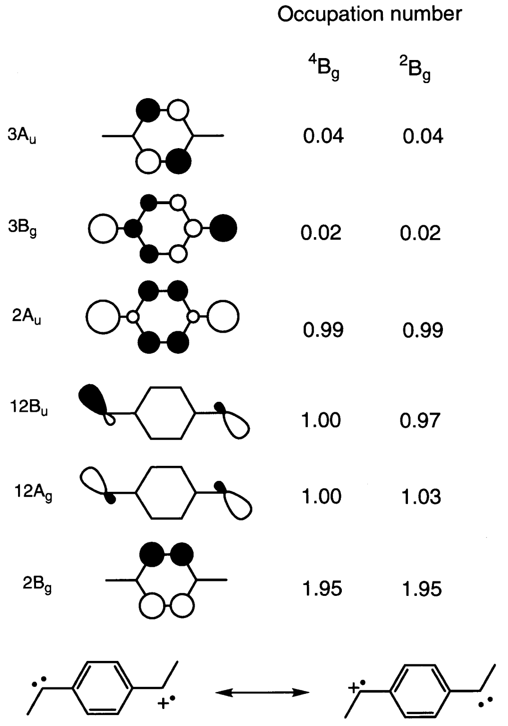

Fig. 5. Active MOs and their occupation numbers for $\mathbf{1}^+$.

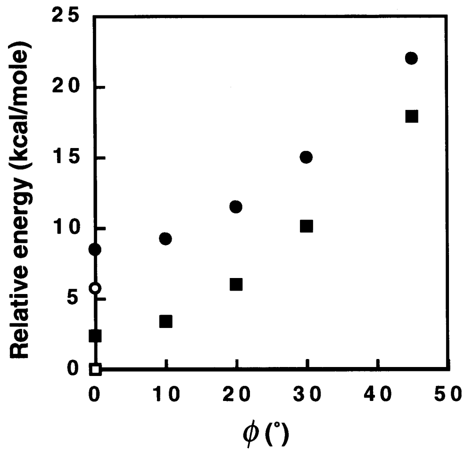

Fig. 6. Relative energy (kcal mol^{-1}) vs dihedral angle ϕ (°) (see text) of *anti*-$\mathbf{1}^+$; the doublet state (solid circle) and the quartet state (solid square). Circle and square at $\phi = 0°$ correspond to the doublet and quartet states of *syn*-$\mathbf{1}^+$, respectively.

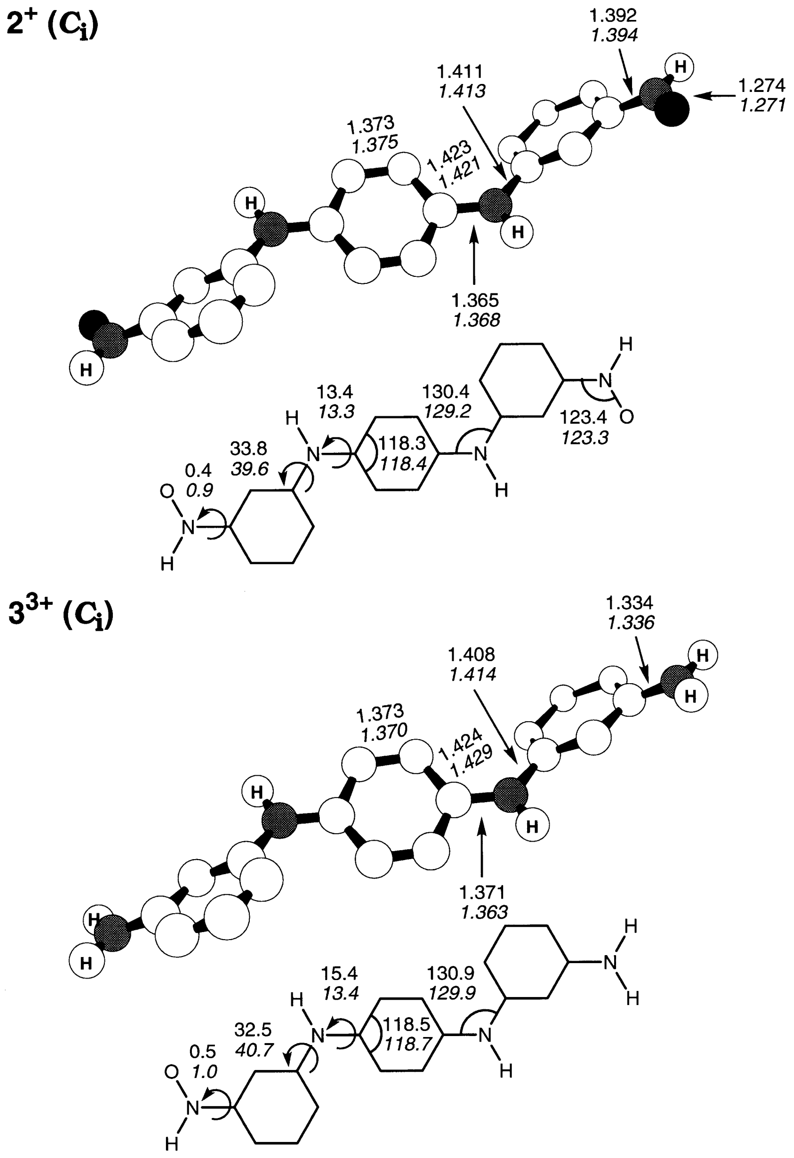

Fig. 7. Important bond lengths (Å) and angles (°) for the doublet (italics) and quartet states of $\mathbf{2}^+$ and $\mathbf{3}^+$ at the B3LYP/6-31G* level of theory.

we hereafter focus only on the *anti*-form in order to compare with the results of 3- and 4-site model compounds which plausibly take the *anti*-forms.

Next, we investigated the effect of π-conjugation between the π-orbital of the *p*-phenylene and the p-orbitals of carbene centers. It is anticipated that the transfer integral between two sites decreases with increase of the dihedral angle (ϕ) between *p*-phenylene and carbene planes. This can lead to destruction of the double-exchange interaction. As shown in Fig. 6, however, it was confirmed that the relative energy remains unchanged to large extent as to the dihedral angle ϕ, clearly indicating the robustness of the double-exchange interaction.

Let us now turn our discussion to the 2-site models using more realistic model polymers shown in Fig. 2. In this case, nitroxide or aluminum radical cation is attached to the polymer backbone in *meta*-substitution pattern. We have carried out the B3LYP/6-31G* calculations for these model compounds. Fig. 7 illustrates the optimized geometries of the doublet (^2A_u) and quartet (^4A_u) states for cationic species of N,N′-bis(m-(*N*-oxylamino)phenyl)-*p*-phenylenediamine (**2**) and N,N′-bis(m-aminophenyl)-*p*-phenylenediamine dication ($\mathbf{3}^{2+}$). In both $\mathbf{2}^+$ and $\mathbf{3}^{3+}$, the two states have similar geometries with the exception of the dihedral angle between the central and peripheral phenyl planes. More noteworthy is that spin density on the central two nitrogen atoms has the same sign (Fig. 8). This suggests that the double-exchange interaction can be expected for these model molecules. In fact, the doublet–quartet splitting energy (ΔE_{D-Q}) for $\mathbf{2}^+$ was calculated to be 0.8 kcal mol^{-1}, clearly indicating high-spin ground state of $\mathbf{2}^+$. In contrast to $\mathbf{2}^+$, the value of ΔE_{D-Q} for $\mathbf{3}^{3+}$ was

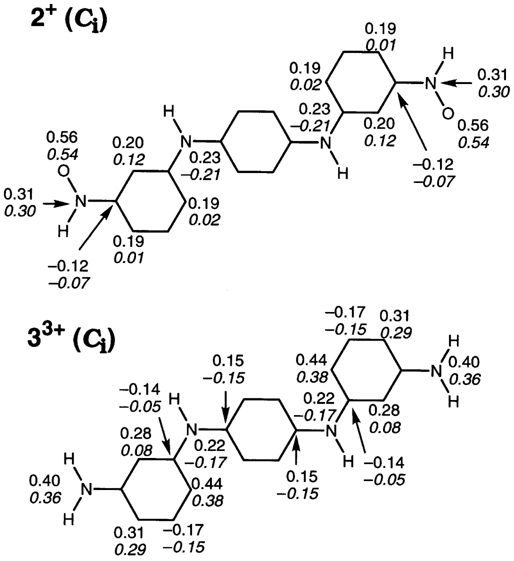

Fig. 8. Mulliken spin density for the doublet (italics) and quartet states of $\mathbf{2}^{+}$ and $\mathbf{3}^{3+}$.

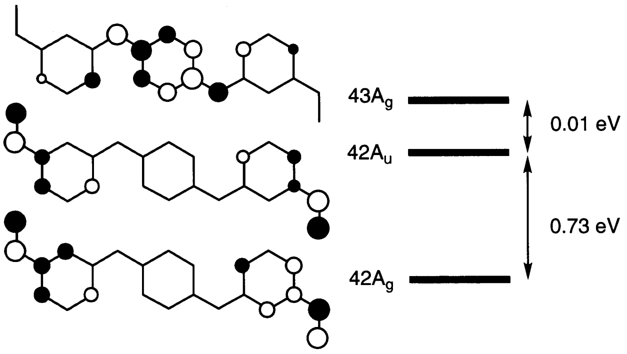

Fig. 9. Schematic drawings of the three singly-occupied MOs for the quartet state of $\mathbf{2}^{+}$.

estimated to be -0.2 kcal mol^{-1}. However, it should be noted that the spin contamination for the $^{2}A_u$ of $\mathbf{2}^{+}$ and $\mathbf{3}^{3+}$ is conspicuous as compared to that for the corresponding $^{4}A_u$ states (Table 1). Therefore, as far as the 2-site model is concerned, the double-exchange interaction exerts a great influence on the spin-preference. This situation is also explainable in terms of MO theory. The frontier MOs of $\mathbf{2}^{+}$ are depicted in Fig. 9. Three singly occupied MOs are quasi-degenerate and overlap each other in their spatial distributions, suggesting a strong exchange energy, which favors the high-spin state.

3.2. 3-site model

Let us now attempt to extend the oligomer model study into 3-site model. Hereafter we confine ourselves to an oligomer of poly(*p*-phenylenecarbene) (**4**, Fig. 10). Schematically shown in Fig. 10, when one electron is removed from 3-site system, the doublet, quartet, and sextet states are considered as the competing spin states. The B3LYP/6-31G* geometries for $\mathbf{4}^{+}$ are shown in Fig. 11. One can see that the optimized geometries of each state are in remarkable contrast with the corresponding 2-site model. As for the sextet state (^{6}A), $\mathbf{4}^{+}$ has a planar structure and, therefore, the C–C–C angle around the central carbenic center increases (150.3°). On the other hand, the optimized structures for quintet (^{4}B) and doublet (^{2}B) states show the linear configuration of the central carbenic center. As influenced by these geometrical changes, the quartet–sextet (doublet–sextet) splitting energy was calculated to be -18.2 (-13.1) kcal mol^{-1}, indicating low-spin-correlation for $\mathbf{4}^{+}$ (Table 2). At the geometry for the sextet state, the doublet and quartet states are still 7.1 and 6.1 kcal mol^{-1}, respectively, lower in energy than the sextet, indicating strong antiferromagnetic spin-correlation. One-electron oxidation of **4** corresponds to $x = 1/3$, and hence lightly doped poly(*p*-phenylenecarbene) would not lead the spin-polarized polymer.

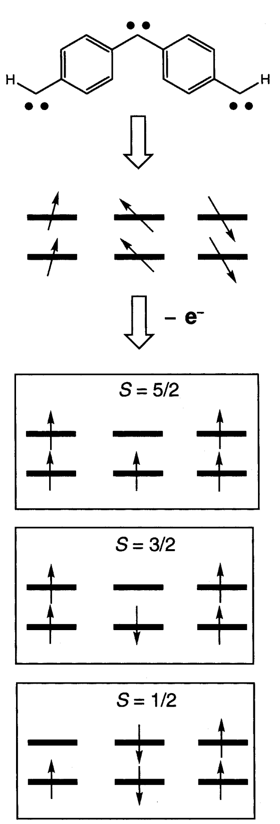

Fig. 10. 3-site model compound (**4**) for poly(*p*-phenylenecarbene) and possible spin configurations for $\mathbf{4}^{+}$.

3.3. 4-site model

Turning now to the 4-site model for poly(*p*-phenylenecarbene) (**5**, Fig. 12), some oxidation states can be taken into consideration: (i) mono-cation ($x = 1/4$) and (ii) dication ($x = 1/2$). As shown in Fig. 12, there exist

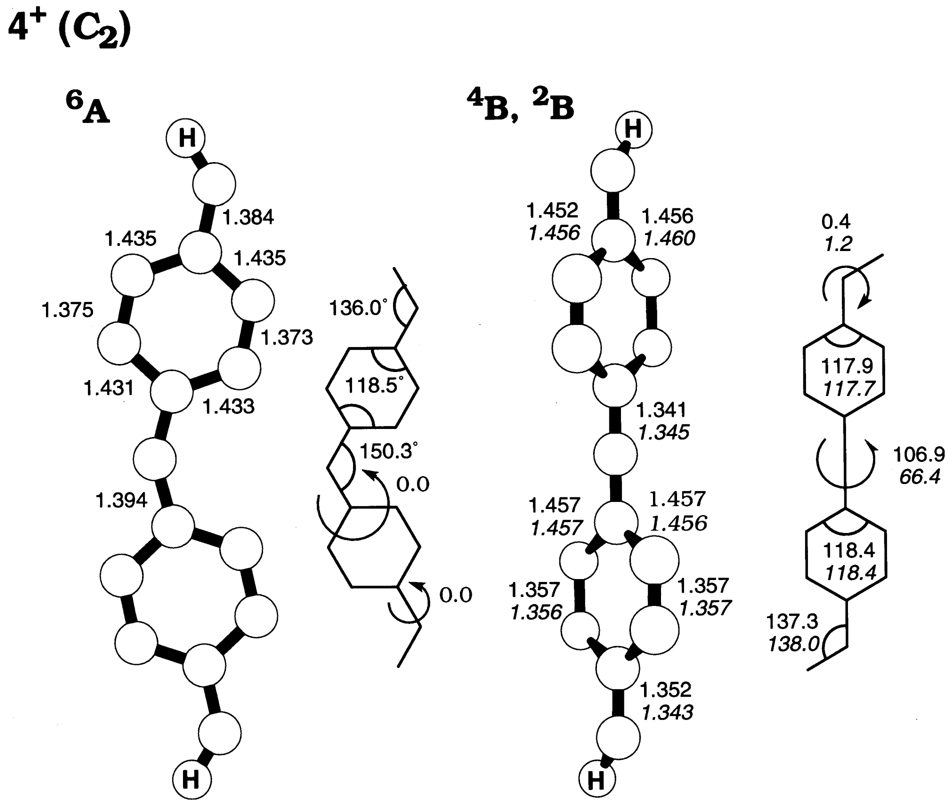

Fig. 11. Important bond lengths (Å) and angles (°) for the sextet, quartet, and doublet (italics) states of $\mathbf{4}^+$ at the B3LYP/6-31G* level of theory.

the doublet and octet states for $\mathbf{5}^+$ and the singlet, triplet, and septet states for $\mathbf{5}^{2+}$. Fig. 13 illustrates the B3LYP/6-31G* optimized structures for two low-lying states of $\mathbf{5}^+$ and $\mathbf{5}^{2+}$. In the high-spin state (^8A_g) of $\mathbf{5}^+$, the dihedral angles between the adjacent phenyl rings are small enough to judge planar structure like the high-spin state of $\mathbf{4}^+$. However, it was found that $\mathbf{5}^{2+}$ has quite large dihedral angles. On the other hand, the competing low-spin states of both $\mathbf{5}^+$ and $\mathbf{5}^{2+}$ adopt a linear structure like the low-spin state (^4B) of $\mathbf{4}^+$. Consequently, in both oxidation states of **5**, the low-spin state with the linear geometry was predicted to lie below the corresponding high-spin state (Table 3). However, it should be noted that, at the geometry for the high-spin state, the low-spin states (^1A_g and ^3A_u) of $\mathbf{5}^{2+}$ are 72.9 and 27.7 kcal mol^{-1} higher in energy than

Table 2
Relative energies and $\langle S^2 \rangle$ values for $\mathbf{4}^+$

State	Calculation	E (Hartree)	E_{rel} (kcal mol^{-1})[a]	$\langle S^2 \rangle$
^{2}B	B3LYP/6-31G*	−577.0747	−13.1	1.76
			−7.1[b]	1.85[b]
^{4}B	B3LYP/6-31G*	−577.0828	−18.2	3.87
			−6.1[b]	3.79[b]
^{6}A	B3LYP/6-31G*	−577.0538	0	8.81

[a] Energy relative to the high-spin state.

[b] Single point calculation at the ^{6}A geometry.

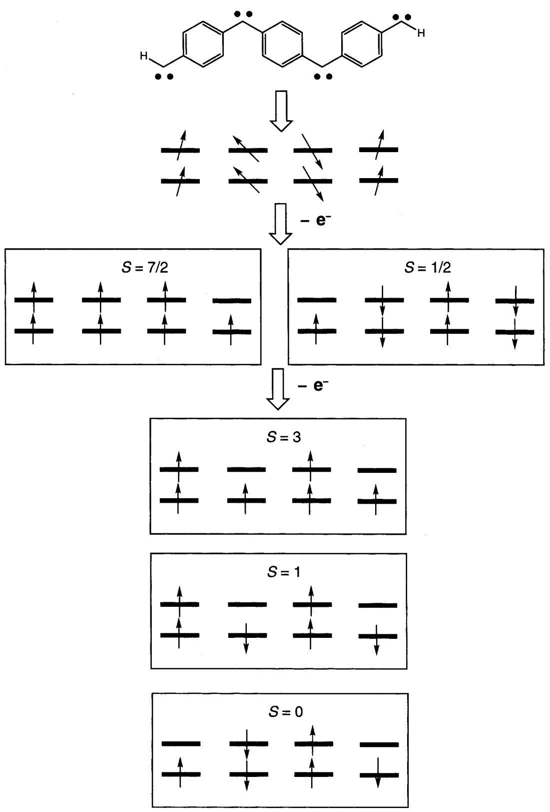

Fig. 12. 4-site model compound (**5**) for poly(p-phenylenecarbene) and possible spin configurations for $\mathbf{5}^+$ and $\mathbf{5}^{2+}$.

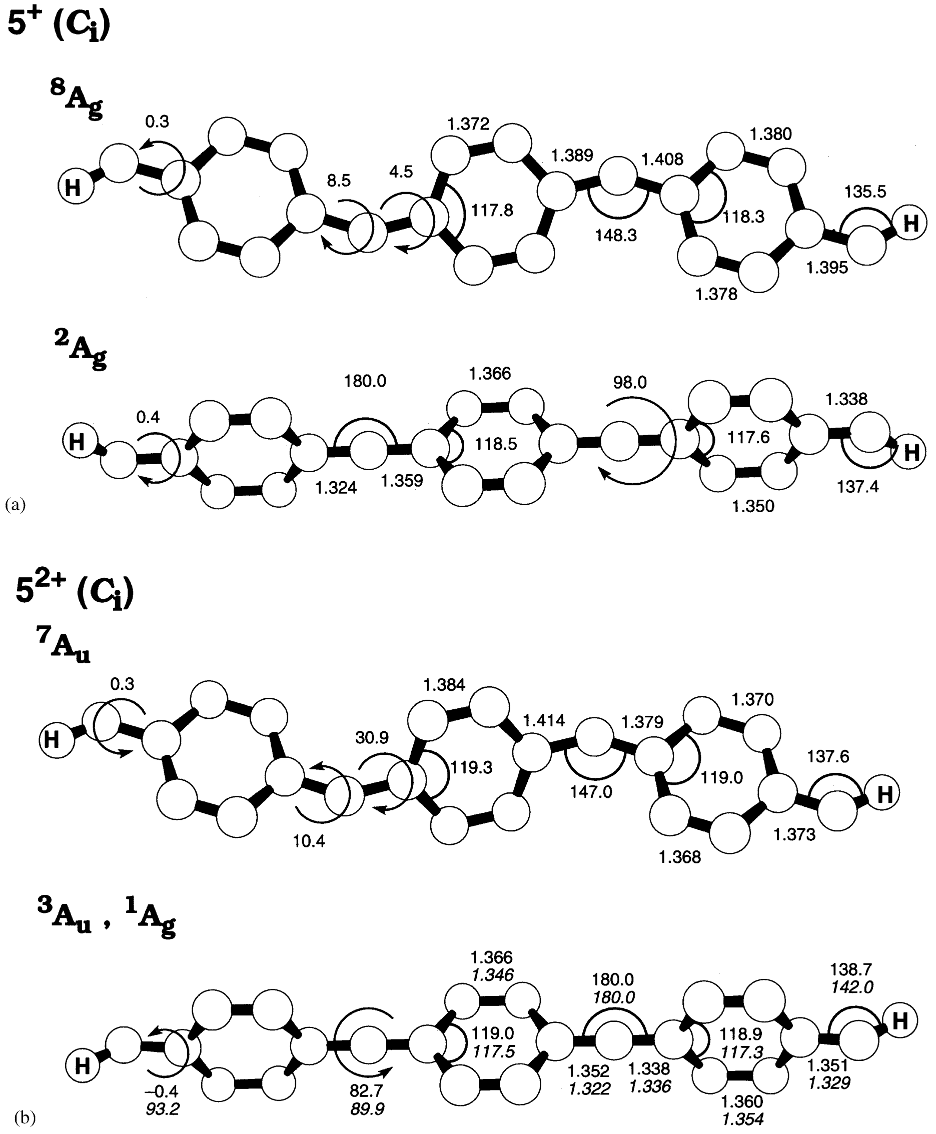

Fig. 13. Important bond lengths (Å) and angles (°) for (a) the octet and doublet states of $\mathbf{5}^+$ and (b) the septet, triplet, and singlet (italics) states of $\mathbf{5}^{2+}$ at the B3LYP/6-31G* level of theory.

Table 3
Relative energies and $\langle S^2 \rangle$ values for $\mathbf{5}^+$

State	Calculation	E (Hartree)	E_{rel} (kcal mol^{-1})[a]	$\langle S^2 \rangle$
$\mathbf{5}^+$				
^2A_g	B3LYP/6-31G*	−846.1803	−40.8	1.92
			−22.7[b]	3.12[b]
^8A_g	B3LYP/6-31G*	−846.1152	0	15.81
$\mathbf{5}^{2+}$				
^1A_g	B3LYP/6-31G*	−845.8089	−3.7	0
			72.9[b]	0[b]
^3A_u	B3LYP/6-31G*	−845.8097	−4.2	2.94
			27.7[b]	2.26[b]
^7A_u	B3LYP/6-31G*	−845.8030	0	12.10

[a] Energy relative to the high-spin state.

[b] Single point calculation at the geometry of the corresponding high-spin state.

the corresponding high-spin state (^7A_u), while the low-spin state (^2A_g) of $\mathbf{5}^+$ is 22.7 kcal mol^{-1} lower in energy than the ^8A_g state. This means that $\mathbf{5}^{2+}$ can be a high-spin molecule if we can oxidize **5** under geometrical constraint. More importantly, these results suggest that, when the hole density deviates from $x = 1/2$, oligomers of poly(p-phenylenecarbene) can no longer retain the high-spin-correlation.

4. Conclusion

We have studied the electronic structures of oligomer model compounds for the promising spin-polarized molecular wire on the basis of quantum chemical calculations.

The following conclusions can be drawn:

i) In 2-site model compounds, it is predicted that the high-spin-correlation can be accomplished by the double-exchange mechanism.
ii) For 3- and 4-site model compounds for poly(*p*-phenylenecarbene), on the other hand, drastic deformation in geometry of the competing low-spin states can take place by oxidation process, resulting in the low-spin-correlation.
iii) If conformation-fixing is possible, the double-exchange interaction is prevailing for the dication of 4-site model. This suggests that the preponderance of the double-exchange interaction strongly depends on the hole density.

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research from Japan Society for the Promotion of Science (JSPS). Numerical calculations were partly carried out at the Supercomputer Laboratory of the Institute for Chemical Research of Kyoto University.

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