

Density functional study of intramolecular ferromagnetic interaction through mphenylene coupling unit (I): UBLYP, UB3LYP, and UHF calculations

Masaki Mitani, Hiroki Mori, Yu Takano, Daisuke Yamaki, Yasunori Yoshioka, and Kizashi Yamaguchi

Citation: The Journal of Chemical Physics **113**, 4035 (2000); doi: 10.1063/1.1286418 View online: http://dx.doi.org/10.1063/1.1286418 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/113/10?ver=pdfcov Published by the AIP Publishing

Articles you may be interested in

Unrestricted density functional theory based on the fragment molecular orbital method for the ground and excited state calculations of large systems J. Chem. Phys. **140**, 144101 (2014); 10.1063/1.4870261

Product branching ratios in photodissociation of phenyl radical: A theoretical ab initio/Rice–Ramsperger–Kassel–Marcus study J. Chem. Phys. **136**, 234305 (2012); 10.1063/1.4726455

Density-functional study of intramolecular ferromagnetic interaction through m-phenylene coupling unit (II): Examination of functional dependence J. Chem. Phys. **113**, 10486 (2000); 10.1063/1.1290008

Density functional theory with fractionally occupied frontier orbitals and the instabilities of the Kohn–Sham solutions for defining diradical transition states: Ring-opening reactions J. Chem. Phys. **111**, 7705 (1999); 10.1063/1.480108

Density functional study of intramolecular ferromagnetic interaction through m-phenylene coupling unit. III. Possibility of high-spin polymer J. Chem. Phys. **111**, 1309 (1999); 10.1063/1.479317



This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP 136.165.238.131 On: Tue, 23 Dec 2014 00:02:06

Density functional study of intramolecular ferromagnetic interaction through *m*-phenylene coupling unit (I): UBLYP, UB3LYP, and UHF calculations

Masaki Mitani, Hiroki Mori, Yu Takano, Daisuke Yamaki, Yasunori Yoshioka, and Kizashi Yamaguchi^{a)} Department of Chemistry, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan

(Received 22 December 1998; accepted 4 May 2000)

Polyradicals comprised of *m*-phenylene-bridged organic radicals are well known as building blocks of organic ferromagnets, in which radical groups are connected with each other at the *meta* position in the benzene ring, and the parallel-spin configurations between radical sites are more stabilized than the antiparallel ones. Topological rules for spin alignments enable us to design organic high-spin dendrimers and polymers with the ferromagnetic ground states by linking various radical species through an *m*-phenylene unit. However, no systematic *ab initio* treatment of such spin dendrimers and magnetic polymers has been reported until now, though experimental studies on these materials have been performed extensively in the past ten years. As a first step to examine the possibilities of ferromagnetic dendrimers and polymers constructed of *m*-phenylene units with organic radicals, we report density functional and molecular orbital calculations of six m-phenylene biradical units with radical substituents and polycarbenes linked with an *m*-phenylene-type network. The relative stability between the spin states and spin density population are estimated by BLYP or B3LYP and Hartree-Fock calculations in order to clarify their utility for constructions of large spin denderimers and periodic magnetic polymers, which are final targets in this series of papers. It is shown that neutral polyradicals with an *m*-phenylene bridge are predicted as high-spin ground-state molecules by the computations, while *m*-phenylene-bridged ion-radical species formed by doping may have the low-spin ground states if zwitterionic configurations play significant roles to stabilize low-spin states. Ab initio computations also show an important role of conformations of polyradicals for stabilization of their high-spin states. The computational results are applied to molecular design of high-spin dendrimers and polymers. Implications of them are also discussed in relation to recent experimental results for high-spin organic molecules. © 2000 American Institute of Physics. [S0021-9606(00)30829-7]

I. INTRODUCTION

Recently new materials with novel functional properties have attracted significant attention both experimentally and theoretically. Molecule-based magnetic compounds have been noticed as one of such functionality materials¹⁻⁷ because they may exhibit superparamagnetism, ferro- or ferrimagnet, magnetic conductor or metal, spin-mediated superconductor, etc. Magnetic properties of organic molecules may be controlled or switched by both chemical and physical techniques such as hole doping and photoexcitation. Magnetic dendrimers and polymers would be precursors to obtain tunable magnets with high transition temperature, since an effective exchange interaction between spins is much larger within a molecule than between molecules. Magnetic molecules with strong throughbond exchange interactions are not only interesting to investigate chemical physics of spins in mesoscopic systems but also important as building blocks for magnetic materials from the practical viewpoint of materials synthesis.

Molecule-based magnetic compounds with throughbond exchange interactions are constructed of spin sources and coupling units. Various types of such materials can be designed by linking organic radicals or transition metals to π -conjugation groups, in conformity with spin alignment rules, which have been proposed by several groups.⁸⁻¹⁶ For example, ferro- or antiferromagnetic ground state of organic polyradicals can be predicted by topological coupling modes of spins via linking groups, for instance, the m or p and oposition(s) in a benzene ring. Dendrimers and polymers comprised of these high-spin units may indicate ferromagnetic characters unless their planar conformations are completely prevented by steric repulsions. Recently experimental efforts to synthesize magnetic oligomers, dendrimers, and polymers have been made extensively, and energy gaps between highand low-spin states in these species have been determined by the ESR, SQUID, and other techniques.¹⁻⁷ In spite of great development of the experiments, theoretical work at the ab *initio* level is still insufficient at present.

From experimental^{17–28} and theoretical^{11,13,14,29–31} studies of magnetic interactions, well-known organic magnetic molecules with the ferro(antiferro)magnetic ground state are

0021-9606/2000/113(10)/4035/17/\$17.00

4035

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP 136.165.238.131 On: Tue, 23 Dec 2014 00:02:06

^{a)}Electronic mail: yama@chem.sci.osaka-u.ac.jp



FIG. 1. (a)–(c) Schematic illustrations of ferro- or antiferromagnetic spin coupling for phenylene-bridged organic radicals linked at (a) *meta*-, (b) *para*-, and (c) *ortho*-positions in the benzene ring.

m-(p- or o-) phenylene-bridged organic polyradicals. The meta-isomers have usually more stable high-spin states with a parallel spin configuration than low-spin states with an antiparallel spin configuration between radical sites. The situation is reversed in the case of *para-* and *ortho-*isomers, as shown in Figs. 1(a)-1(c) schematically. In this series of ab initio computational studies, we mainly examine *m*-phenylene-bridged systems for both molecule and polymer cases by density functional and molecular orbital treatments, because we are interested in the intramolecular ferromagnetic interactions. Previously ab initio unrestricted Hartree-Fock (UHF) and UHF Møller-Plesset (UMP) and coupled-cluster (UCC) calculations including electron correlations were performed for *m*-phenylenebis(methylene) 1.²⁹⁻³¹ The computational results are consistent with the experiments.^{18,19} However, these precise MO calculations are hardly applicable to large clusters or periodic systems.

Density functional theory (DFT) developed in solid state physics^{32,33} has been accepted as an alternative approach to overcome the electron correlation problem.^{34,35} Nowadays, DFT calculations are widely used in computational chemistry^{36–38} because of their simple procedures in practical applications to large molecules and polymers. With regard to early studies for infinite magnetic polymers, any *ab initio* crystal orbital investigations have not been reported, except our recent work for phenylenevinylene-bridged polymers with a methylene radical,³⁹ while only semiempirical treatments have already been carried out.^{40–51} Judging from the previous result,³⁹ the DFT-based crystal orbital method may be a reasonable tool for theoretical studies of periodic polymers. However, the applicability of DFT computations to open shell systems such as organic radicals or transition



FIG. 2. Molecular structure of a *m*-phenylene molecule. Spin sources of organic radicals 1-6 are indicated by the symbol X.

metals has not been established sufficiently yet, although many approximated exchange and correlation functionals have also been proposed by various authors until now. Therefore, the reliability of approximated functionals should be compared with correlated MO methods such as complete active space (CAS) SCF and CASPT2 methods^{52–54} in order to determine which functional can describe magnetic properties in molecules and polymers suitably.

In this series of papers I-III, we have challenged to solve these problems described above using recently developed program series of CRYSTAL that include Hartree-Fock and density-functional approximations.^{55–57} In Part I, we examine ferromagnetic interactions between radical spins through *m*-phenylene unit to clarify which system becomes a possible monomer in a high-spin polymer. Molecular structures of *m*-phenylene molecules examined in this paper are given in Fig. 2, together with the numbering of atoms. Organic radical groups are denoted by the symbol X. Six species with X=CH (1), CH₂ (2), NH (3), NH₂⁺ (4), BH₂⁻ (5), and $N^{-}(6)$ are considered as spin sources. These molecules contain neutral, cation, and anion radicals of carbon, nitrogen, and boron atoms. Therefore, the effects of positive or negative charge and heteroatoms for spin states can be investigated systematically. Very recently, ab initio UHF and UMP calculations of several isoelectronic series to 1 [X=Mn(II),Cu(II)] have been carried out.^{58,59}

Present UHF and DFT calculations of 1 clarify the scope and limitation of the broken-symmetry approach toward molecular magnetism. Variations of effective exchange integrals with conformations of radical groups are studied in the case of *m*-phenylene bis(methyl) 2, since recent experiments have clearly demonstrated that 2 becomes a singlet ground state if its planar conformation is completely destroyed. Biphenylbis(methyl)s (7) are examined in relation to topological rules for spin alignments in *m*-phenylene bridged systems. The polycarbenes $(1)_n$ linked with an *m*-phenylene bridge are also examined to elucidate the size dependency of the effective exchange integrals. The computational results for 1-7and $(1)_n$ are applied to the molecular design of high-spin polymers (8–16) and dendrimers (17–23) (see Figs. 11 and 12). Finally, the implications of the present calculated results are discussed in relation to the recent synthesis of dendrimerlike high-spin polyradicals.⁶⁰⁻⁶⁵

II. THEORETICAL BACKGROUNDS

A. Model Hamiltonians

Magnetism and related phenomena such as spinmediated superconductivity are characteristic problems in strongly electron correlated systems, which have received current interest in relation to the high- T_c superconductivity in copper oxides. Polyradical species under consideration are also regarded as such electron correlated systems. Past decades, several theoretical models have been used for explanations of spin alignments in these species.^{1–7} The UHF and spin-polarized DFT computational results can be used to clarify foundations of the models and their mutual relationships. First of all, we therefore examine effective models, basic concepts, and computational procedures used in this paper, and clarify their relationships.

The effective exchange interactions between magnetic sites in high- or low-spin polyradicals have been described by the isotropic spin Hamiltonian model, namely the Heisenberg model (HB), from the experimental grounds⁶⁶

$$H(\text{HB}) = -2\Sigma J_{ab} \mathbf{S}_{\mathbf{a}} \cdot \mathbf{S}_{\mathbf{b}},\tag{1}$$

where S_a and S_b represent spins at sites *a* and *b*, respectively. J_{ab} is the effective exchange integral, which can be experimentally determined by the measurement of magnetic susceptibility and other experimental techniques. The Heisenberg model in Eq. (1) is reduced to its classical version if spin is regarded as a classical spin vector in order to obtain pictorial understanding of spin alignments,⁶⁷

$$H(\text{CHB}) = -2\Sigma J_{ab} S_a S_b \mu_a \cdot \mu_b$$
$$= -2\Sigma J_{ab} S_a S_b \cos \theta_{ab}, \qquad (2)$$

where θ_{ab} is the angle between spin vectors μ_a and μ_b . Under this approximation, the singlet and triplet spin couplings are described by the antiparallel ($\theta_{ab} = 180^\circ$) and parallel ($\theta_{ab} = 0^\circ$) spin alignments, respectively. Such spin vector presentations of *m*-, *p*- and *o*-phenylenebis(methyl) **2** are given in Fig. 1, where the spin of a π electron on each carbon atom is schematically depicted by an up or a down arrow. The spin alignments often have the magnetic symmetry (*M*), which is characterized by the magnetic group^{68,69}

$$M = H + T(P - H), \tag{3}$$

where *P* and *H* denote the spatial symmetry of radical species and its subgroup, respectively, and *T* is the time-reversal symmetry operation for spin inversion. The magnetic group (*M*) has been utilized to characterize spin alignments in polyradicals species; spin alignments with the high magnetic symmetry tend to become the ground spin structures in general.^{68,69}

The Hückel theory has been used to elucidate molecular orbital (MO) energy levels as shown in Fig. 1, and Hund's rule is applied to explain the high-spin ground state of 2 with the degenerated nonbonding MOs (NBMOs), which are completely characterized by the spatial symmetry *P*. How-

ever, it cannot provide the high- and low-spin energy gap directly. The most general space-spin MO formalism for molecular magnetism⁶⁹ is given by the generalized Hartree– Fock (GHF) or generalized DFT (GDFT) approach. The GHF (GDFT) solutions for polyradicals can be constructed considering the magnetic double group, which is given by the direct product $G=T\times S\times P$, where *S* denotes the spin rotation. The GHF solution is expressed by a Slater determinant constructed of general spin orbitals (GSO),⁷⁰

$$\Phi(\text{GHF}) = |\varphi_1 \varphi_2 \varphi_3 \cdots \varphi_n|, \qquad (4)$$

where

$$\varphi_i = \varphi_i^+ \alpha + \varphi_i^- \beta. \tag{5}$$

The GSO in Eq. (5) is also used for GDFT with a noncolinear spin structure. As shown previously,⁷⁰ a typical example described by the GHF (GDFT) solution is the triangular radical cluster with the D_{3h} symmetry. The GHF (GDFT) solution exhibits the so-called triangular spin alignment with the 6m2 magnetic symmetry.⁶⁸ For example, spin structures of several nonalternant hydrocarbons without bond alternation are described by the noncolinear spin alignment given by the GHF (GDFT) solution.⁶⁹ These situations are similar to several cluster forms of Mn oxide and Fe sulfide with strong spin frustration.

The GHF solutions often reduce to the unrestricted Hartree–Fock (UHF) solutions with collinear (up or down) spin alignments in Fig. 1, particularly in the case of alternant hydrocarbons under consideration. The UHF solutions are defined by the spin-polarized different-orbitals-for-differentspins (DODS) molecular orbitals, namely GSO reduces to DODS,

$$\Psi_i^{\pm} = \cos\frac{\omega_i}{2}\phi_i \pm \sin\frac{\omega_i}{2}\phi_i^*, \qquad (6)$$

where ϕ_i and ϕ_i^* are the bonding and antibonding UHF natural orbitals (UNO), respectively. Their occupation numbers, n_i and n_i^* are given by the orbital overlap $T_i = \langle \psi_i^+ | \psi_i^- \rangle$ between the DODS MOs as

$$n_i = 1 + T_i, \quad n_i^* = 1 - T_i$$
(7)

The DODS MOs are obtained by solving the Kohn-Sham equation in the case of spin-polarized density functional theory (UDFT) methods. The natural orbitals and their occupation numbers of UDFT and hybrid-type UDFT (for example, UB3LYP) solutions are determined by diagonalizing the total density. The natural orbitals are used for the explanation of orbital interactions in polyradical species. The occupation numbers of the natural orbitals by UHF or UDFT are used for the selections of complete active space (CAS) for successive configuration interaction (CI).69,71 The CASCI, CASSCF, and CASPT2 calculations are performed for elucidations of the direct SOMO-SOMO interaction and throughbond indirect exchange interactions. These are also utilized to clarify the nature of exchange and correlations involved in UHF and UDFT. Figure 3 illustrates computational schemes and basic concepts toward molecular magnetism.

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP



B. Correlation and spin correlations

Here, the above Heisenberg, UHF and UDFT models are briefly considered from the viewpoint of correlation and spin correlation. As shown previously,⁷² the magnitude of the orbital mixing parameter ω_i in Eq. (6) is usually overestimated under the UHF approximation, showing large atomic spin densities for π -radical species. For example, the *ab initio* UHF calculation of a *m*-phenylene biradical indicates that the magnitude of atomic spin densities on carbon atoms is almost 1.0 as in the case of the spin vector expressions in Fig. 1 and the classical Heisenberg model in Fig. 3. On the other hand, the orbital mixings in Eq. (6) via the spin polarization effect are rather weak under the UDFT approximation, and therefore phenyl ring is regarded as the closed-shell aromatic framework with moderately induced spin densities, in accord with the experiments.²³ Therefore, UDFT is particularly useful for theoretical calculations of spin densities of organic π radicals. The situation should be similar to polyradicals as shown below.

The spin densities appear even in the singlet state under both UHF and UDFT approximations because of the broken spin symmetry. In fact, they disappear after the spin projection of singlet UHF and UDFT solutions into the pure singlet ones. So, they are often regarded as spin contamination in quantum chemistry. However, spin densities in the low-spin state play a key role for the qualitative understanding of antiferromagnetic spin correlation.^{73–75} Here, the role of spin densities in the broken-symmetry wave functions is clarified by considering pair and spin correlation functions. The pair function $P_2^f(r_1, r_2)$ of parallel spin pairs are given by density P_1 and spin density Q_1 obtained by the DODS molecular orbitals,^{73,74}

$$P_{2}^{f}(r_{1},r_{2}) = \{ [P_{1}(r_{1})P_{1}(r_{2}) - P_{1}(r_{1},r_{2})^{2}] + [Q_{1}(r_{1})Q_{1}(r_{2}) - Q_{1}(r_{1},r_{2})^{2}] \} / 2.$$
(8a)

Similarly, the pair function $P_2^c(r_1, r_2)$ of antiparallel spin pairs is expressed by

$$P_2^c(r_1, r_2) = [P_1(r_1)P_1(r_2) - Q_1(r_1)Q_1(r_2)]/2.$$
 (8b)

The correlation effects of the same and opposite spins are described by these functions, respectively. The pair function of the same spin clearly vanishes for $r_2 \rightarrow r_1$, since two terms in density and spin density become equal, respectively, and cancel exactly. This type of correlation prevents two

electrons of the same spin from being found at the same point in space. Thus there exists a Fermi hole in the same spin pairs. The pair function of opposite spin, however, does not vanish for $r_2 \rightarrow r_1$ as^{73,74}

$$P_{2}^{c}(r) = [P_{1}(r)^{2} - Q_{1}(r)^{2}]/2$$

= $P_{1}(r)[P_{1}(r) - Q_{1}(r)^{2}/P_{1}(r)]/2.$ (8c)

The true pair function of different spins should vanish for $r_2 \rightarrow r_1$ due to the Coulomb repulsion between different spins. Thus spin density is closely related to Coulomb correlation between different spins, and its magnitude directly expresses the size of the Coulomb hole under the spin polarized UHF and UDFT approximations.^{73–75}

The pair function by the UDFT method is given by⁷⁵

$$P_{2}(r) = P_{2}^{c}(r) + P_{2}^{f}(r) = P_{1}(r)[P_{1}(r) + n_{\rm XC}(r)], \quad (8d)$$

where $n_{\rm XC}(r)$ denotes the exchange-correlation hole. Equation (8d) reduces to Eq. (8c) if the wave function is restricted to a Slater determinant. Thus, spin densities are closely related to the on-site Coulomb repulsion in both UHF and UDFT approaches. The large atomic spin densities on a phenyl ring by UHF mean the strong on-site Coulomb repulsion. This, in turn, indicates that UHF overestimates the magnitude of both spin density and an effective exchange integral. On the other hand, UDFT often underestimates it in the case of strong correlation systems.⁵⁸ The hybrid DFT method such as UB3LYP involving the UHF exchange potential may be regarded as a practical procedure to optimize the correlation effect.

The spin correlation functions $K_2^c(r_1, r_2)$ is defined by using the second-order density matrix as⁷⁴

$$K_{2}^{c}(r_{1},r_{2}) = \int \int \mathbf{S}(1) \cdot \mathbf{S}(2) \rho_{2}(r_{1},r_{2};r_{1}',r_{2}') ds_{1} ds_{2}$$
$$= Q_{1}(r_{1})Q_{1}(r_{2})/4.$$
(9)

The spin density product term $Q_1(r_1)Q_1(r_2)$ is negative for the singlet pair while positive for the triplet pair, and therefore the sign of spin densities is closely related to a ferro- or antiferromagnetic spin correlation function. Thus several theoretical models in Fig. 3 are mutually related via the spin exchange phenomena in Eq. (1).^{73,74} The spin vector model in Fig. 1 is nothing but the pictorial expression of spin correlations. The spin density and spin correlation function can be observed in the antiferromagnetically ordered state,⁷⁶ and they are useful indices to express exchange-correlation phenomena in small radical clusters. This view^{73,74} is consistent with the recent pair-density interpretation of spin-density functional theory.⁷⁵ Polyradicals in mesoscopic size would be particularly interesting from the theoretical viewpoint described above.

C. Computation of effective exchange integral

The sign and magnitude of effective exchange integrals between spins in Eq. (1) play important roles to determine magnetic behaviors of polyradicals. The J_{ab} values have been regarded as experimentally determined parameters. Recent developments of the ab initio computational techniques have enabled us to calculate J_{ab} values for polyradical species, leading to the design of the molecular magnet. As mentioned above, spin projection should be carried out in order to obtain the effective exchange integrals (J_{ab}) because of spin contaminations in spin-polarized DFT and UHF methods. A useful scheme for spin projection has been developed on the basis of the isotropic Heisenberg Hamiltonian combined with UHF and UDFT calculations.⁷⁷⁻⁷⁹ Spin projections of these solutions are performed assuming energy splittings of the Heisenberg model, providing a practical computational scheme for effective exchange integrals as

$$J_{ab}^{(1)} = \frac{E(\mathrm{LS}) - E(\mathrm{HS})}{\mathrm{^{HS}}\langle\hat{S}^2\rangle - \mathrm{^{LS}}\langle\hat{S}^2\rangle},\tag{10}$$

$$J_{ab}^{(2)} = \frac{E(\text{LS}) - E(\text{HS})}{4S_a S_b},$$
(11)

where $S_c(c=a,b)$ denotes the size of spin at the *c* site, and differences for *E* and those of $\langle \hat{S}^2 \rangle$ are evaluated from total energies and total spin angular momentums at low- and highspin (LS and HS) states, respectively. We have applied Eq. (10) to a wide variety of organic and inorganic compounds.^{11,13,29–31,59} Equation (11) can be also utilized if the orbital overlap between magnetic orbitals is negligible.

Reliability of this computational scheme of J_{ab} values will be examined by using succeeding UHF natural orbital (UNO) CI and DFT natural orbital (DNO) CI calculations. The UNO or DNO CASCI, CASSCF, and CASPT2 results are given in Sec. IV. Thus several computational models and underlying concepts are closely related. Figure 3 illustrates an important role of DFT computations for a theoretical investigation of molecular magnetism. All the calculations in this study were performed by GAUSSIAN 94^{80} and CRYSTAL 95 program packages.⁵⁵⁻⁵⁷ Becke's⁸¹ and Becke's three-parameter⁸² exchanges with the Lee-Yang-Parr⁸³ correlation and Hartree-Fock approximations were used in spin-polarized DFT (UBLYP and UB3LYP) and unrestricted MO (UHF) calculations, respectively. DFT and MO results were obtained with Pople's 4-31G basis set.⁸⁴ Moreover, basis set dependency was checked by using the UBLYP method with Pople's 6-31G* basis set.⁸⁵

As shown previously,⁸⁶ the UDFT and UHF calculations are feasible even for multicenter polyradicals such as oligomer of triplet carbene $(CH_2)_{11}$, for which the CAS-based approach is not applicable. Since the total energies of the HS and LS UHF (or DFT) solutions correspond to those of the Heisenberg models, respectively, the energy gap can be used to estimate the effective exchange integrals $(J_{ab})^{86}$ as

$$J_{ab}^{(2)} = \frac{E(\text{LS}) - E(\text{HS})}{4(N-1)S_a S_b},$$
(12)

where *N* is the number of spin sites in one-dimension chains $(S_aS_b)_n$ (n=N/2) under consideration. The S_a and S_b are the sizes of spin at sites *a* and *b*. On the other hand, the spin projection of spin-polarized wave functions is a difficult task, if orbital overlaps between radical orbitals are significantly large. The approximate spin projections⁸⁶ are feasible for UHF-based and spin-polarized DFT methods to calculate potential curves for dissociations from the strong overlap to the weak overlap region. To this end, we have considered an approximate but size-consistent spin projection procedure, where the denominator in Eq. (12) is modified so as to reproduce the extremal values of the total spin angular momentum in both regions as⁸⁶

$$\Delta = {}^{\mathrm{HS}} \langle S^2 \rangle - {}^{\mathrm{LS}} \langle S^2 \rangle - S_a g(N) [{}^{\mathrm{LS}} \langle S^2 \rangle - S_r(S_r + 1)],$$
(13)

where

$$g(N) = (N-2)^2/N$$
 (N>2 and even numbers), (14)

or

$$=(N-3)$$
 (N>3 and odd numbers), (15)

and S_r denotes the exact spin angular momentum for clusters under discussion:

$$S_r = n(S_a - S_b) \quad (N = 2n),$$
 (16)

or

$$= n(S_a - S_b) + S_a \quad (N = 2n + 1).$$
(17)

The effective exchange integrals by the approximate spin projection are, therefore, given by 86

$$I_{ab}^{(1)} = \frac{E(\mathrm{LS}) - E(\mathrm{HS})}{\Delta}.$$
 (18)

The $J_{ab}^{(1)}$ value almost reduces to that of Eq. (12) in the weak overlap region, whereas it should be different from $J_{ab}^{(2)}$ in the strong overlap region, where the spin contamination effects in UHF and spin-polarized DFT wave functions are more or less decreased.

III. CALCULATED RESULTS

A. Total energies, high- and low-spin energy gaps

Geometries for both of low (LS) and high-(HS) spin states of biradicals 1-6 in Fig. 2 were optimized by the energy gradient techniques at UBLYP/4-31G and UB3LYP/4-31G levels (see EPAPS, Ref. 87). These computations revealed the fully optimized geometrical parameters for each of molecules 1-6. The structures optimized by the UBLYP/4-31G method were assumed in UBLYP/6-31G* and UHF/4-31G calculations for a methodological comparison. The UBLYP results for bond lengths were generally longer than

TABLE I. Energy gaps between low- and high-spin states both spin states of *m*-phenylene molecules 1-6 by UBLYP, UHF, and UB3LYP methods.^{a,b}

System	Spin state	UHF/4-31G	UB3LYP/4-31G	UBLYP/4-31G	UBLYP/6-31G*
Molecule 1	$\Delta E (4J^{(2)}_{ab})^{c}$	11 103	2530	1750	1732
(X=CH) Molecule 2	$\Lambda F(I^{(2)})^{c}$	10 721	2393	1586	1561
(X=CH ₂)	$\Delta E(J_{ab})$	10 721	2375	1500	1501
Molecule 3	$\Delta E(J^{(2)}_{ab})^{c}$	13 347	2890	1953	2069
(X=NH)	t = (-(2)) a	10.522	1456	222	201
Molecule 4 $(X = NH^+)$	$\Delta E(J_{ab}^{(2)})^{c}$	10 523	1456	232	281
Molecule 5	$\Delta E(J_{ab}^{(2)})^{c}$	7233	941	321	346
$(X=BH_2^-)$					
Molecule 6	$\Delta E(J^{(2)}_{ab})^{c}$	-227	-222	-336	-362
(X=N)					

^aUBLYP/4-31G optimized geometries for low- and high-spin states were assumed in UBLYP/6-31G* and UHF/4-31G calculations.

^bThe energy gap is defined as $\Delta E = E$ (low-spin)-*E*(high-spin) and ΔE values are shown in cm⁻¹.

 $^{c}J_{ab}$ values by Eq. (11).

UB3LYP results by an amount of about 0.01 Å. Both methods gave almost the same values for bond angles. Concerned with the structures of radical sites, X1C2 lengths were somewhat longer in LS states than in HS states. HX1C2 angles were larger and smaller in 1 and 3 than in other molecules, respectively. Both C2C3 and C2C4 bonds were elongated in HS states than in LS states. However, the tendency for the C2C4 bond is reversed in 4 and 5. No change in bond angles was found between both spin states of each molecule. Bond alternations appear in all of the molecules except HS states of charged molecules 4 and 5. From the optimized values for bond angles in the benzene ring, it was found that the deformation in a six-membered ring seems to be relatively remarkable in 5 and 6.

Total energies for low- (LS) and high- (HS) spin states of 1-6 and energy gaps between them, $\Delta E = E(LS)$ -E(HS), were calculated by UBLYP, UHF, and UB3LYP methods. Table I⁸⁸ summarizes the energy gaps, ΔE , at the optimized geometries. All the results from three types of calculations indicate that molecules 1–5 have positive ΔE , while that molecule 6 has negative ΔE . Positive and negative gaps mean the high- and low-spin ground states, respectively. Basis set dependency is small in the evaluation of relative stabilities for all of molecules 1-6 by UBLYP calculations. The ΔE values for 1–5 increase in the order UBLYP<UB3LYP<UHF. This ordering for UB3LYP can be explained from the fact that the B3 exchange functional is a hybrid type involving both UDFT and UHF exchange terms. The UHF method predicts almost similar stability for high-spin states of these molecules [for example, $\Delta E(3)/\Delta E(4)$ and $\Delta E(3)/\Delta E(5) = 1.1$ and 1.6, respectively], while the UBLYP method indicates that the ferromagnetic interactions in neutral molecules 1-3 are much larger than those of charged molecules 4 and 5 [for example, $\Delta E(3)/\Delta E(4)$ and $\Delta E(3)/\Delta E(5) = 8.4$ and 6.1, respectively]. UB3LYP also shows the tendency similar to UBLYP, though the discrepancy between neutral and charged molecules decreases [for example, $\Delta E(3)/\Delta E(4)$] and $\Delta E(3)/\Delta E(5) = 2.0$ and 3.1, respectively]. UB3LYP results are biased toward UHF estimations because of the inclusion of an UHF exchange potential by 20%.

Although the magnitude of ΔE values significantly depends on calculation methods as described above, both UDFT and UHF MO methods indicate that three neutral molecules 1-3 are regarded as stable high-spin molecules. The ΔE values by the UHF seem too large, as compared with the experimental values for 1 and 2.^{17–28} DFT calculations predict small positive ΔE values for charged molecules 4 and 5, while UHF predicts large positive gaps. On the other hand, 6 is a singlet biradical with small negative energy gaps by both UHF and UDFT. Molecules 1-3, together with 4 and 5, are useful building blocks of high-spin polyradicals of the denderimer type, and other extended structures.

From Hund's rule in Fig. 1, the high- and low-spin gaps should be related to the SOMO-SOMO orbital energy gaps. We list splitting widths of singly occupied orbitals for highspin states of 1-5 by UBLYP, UHF, and UB3LYP calculations in Table II.⁸⁹ Table II shows that a molecule with small (large) splitting exhibits the tendency of a large (small) ΔE value. Especially, the tendency is clearly enhanced in UBLYP calculations. The relationship between the splitting width and the relative stability can be qualitatively understood as the following simple consideration. Since singly occupied orbitals are nearly degenerate in molecules 1-3, the parallel-spin configuration in Fig. 1 is stable according to Hund's rule. On the other hand, in molecules 4 and 5, due to the large splitting between singly occupied orbitals, one of the unpaired electrons must lie in a higher orbital and the parallel-spin configuration becomes energetically unfavorable. Therefore, singlet ground state should be resulted if the SOMO-SOMO energy gaps in *m*-phenylene-type biradicals exceed a certain threshold because of polar effects by heteroatoms. This tendency has been indeed observed by the experiments.²⁸ The DFT methods are useful enough for qualitative computations of the high- and low-spin energy gaps in polyradicals.

TABLE II. Splitting widths of singly occupied orbitals for high-spin states of *m*-phenylene molecules 1-5 by UBLYP/4-31G, UHF/4-31G, and UB3LYP/31G methods.^{a,b}

UBLYP/4-31G
$0.005\ 02(0.137)^{c}$
$0.00173(0.047)^{\circ}$
0.005 77(0.157) ^c
0.005 00(0.136) ^c
0.034 22(0.931) ^c
0.012 82(0.349) ^c

^aUBLYP/4-31G optimized geometries for high-spin states were assumed in UHF/4-31G calculations.

^bSplitting widths are shown in a.u.

^cValues in eV are given in parentheses.

B. Spin densities and shapes of molecular orbitals

As discussed in Sec. II, spin densities play essential roles in the spin-polarized DFT and UHF approximations. Atomic spin populations on a radical X1 site and benzene C2–C5 atoms are depicted in Figs. 4(a)-4(f). The alternating sign of spin density is found along the paths linking both radical sites of X1-C2-C3-C2-X and X1-C2-C4-C5-C4-C2-X1. This is caused by the spin polarization (SP) effect to stabilize the high-spin state. As well as ΔE values, we can clearly distinguish UHF results from UBLYP and UB3LYP results by large spin densities. Particularly, UHF overestimates the spin polarization on a benzene ring in contrast to DFT, though the SP effect by these methods is expressed by the same orbital mixing between the bonding and antibonding MOs on phenyl rings, as shown in Eq. (6). The overestimation in spin densities by UHF calculations has already been remarkable for other magnetic systems, leading to an approximate spin projection, even for qualitative purposes, as shown in our previous work.^{39,70} UBLYP/6-31G* and UB3LYP/4-31G give slightly smaller and larger densities in an absolute value than UBLYP/4-31G, respectively. The amplitude of spin polarization in 4 and 5 with small ΔE values is somewhat lower than that in 1–3 with large ΔE values. On the other hand, very weak spin polarization does occur on benzene



FIG. 4. (a)–(f) Atomic spin populations on a radical X1 site and benzene C2–C5 atoms for the high-spin state of an *m*-phenylene (a) molecule 1-(f) molecule **6** by UBLYP/4-31G, UBLYP/6-31G*, UHF/4-31G, and UB3LYP/4-31G methods.

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP



(b) Molecule 4 (X=NH⁺₂·)

FIG. 5. (a),(b) Schematic illustrations of the highest occupied one-electron orbitals for the low- and high-spin states of *m*-phenylene (a) molecules 1, 2, 3, and 5, and (b) molecule 4.

ring of **6** with negative ΔE value but spins are almost localized on the radical sites.

From the above results, the magnitude of spin densities on a benzene ring is closely related to the high- and low-spin energy gaps. To elucidate reasons of this relationship, the highest occupied one-electron orbitals and corresponding spin configurations for both low- and high-spin states of **1–5** are schematically illustrated in Figs. 5(a) and 5(b) and Figs. 6(a)-6(d), respectively. From Fig. 5(a), singly occupied π orbitals are localized in neutral molecules **1–3**, while, from Fig. 5(b), those are delocalized in charged molecules **4** and **5**. This, in turn, indicates that SOMO spins in **4** and **5** are more or less delocalized because of intramolecular charge-transfer (spin delocalization) effects, which stabilize the low-spin state. The spin delocalization is therefore responsible for the large orbital energy gaps and small singlet-triplet energy gap in 4 and 5.

The π -SOMOs for low-spin states are approximately given by the mixing of π SOMOs for high-spin states, since these are good approximations to the UHF natural orbitals (UNO) or DFT natural orbitals (DNO) in Eq. (6),

$$\psi^{\pm} = \cos\frac{\omega}{2} \,\psi_{\text{SOMO}}(S) \pm \sin\frac{\omega}{2} \,\psi_{\text{SOMO}}(A), \tag{19}$$

where ω is close to 90° for molecules **1–5**. The almost equal mixing provided the broken symmetry SOMOs that were largely localized on the left and right radical centers, respectively, as illustrated in Fig. 5. This is responsible for a singlet biradical configuration, leading to the DODS orbital picture of polyradicals under the UDFT and UHF approximations. The situation is the same for the σ -radical orbitals of **1**. Then, **1** has a tetraradical character with the unpaired electrons in π and σ orbitals for both the singlet and quintet

TABLE III. Total energies of the singlet and triplet states and energy gaps between them for σ - or π -type biradical configuration of *m*-phenylene molecules **2** and **6** by UBLYP/4-31G, UB3LYP/4-31G, and UHF/4-31G methods.^{a,b}

System	Radical	Method	Singlet	Triplet	$\Delta E(J^{(2)}_{ab})^{\rm e}$
Molecule 2^{c} (X=CH ₂)	π	UBLYP/4-31G	-309.029 43	-309.036 66	1586
Molecule 2^d (X=CH ₂)	σ	UBLYP/4-31G	-308.97403	-308.97302	-222
Molecule $6^{c} (X=N^{-})$	σ	UHF/4-31G	-337.645 17	-337.644 14	-227
Molecule 6 (X=N ⁻)	π	UHF/4-31G	-337.58295	-337.632 49	10 873
Molecule 6 (X=N ⁻)	σ	UB3LYP/4-31G	-339.795 43	-339.794 31	-242
Molecule 6 (X=N ⁻)	π	UB3LYP/4-31G	-339.741 85	-339.75011	1656
Molecule 6 (X=N ⁻)	σ	UBLYP/4-31G	-339.667 31	-339.665 55	-370
Molecule 6 ($X=N^{-}$)	π	UBLYP/4-31G	-339.615 03	-339.619 40	873

^aTotal energies are shown in a.u.

^bEnergy gap is defined as $\Delta E = E(\text{singlet}) - E(\text{triplet})$ and ΔE values are shown in cm⁻¹.

^cResults in Table I are given.

^dStandard geometries were assumed as CC and CH bond lengths and bond angles are 1.40 Å, 1.08 Å, and 120°, respectively.

 ${}^{e}J_{ab}$ values by Eq. (11).

states. In the quintet state, triplet methylenes on radical sites in the *m*-phenylene skeleton couple with each other ferromagnetically, while they couple antiferromagnetically in the singlet state. The stability of the quintet state comes from ferromagnetic spin coupling via the Coulombic exchange interaction between SOMOs, which is the origin of Hund's rule in Fig. 1, and spin-polarization effect linking path of two radical sites, as shown in Fig. 4(a). The CASCI and CASSCF calculations are crucial to elucidate relative contributions of these terms, as shown in Sec. IV. 2, 3, 4, and 5 have π -biradical orbitals on two separated radical sites, as shown in Figs. 5(a) and 5(b). These have the π -radical lobes on sites C3 and C4, leading to the ferromagnetic spin coupling between two radical sites X1 through the Coulombic exchange effect. In fact, C3 and C4 have large positive spin densities, as shown in Figs. 4(b), 4(d), and 4(e).

The Coulombic (potential) exchange integral between SOMOs is given by 90

$$K_{ab} = \langle \psi^{+} \psi^{-} | \psi^{+} \psi^{-} \rangle \cong \sum_{i} (C_{i}^{+})^{2} (C_{i}^{-})^{2} U, \qquad (20)$$

where C^{\pm} are the LCAO coefficients of SOMOs ($\psi^{\pm} = \Sigma C_i^{\pm} \chi_i$), and *U* is the on-site Coulombic repulsion integral. The K_{ab} value is not zero if ψ^+ and ψ^- have the overlapping region: for example, the coefficient at the C3 site in Fig. 5. The effective exchange integral (J_{ab}) via the SOMO–SOMO interaction is close to K_{ab} because

$$J_{ab}(\text{SOMO-SOMO}) \cong K_{ab} - CS_{ab}^2(C:\text{const}), \qquad (21)$$

where S_{ab} is the orbital overlap integral between SOMOs, and $S_{ab} = \langle \psi^+ | \psi^- \rangle \cong 0$ for molecules **1–5**. The key point is that the Coulombic exchange integral K_{ab} in Eq. (20) is not zero even if $S_{ab} = \langle \psi^+ | \psi^- \rangle \cong 0$, leading to Hund's rule $(J_{ab} > 0)$ in Fig. 1.

Next, let us consider the molecule **6** with the singlet ground state. This is different case from **1–5** with the high-spin ground states. Figure 6(d) schematically shows orbital diagrams and spin configurations for singlet and triplet states of **6**. In the stable singlet state, **6** exhibits an antiferromagnetic spin coupling between σ orbitals of two radical sites.

Since the LCAO coefficient at the C3 site is very small, the K_{ab} value is negligible for **6**, in conformity with the singlet ground state expressed by Fig. 6(d). In the triplet state, four highest occupied α orbitals order as $\sigma\sigma\pi\pi$ while corresponding β orbitals as $\pi\pi$ (occupied) and $\sigma\sigma$ (unoccupied). The π and σ orbitals are doubly and singly occupied orbitals, respectively. In conclusions, the DODS MO description by DFT are useful for a qualitative understanding of orbital interactions in polyradicals and provide reasonable spin populations of them.

C. Importance of orbital symmetries and conformation for ferromagnetic interactions

The orbital configurations in Fig. 6 clearly demonstrated an important role of orbital symmetry (whether π or σ radical) for active control of spin alignment (ferro- or antiferromagnetic coupling). By altering the arrangement of occupied and virtual β orbitals in the triplet state of **6**, the configuration of the π -radical will be produced, being similar to 3 with π -radicals in which the triplet state is more stable than the singlet state. DFT and UHF/4-31G calculations were performed for this π -radical state of 6. The results are given in Table III. From Table III, the relative stability is predicted to be E(singlet) > E(triplet) for a π biradical, indicating the spin crossover from antiferro- and ferromagnetic coupling by the orbital rotation. From spin population analysis, we also find that the spin polarization on the benzene ring is recovered in the triplet π -radical state of **6**, as given in Fig. 7(a). Thus, it can be concluded that σ radicals induce the very weak spin polarization on the σ -electron system in the phenyl ring, as shown in Fig. 7(b), and organic radicals are linked with weak antiferromagnetic interactions. This effect arises from the weak mixing between the bonding and antibonding σ orbitals within the benzene ring,

$$\psi_{\sigma}^{\pm} = \cos\frac{\kappa}{2} \,\sigma \pm \sin\frac{\kappa}{2} \,\sigma^*, \tag{22}$$

where $0^{\circ} < \kappa \ll 90^{\circ}$.





(c) UHF Natural Orbitals and occupation numbers for m-phenylenebis(methylene) in the quintet (singlet) state

FIG. 7. (a) Spin structure for the triplet state of **6** with a π -radical character by the UHF/4-31G method. (b) Schematic representation of the spin structure for the singlet state of twisted **2** with a σ -radical character. (c) Symmetries and occupation numbers of UNO for the high-spin π -radical state of **1** (values for the low spin are in parentheses).

On the other hand, π radicals couple ferromagnetically via the large Coulombic exchange and spin polarization on the π -electron system network. The natural orbital analysis is a useful method to elucidate this spin polarization (SP) of a π electron in the π -radical state of 1–5. Figure 7(c) shows the symmetry and occupation numbers of π -type bonding and antibonding UNOs of the highest- (HS) and lowest- (LS) spin state of 1. The occupation numbers of the antibonding NOs are not negligible for HS, but negligible for LS. This shows the large SP stabilization of HS, in contrast to LS. The UHF method overestimates the SP effect for HS, and this is the reason why it provides the overestimation of the HS-LS energy gap of 1. The natural orbital analysis of 2-5 also shows the same conclusion. On the other hand, the natural orbital analysis of the UDFT solutions indicated small occupation numbers of antibonding DNOs, even for HS, in conformity with the reasonable HS-LS energy gap. However, shapes and symmetry of UNO and DNO are reasonable, since they are mainly responsible for the kinetic energy part of electron motion, though the electron-electron exchange



FIG. 8. Molecular structure of deformed molecule 2 with artificial σ -radical orbitals by rotation of CH₂ groups.

interaction part is quite different between DFT and UHF, as shown in Sec. II. Therefore both UNO and DNO are utilized for successive CASCI, as described in Sec. IV.

Recent experiments⁶⁰⁻⁶⁵ clearly demonstrated that conformations of radical groups play crucial roles to determine the HS-LS energy gaps. These findings should be related to the orbital symmetry. To confirm this prediction, CH₂ radical groups of **2** are rotated by θ 1 and θ 2 degrees around each of the C(radical)–C(benzene) bonds, respectively, that is, the molecular plane of the radical group was placed so as to be perpendicular to the benzene ring at $\theta 1 = \theta 2 = 90^{\circ}$, as given in Fig. 8. UHF and UDFT/4-31G calculations were performed for this σ -radical state of **2**, as shown in Table III. The singlet state indeed becomes more stable than the triplet state, in conformity with the orbital symmetry rule. This indicates that spin crossover from the high spin to the low spin occurs in the course of internal rotations of CH₂ groups, as depicted in Fig. 8. Rotation angles $\theta 1 = \theta 2 = 0^{\circ}$ correspond to the original π radical and $\theta 1 = \theta 2 = 90^{\circ}$ to the σ radical. The J_{ab} values were evaluated from UBLYP/4-31G calculations with a spin-projection procedure by applying Eq. (10). Figure 9 shows the dependence of J_{ab} values in internal rotations of CH₂ groups. Figure 9 clearly shows that the change from the π - to the σ -radical state depends on ($\theta 1, \theta 2$) values, and $(\theta 1, \theta 2) = (45^{\circ}, 90^{\circ}), (60^{\circ}, 75^{\circ}), (60^{\circ}, 90^{\circ}),$ $(75^{\circ}, 75^{\circ})$, $(75^{\circ}, 90^{\circ})$, and $(90^{\circ}, 90^{\circ})$ give negative J_{ab} values that mean the singlet ground state with the antiferromagnetic coupling. The rotation of both CH₂ groups is essential to destroy the ferromagnetic state stabilized by π conjugation between radical sites, since positive J_{ab} values under $\theta 1$



FIG. 9. Variations of J_{ab} values under CH₂ rotations by θ 1 and θ 2 obtained from UBLYP/4-31G calculations with spin projection.

=0°, 15°, and 30° (white marks) are kept even at $\theta 2 = 90^{\circ}$. Thus, the rigid structures will be crucial in order to accomplish high-spin polyradicals. The DFT calculations can be used to elucidate variations of J_{ab} values with conformational changes in polyradicals.

D. Topological rules for spin alignments in biphenylbis(methyl)

Several spin alignment rules have been derived on the basis of the model Hamiltonians in Fig. 3. Biphenylbis (methyl) 7 is one of the most important test molecules for these rules. The NBMO rule⁸ in Fig. 1 predicts the high-spin ground state for the [3,3'] isomer of 7, while the VB^{9,10} and spin vector models¹¹ predict the low-spin ground state. The ESR experiment supports the latter prediction.⁶ Therefore, it is very interesting to examine whether DFT calculations can reproduce the experimental tendency. Here we investigate variations of energy gap (ΔE) and effective exchange integral (J_{ab}) with changes of substitution positions of the CH₂ group, which are illustrated in Fig. 10. Computations were carried out assuming planar conformations and standard C-C (1.40 Å) and C-H (1.08 Å) distances. Table IV summarizes the calculated results. The ΔE and J_{ab} values are largely negative (antiferromagnetic) for the [4,4'], [2,4'], and [2,6'] isomers because these have the closed-shell valence-bond (VB) structures, as illustrated by (b), (c), and (d) in Fig. 10. The same situation appears in the case of para-phenylenebis(methyl) in Fig. 1. The J_{ab} values with and without spin projections by Eqs. (10) and (11) are different since the orbital overlap integrals (S_{ab}) between SO-MOs are large for these VB configurations. On the other hand, the *m*-phenylenebis(methyl) structure is feasible for the [2,3'] or [2,5'] and [3,4'] isomers of biphenyl 7, as shown in Figs. 10(e) and 10(f). The J_{ab} values are calculated



FIG. 10. (a) Molecular or (b)–(g) valence–bond structures and (h) spin vector model for isomers of biphenylbis(methyl) 7.

to be positive (ferromagnetic) by UB3LYP, but they are negative for [2,3'] and [2,5'] by UBLYP. The orbital overlap term ($|-CS_{ab}^2|$) becomes larger than the Coulombic exchange term (K_{ab}) under the UBLYP approximation since UBLYP overestimates the hydrogen bonding interactions at

TABLE IV. Energy gaps and effective exchange integrals for isomers of biphenylbis(methyl) **7** by UBLYP/4-31G and UB3LYP/4-31G methods.^a

Method Isomer ^b	UE	33LYP	UBLYP		
	$J^{(1)\mathrm{d}}_{ab}$	$\Delta E^{\rm c}(J^{(2)}_{ab})^{\rm e}$	$J^{(1)\mathrm{d}}_{ab}$	$\Delta E^{\rm c}(J^{(2)}_{ab})^{\rm e}$	
[4,4']	-2042	-2467	-2032	-3416	
[2,4']	-1400	-1591	-1376	-2022	
[2,6']	-952	-1045	-973	-1278	
[2,3']	114	122	-214	-236	
[2,5']	142	151	-191	-214	
[3,4']	678	709	450	457	
[3,3']	-310	-302	-207	-210	
[3,5']	-314	-306	-214	-218	

^a ΔE and J_{ab} values are listed in cm⁻¹.

^bMolecular structures and radical positions for isomers are illustrated in Fig. 10.

^c ΔE is equivalent to J_{ab} without spin projection [see Eq. (11)] in the case of **7**.

^dValues after spin projection are given [see Eq. (10)]. ${}^{e}J_{ab}$ values by Eq. (11).

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP:



FIG. 11. (a) *m*-phenylene-type polycarbene with N=10 (decamer) and spin alignments for high- (HS) and low-spin (LS) states. (b)–(c) Spin densities calculated for HS and LS states, respectively, by UBLYP/4-31G. The values by UB3LYP are given in parentheses.

C2' and C3 positions. This means that UBLYP may often bias to the low-spin side because of too much electron delocalization. Further detailed studies will be performed for comparisons of exchange and correlation functionals in this regard. The orbital overlap and Coulombic exchange terms are essentially zero for the [3,3'] and [3,5'] isomers because of no SOMO-SOMO interaction [Eq. (21)], which can be understood by the VB structure (g) in Fig. 10. The throughbond exchange interaction via the spin polarization (SP) and electron correlation (EC) mechanisms plays an important role in this case, leading to the low-spin VB structure (h), where the classical arrow notation of spins is utilized like the classical Heisenberg model. The J_{ab} values for the [3,3'] and [3,5'] isomers are calculated to be negative by UBLYP and UB3LYP, in accord with the VB and Heisenberg models. UBLYP and UB3LYP include the SP plus EC effects appropriately via the exchange-correlation functionals. The calculated results for all the isomers of biphenyl 7 by UB3LYP are formally explained by the spin vector models¹¹ in Fig. 1. The situation is the same, even for dendrimers and polymers, as shown in the last section of this paper and Part III of this series. Therefore, DFT computations may be concluded to be useful for theoretical investigations of spin alignments in polyradicals.

E. Size effect in effective exchange interactions in polycarbenes

In order to demonstrate the utility of the brokensymmetry (BS) approach, here we performed polycarbene oligomers linked with *m*-phenylene bridges as shown in Fig. 11 and **8** in Fig. 12. The optimized CCC angle for the methylene site of **1** was assumed for the oligomers. Table V summarizes the calculated results. From Table V, the calculated J_{ab} values for each oligomer increase in the order UBLYP<UB3LYP \ll UHF. The J_{ab} values by UBLYP and UB3LYP are about 230 and 380 cm⁻¹ for decamer (N= 10), respectively, while the calculated J_{ab} values by UHF is over than 2000 cm⁻¹, even for hexamer. The J_{ab} values by UBLYP and UB3LYP, and unprojected UHF decrease monotonically with the increase of cluster size, though the J_{ab} values by APUHF exhibit a complex behavior because of strong spin polarization. Then, the J_{ab} values for large oligomers can be estimated by using the fitting curves of the calculated results with the single exponential functions,

$$J_{ab} = -a \exp(-x) + b, \qquad (23)$$

where *x* denotes the size of oligomers, and *a* and *b* are the fitting parameters. The estimated J_{ab} values and *a* and *b* parameters are shown in Table V.⁹¹ The J_{ab} values for oligomers with N>10 are estimated to be almost constant, showing the saturation. This indicates that polycarbenes linked with *m*-phenylene bridges exhibit the ferromagnetic exchange coupling, even if their sizes are very large. Probably the same situation is expected for other radical components examined in this paper. Therefore, we can construct several polyradical network systems with the high-spin ground states, as shown in Sec. V.

As shown in Fig. 11, the calculated spin densities on the carbene sites are parallel (ferromagnetic) and antiparallel (antiferromagnetic) for the highest-spin (HS) and lowest-spin (LS) states, respectively, in accord with the classical arrow notations in Figs. 11 and 12, though they disappear for the latter singlet state after approximate spin projection. The spin densities on carbene sites in the HS state are about 1.51 (1.62) by UBLYP(UB3LYP)/4-31G, while they are 1.54 (1.63) and -1.54 (-1.63) for spin-up and spin-down sites, respectively, in the LS state. Then, the spin correlation function between the nearest radical sites given by Eq. (9) is negative for the LS state, showing the antiferromagnetic short-range order. It is noteworthy that the total number of spins is 20 for decamer, and therefore the active orbitals for CASSCF become over 20, indicating that its CAS-based treatments are impossible. This is one of the reasons why the broken-symmetry approaches are practical and useful for qualitative purposes. We may conclude that UDFT calculations are indeed applicable to theoretical investigations of molecular magnetism in large polyradicals.



FIG. 12. Possible *m*-phenylene skeletons as coupling units for extended systems of organic magnetic polymers.

IV. CASCI, CASSCF, AND CASPT2 CALCULATIONS

A. Phenylenebis(methylene)

Results of energy gap and spin density obtained from DFT and UHF MO calculations are significantly different from each other, as we have described in preceding sections. In order to elucidate reliabilities of spin-polarized computations, we have performed the CASCI, CASSCF, and CASPT2 calculations of the highest- and lowest-spin states of *meta-* and *para-*phenylenebis(methylene) 1(X=CH).²⁹ The complete active space (CAS) was selected by the use of the occupation numbers of UHF NO (UNO) and DFT NO (DNO). Table VI summarizes the calculated J_{ab} values. The UNO CASCI by the use of four active orbitals and four active electrons {4,4} provide the SOMO–SOMO direct interaction part of the J_{ab} values given by Eq. (21),

 $J_{ab}(\text{SOMO-SOMO}) = J_{ab}(\text{CASCI}\{m,n\}),$

where $\{m,n\}$ means the SOMO–SOMO interaction space. This is about 190 cm⁻¹. The CASSCF refinement is minor, showing that UNO is a good approximation to CASSCF natural orbitals. The remaining spin polarization (SP) plus electron correlation (EC) terms can be estimated by expanding CAS space,

$$J_{ab}(\text{SP+EC}) = J_{ab}(\text{Total}) - J_{ab}(\text{SOMO}-\text{SOMO}).$$
 (25)

The UNO CASCI, and CASSCF results by use of the ten active orbitals and ten active electrons. {10,10} predicts that the total J_{ab} values are larger than 400 cm⁻¹. The same conclusion is resulted by the CASSCF second-order perturbation (PT2) calculations: namely, 403, 406, and 520 cm⁻¹ by CASPT2(D){4,4}, CASPT2(N) {4,4}, and CASPT2(N){6,6}, where D and N mean the diagonal and nondiagonal approximations.⁵³ Judging from the CASSCF

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 136 165 238 131 On: Tue, 23 Dec 2014 00:02:06

(24)

TABLE V. Effective exchange integrals (J_{ab}) for polycarbene oligomers linked with *m*-phenylene bridges **8** by UHF/4-31G, UB3LYP/4-31G, and UBLYP/4-31G methods.^{a,b}

System	UHF/4-31G	UB3LYP/4-31G	UBLYP/4-31G
dimer trimer tetramer pentamer hexamer decamer dodecamer tetradecamer hexadecamer	$\begin{array}{c} 2126 \ (2472)^{c} \\ 1971 \ (2156)^{c} \\ 2028 \ (2111)^{c} \\ 2254 \ (2039)^{c} \\ 2305 \ (2036)^{c} \\ \ (2025)^{d} \end{array}$	559.2 $(568.5)^{c}$ 448.4 $(454.8)^{c}$ 417.3 $(422.3)^{c}$ 402.4 $(406.4)^{c}$ 393.0 $(396.8)^{c}$ 377.9 $(380.2)^{c}$ 388.2 ^d $(391.8)^{d}$ 388.2 ^d $(391.8)^{d}$ 388.2 ^d $(391.8)^{d}$	$\begin{array}{c} 372.5 \ (375.1)^{c} \\ 284.7 \ (286.5)^{c} \\ 259.2 \ (206.9)^{c} \\ 247.7 \ (249.6)^{c} \\ 240.1 \ (242.3)^{c} \\ 223.6 \ (227.3)^{c} \\ 235.2^{d} \ (237.5)^{d} \\ 235.2^{d} \ (237.5)^{d} \\ 235.2^{d} \ (237.5)^{d.e} \end{array}$
u	(3249)	1204 (1309)	1019 (1019)

 ${}^{a}J_{ab}$ values are listed in cm⁻¹.

^bStandard geometries were assumed as CC at the benzene site, CC at the carbene site and CH bond lengths and bond angles are 1.40, 1.40 and 1.08 and 120, 135, 120 degrees, respectively.

 ${}^{c}J_{ab}$ values without an approximated projection method [Eq. (12)] in parentheses.

^dEstimated values by the extrapolation [Eq. (23)].

^eThese are b values in Eq. (23).

 f_a values in Eq. (23) are given.

and CASPT2 results, the SOMO–SOMO direct exchange interaction is smaller than one-half of the total exchange interaction,

$$W = J_{ab}(\text{SOMO}-\text{SOMO})/J_{ab}(\text{Total}) < \frac{1}{2}.$$
 (26)

The remaining SP plus EC term should be related to the sign and magnitude of spin densities under the spin-polarized approximation, as shown in Sec. II. Then the SP plus EC effects can be grasped by the simple valence-bond (VB) picture given by the spin vector model in Fig. 1. Both the SOMO–SOMO interaction model via the Coulombic exchange K_{ab} (Hund's rule) and the VB model via the SP plus EC effects are equally applicable for a qualitative explanation of the high-spin ground state of **1**. This is the reason why both MO and VB explanations work well for *m*-phenylene bridged polyradicals **1–5**; namely, both explanations are possible depending on the taste and training of researchers.^{1–5}

In order to elucidate the role of σ -orbital, UNO CASCI{10,10} calculations were performed by including the σ -orbital instead of the π orbital. The J_{ab} values by the π -CI and σ -CI are 630 and 403 cm⁻¹, respectively, showing that the σ orbital contributes to stabilizing the low-spin state.

This is wholly compatible with the preceding arguments on the orbital symmetry control of the effective exchange interactions in 3 and 6.

Judging from the J_{ab} values in Tables I and VI, BLYP can reproduce the J_{ab} values by CASSCF and CASPT2. UHF overestimated the J_{ab} values, because of a large spin polarization effect, while the UNO CASCI{10,10} provides reasonable J_{ab} values, indicating that it can include the SP plus EC effects in a well-balanced manner. The CASCI by the use of UBLYP NO (BNO) and USLYP NO (SNO) were also carried out for comparison, as shown in Table VI. Both provided similar results CASCI for *m*or *p*-phenylenebis(methylene), since BNO and SNO are not so different. The B(S)NO CASCI{10,10}, together with UNO CASCI{10,10}, reproduced the J_{ab} value by BLYP. This in turn indicates that UBLYP includes the SP plus EC effects via the exchange-correlation functional. In conclusion, CASCI by the use of its own NO is desirable for a theoretical confirmation of UHF and DFT approaches to magnetic molecules.

B. Biphenylbis(methyl)

The UNO CI calculations of the [3,3'] and [4,4'] isomer of 7 were performed in order to confirm the UDFT results, as shown in Table VI. The J_{ab} value of the [3,3'] isomer by UNO CASCI{4,4} is almost zero since the potential exchange term K_{ab} in Eq. (20) becomes zero, in contrast to the case of 1. The SOMO-SOMO interaction is essentially zero in this case, as expected from Fig. 10(g). The weight w in Eq. (26) is only 3%. The simple NBMO rule is broken down for 7, showing an important role of secondary orbital interactions. In fact, the UNO CASCI {8,8} provides the large negative J_{ab} value, showing that the SP plus EC correlations of the closed-shell electrons play a crucial role for an antiferromagnetic exchange interaction in the [3,3']isomer. This is the reason why the VB and spin vector model in Fig. 10(h) work well for a qualitative explanation of its spin alignment.

The UNO CASCI{4,4} for the [4,4'] isomer shows the large negative J_{ab} value because of the nonzero SOMO–SOMO orbital overlap ($S_{ab} \neq 0$), in accord with the MO description in Fig. 10(b), and dynamical correlation corrections are not important in this case. The BLYP calculations of **7** reproduce the large-scale UNO CI results qualitatively. This broken-symmetry approach is therefore utilized as a practical

TABLE VI. Effective exchange integrals^a calculated by CASCI and CASSCF.

Methods		1 [meta]	1 [para]	7 [3,3']	7 [4,4']
UNO CAS-CL (SCF)	{4, 4}	188(170)	-1992	-7.3	-4.9
UNO CAS-CI (SCF)	{8, 8}	507(519)	-1453 (-1653)	-254	-498
UNO CAS-CI (π)	{10, 10}	677	-1552		
UNO CAS-CI (σ)	{10, 10}	403			
BNO CAS-CI (SNO) ^b	{8, 8}	664(659)	-1942(-2078)		
BNO CAS-CI (SNO) ^b	$\{10, 10\}$	565(565)	-1937 (-2046)		

 ${}^{a}J_{ab}$ values are listed in cm⁻¹.

^bBNO and SNO denote UBLYP NO and USLYP NO, respectively.

This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP

alternative to UNO CI for large polyradicals as shown in the case of polycarbenes (8) in Fig. 12.

Judging from the numerical results for 1 and 7, the UNO CASCI, DNO CASCI, CASSCF, and CASPT2 methods are powerful to elucidate relative contributions of the SOMO-SOMO direct and other indirect orbital interactions and to examine reliabilities of several theoretical models for molecular magnetism and their interrelationships depicted in Fig. 3. The CAS-based computations support use of UBLYP for qualitative studies of effective exchange interactions in polyradical species. However, it is noteworthy that BLYP and B3LYP predict the reverse signs in the case of [2,3']and [2,5'] isomers of 7. This may be a warning for a heavy expectation to UBLYP and UB3LYP. Of course, we can see the functional dependency of DFT results and various approximations for exchange-correlation functionals have already been proposed by the local spin density or generalized gradient procedures.^{92–98} Therefore, we should confirm whether such approximated terms work effectively or not in the study of electronic and magnetic properties of organic radical molecules, particularly charged molecules 3 and 4. In Part II, we report the examination of these subjects. Since CASPT2 computations are impossible for large magnetic molecules, such studies are crucial for developments of effective computational methods.

V. DISCUSSIONS AND CONCLUDING REMARKS

A. Relations to recent experiments

We studied ferromagnetic or antiferromagnetic couplings of organic radicals through *m*-phenylene bridge by spin-polarized BLYP- or B3LYP-DFT and unrestricted HF-MO calculations. In order to find building blocks with a ferromagnetic nature, relative stabilities for the lowest- (LS)and highest- (HS) spin states of six different *m*-phenylenes with a neutral radical or ion-radical substituents were estimated. Judging from these energy gaps by DFT and UHF MO methods, three neutral molecules 1-3 with relatively large HS-LS gaps are useful building blocks to construct organic high-spin dendrimers and polymers with m-phenylene-type networks. In fact, the high-spin ground states of *m*-phenylene bis(phenylmethylene), for which model 1 in Fig. 2 and models 8 in Figs. 11 and 12 are investigated here, are well established on experimental grounds.¹⁷⁻²⁸ Similarly, Schlenk hydrocarbon biradicals with *m*-phenylene bridged biradicals have the triplet ground states,⁶⁴ supporting the computational results for 2. On the other hand, DFT results indicate that the stabilities of highspin states are lower for charged molecules 4 and 5 than for neutral molecules 1-3. Very recently, dianion of bis(dimethylboron)-1,3-phenylene with the model structure 5 was synthesized, and its triplet ground state was confirmed by the ESR technique.⁶⁰ Triarylmethyl-based biradicals with [3,3'] and [3,4']-biphenyl as the spin coupling units were also synthesized, and the former was found to be the singlet state with the S-T gap= -43 cm^{-1} ,⁶¹ while the latter was the triplet ground state. The ESR experiment has already demonstrated that a [3,3']-biphenyl isomer with bis(phenylmethylene) has the singlet ground state.⁶ These observations are wholly consistent with the calculated results for 7 in Table IV. Ground states for alkyl substituted Schlenk hydrocarbon biradicals with the structure 2 were found to be triplet or singlet, depending on conformations of radical substituents.⁶⁴ This finding is consistent with the calculated results for internally twisted biradicals 2.

B. Possibilities of high-spin polymers and dendrimers

The present computational results in Tables I–VI clearly demonstrated that an *m*-phenylene skeleton is a strong ferromagnetic coupling unit because of both Coulombic exchange (K_{ab}) (Hund's rule) and spin polarization effects, and therefore neutral carbon radicals and ion radicals $(B^- \text{ and } N^+)$ generated by doping in Fig. 2 can be utilized as spin sources for organic magnetic polymers, ladders, and sheet, as illustrated by 8-16 in Fig. 12. From the spin vector models in Fig. 1,¹¹ backbone-type polymers **8**, **9**, and **10** should exhibit ferromagnetic spin alignment unless coplanarity of a phenyl ring is prevented largely (see Fig. 10). Similarly, pendanttype polymers 11 and 12 should be ferromagnetic. The ladder 13 has the interchain antiferromagnetic spin alignment because of the weak antiferromagnetic exchange interaction via the spin polarization mechanism, as shown for the [3,3']isomer of 7 in Table V, while the ladders 14 and 15 should have the high-spin ground state. The two-dimensional sheet 16 is also predicted to be ferromagnetic. Recently, an oligomer with type 14 was synthesized, showing the high-spin ground state.⁶³ This encourages further experimental and theoretical investigations of magnetic polymers. Present computations indicate that conformations of magnetic polymers become more and more important with elongation of the polymer length.

In the past decades, many dendrimerlike macromolecules have been synthesized extensively.^{99,100} However, synthesis of high-spin dendrimers are now limited, though extensive experiments have been performed by the Rajca group.⁶⁰⁻⁶⁵ Many possibilities of ferro- and ferrimagnetic spin dendrimers are conceivable from the computational results in Tables I-VI. Figure 13 illustrates several examples (17-23) of such spin dendrimers. Both ferro- and ferrimagnetic denderimers are possible, depending on network structures, as illustrated by spin vector models. For example, 17, 18, 20, 21, and 23 are ferromagnetic because of *m*-phenylene-type spin networks, while **19** and **22** are ferrimagnetic in conformity with *p*-phenylene-type networks. Radical sites in these dendrimers could be formed by electron or hole doping. Very recently Rajca et al. synthesized 23 and demonstrated the high-spin ground state.⁶² Mesoscopic spin dendrimers may be realized in this direction.

C. Concluding remarks

About 15 years ago,¹¹ *ab initio* UHF/STO-3G calculations were performed for several units with radical groups in order to elucidate the sign and magnitude of throughbond effective exchange integrals (J_{ab}) between radical sites. Such qualitative calculations were useful enough for the elucidation of possibilities of magnetic modification of conduct-



FIG. 13. Possible *m*-phenylene skeletons as coupling units for extended systems of organic magnetic dendrimers.

ing polymers such as polyphenylenevinylene and polydiacetylene. However, calculated $|J_{ab}|$ values were too large, actually about one order, as compared with the J_{ab} values estimated by experiments. Post-UHF calculations such as UCCSD(T) and UQCISD(T) were necessary for significant improvement of them.²⁹ Alternately, large-scale UNO CASCI or CASSCF by the use of 6-31G* were used to reproduce the experimental J_{ab} values.²⁹ However, these methods are hardly applicable to polyradicals, and magnetic oligomers. Therefore, we have employed a semiempirical INDO UHF method for computations of J_{ab} values for such large molecules.^{30,31} The method is rather useful because of moderate overestimation of the spin polarization effects.

Here, we have examined the applicabilities of DFT computations to several key problems in molecular magnetism: (1) full geometry optimizations of polyradicals, (2) predictions of high- and low-spin energy gaps, and effective exchange integrals, (3) variations of magnetic properties in isoelectronic series (neutral carbon, cation radical, and anion radical), (4) changes of effective exchange integrals with molecular deformations, and (5) size dependency of the effective exchange integral. The present DFT computations of m-phenylene bridged biradicals and polyradicals have demonstrated that DFT is indeed promising for a theoretical investigation of throughbond effective exchange interactions in large polyradical species. However, BLYP and B3LYP predict the reverse signs of the effective exchange integrals in the case of [2,3'] and [2,5'] isomers of **7**. This may be a warning for describing rapid conclusions on DFT calculations. At least, careful examinations of other exchange and correlation functionals would be necessary to elucidate general applicabilities of DFT methods for radical species. They will be thoroughly performed in Part II of this series.

ACKNOWLEDGMENTS

This work has been partially supported by Grants-in-Aid for Scientific Research on Priority Areas (No. 283, "Innovative synthetic reactions" and No. 401, "Metal assembled complexes") from the Ministry of Education, Science, Sports, and Culture, Japan. One of the authors (M.M.) was also supported by Research Fellowships of the Japan Society for the Promotion of Science for Young Scientists.

- ¹J. S. Miller, A. J. Epstein, and W. M. Reiff, Chem. Rev. 88, 201 (1988).
 ²D. Gatteschi, O. Kahn, J. S. Miller, and F. Palacio, in *Magnetic Molecular Materials* (Kluwer Academic, Dordrecht, 1991).
- ³J. S. Miller and A. J. Epstein, Angew. Chem. Int. Ed. Engl. **33**, 385 (1994).
- ⁴A. Rajca, Chem. Rev. **94**, 871 (1994).
- ⁵O. Kahn, in *Magnetism: A Supramolecular Function*, NATO ASI Series C (Kluwer Academic, Dordrecht, 1996), Vol. 484.
- ⁶K. Itoh, in *Molecular Magnetism* (Gakkai Shuppann Center, Tokyo, 1996) (in Japanese).
- ⁷ The Chemical Society of Japan, in *Kikan Kagaku Sosetsu*, Vol. 35, Organic Solids Based on π -Electron Systems—Molecular Desing, Electronic Properties (Charge & Spin), and Applications—(Gakkai Shuppann Center, Tokyo, 1998) (in Japanese).
- ⁸N. Mataga, Theor. Chim. Acta 10, 372 (1968).
- ⁹A. A. Ovchinnikov, Theor. Chim. Acta 47, 297 (1978).
- ¹⁰D. J. Klein, C. J. Nelin, S. Alexander, and F. A. Matsen, J. Chem. Phys. 77, 3101 (1982).
- ¹¹K. Yamaguchi, Y. Toyoda, and T. Fueno, Synth. Met. 19, 81 (1987).
- ¹²H. Fukutome, A. Takahashi, and M. Ozaki, Chem. Phys. Lett. **133**, 34 (1987).
- ¹³K. Yamaguchi, M. Okumura, J. Maki, and T. Noro, Chem. Phys. Lett. 207, 9 (1993).
- ¹⁴S. Yamanaka, T. Kawakami, M. Okumura, and K. Yamaguchi, Chem. Phys. Lett. 233, 257 (1995).
- ¹⁵N. Tyutyulkov, Pure Appl. Chem. **68**, 345 (1996).
- ¹⁶See also, for examples, Refs. 1–7.
- ¹⁷C. A. Hutchison, Jr. and B. W. Mangum, J. Chem. Phys. 29, 952 (1958).
- ¹⁸K. Itoh, Chem. Phys. Lett. 1, 235 (1967).
- ¹⁹E. Wasserman, R. W. Murray, W. A. Yager, A. M. Teozzolo, and G. Smolinski, J. Am. Chem. Soc. 89, 5076 (1967).
- ²⁰G. Kothe, K. H. Denkel, and W. Summermann, Angew. Chem. Int. Ed. Engl. 9, 906 (1970).
- ²¹ P. Doud, Acc. Chem. Res. 5, 242 (1972).
- ²²G. J. Gleichen, D. D. Newkink, and J. C. Arnold, J. Am. Chem. Soc. 95, 2526 (1978).
- ²³B. B. Wright and M. S. Platz, J. Am. Chem. Soc. 105, 628 (1983).
- ²⁴ Y. Teki, T. Takui, K. Itoh, H. Iwamura, and K. Kobayashi, J. Am. Chem. Soc. **105**, 3772 (1983).
- ²⁵ Y. Teki, T. Takui, H. Yagi, K. Itoh, and H. Iwamura, J. Chem. Phys. 83, 539 (1985).
- ²⁶H. Iwamura, Pure Appl. Chem. 58, 187 (1986).
- ²⁷T. Takui, S. Kita, S. Ichikawa, Y. Teki, T. Kinoshita, and K. Itoh, Mol. Cryst. Liq. Cryst. **176**, 67 (1989).
- ²⁸H. Iwamura, Pure Appl. Chem. **65**, 57 (1993).
- ²⁹ M. Okumura, K. Takada, J. Maki, T. Noro, W. Mori, and K. Yamaguchi, Mol. Cryst. Liq. Cryst. 233, 41 (1993).
- ³⁰D. Yamaki, S. Yamada, G. Maruta, T. Kawakami, W. Mori, and K. Yamaguchi, Mol. Cryst. Liq. Cryst. **279**, 9 (1996).
- ³¹D. Yamaki, S. Takeda, W. Mori, and K. Yamaguchi, Mol. Cryst. Liq. Cryst. **306**, 475 (1997).
- ³²P. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964).
- ³³W. Kohn and L. Sham, Phys. Rev. A **140**, 1133 (1965).

- ³⁴R. G. Parr and W. Young, *Density Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1989).
- ³⁵S. B. Trickey, in *Density Functional Theory of Many-Fermion Systems*, Advances in Quantum Chemistry (Academic, San Diego, 1990), Vol. 21.
- ³⁶J. K. Labanowski and J. W. Andzelm, in Density Functional Methods in Chemistry, (Springer-Verlag, New York, 1991).
- ³⁷J. M. Seminario and P. Politzer, in *Modern Density Functional Theory: A Tool for Chemistry*, Theoretical and Computational Chemistry (Elsevier, Amsterdam, 1995), Vol. 2.
- ³⁸J. M. Seminario, in Ref. 37, Vol. 4.
- ³⁹ M. Mitani, Y. Takano, D. Yamaki, Y. Yoshioka, and K. Yamaguchi, Mol. Cryst. Liq. Cryst. **335**, 613 (1999).
- ⁴⁰C. I. Ivanov, N. Tyutyulkov, and S. Karabunarliev, J. Magn. Magn. Mater. **92**, 171 (1990).
- ⁴¹ K. Mullen, M. Baumgarten, N. Tyutyulkov, and S. Karabunarliev, Synth. Met. 40, 127 (1991).
- ⁴²N. Tyutyulkov, S. Karabunarliev, K. Mullen, and M. Baumgarten, Synth. Met. **52**, 71 (1992).
- ⁴³ N. Tyutyulkov, F. Dietz, K. Mullen, M. Baumgarten, and S. Karabunarliev, Theor. Chim. Acta 86, 353 (1993).
- ⁴⁴ N. Tyutyulkov, F. Dietz, K. Mullen, M. Baumgarten, and S. Karabunarliev, Chem. Phys. **189**, 83 (1994).
- ⁴⁵T. Hughbanks and M. Kertesz, Mol. Cryst. Liq. Cryst. 176, 115 (1989).
- ⁴⁶T. Hughbanks and K. A. Yee, in Ref. 2, pp. 133–144.
- ⁴⁷K. Tanaka, T. Shichiri, and T. Yamabe, J. Mol. Struct.: THEOCHEM 188, 313 (1989).
- ⁴⁸ K. Yoshizawa, A. Chano, A. Ito, K. Tanaka, and T. Yamabe, Synth. Met. 52, 377 (1992).
- ⁴⁹K. Yoshizawa, A. Takata, K. Tanaka, and T. Yamabe, Polym. J. (Singapore) 24, 857 (1992).
- ⁵⁰ K. Yoshizawa, K. Tanaka, and T. Yamabe, Synth. Met. **60**, 279 (1993).
- ⁵¹ K. Yoshizawa, K. Tanaka, and T. Yamabe, J. Phys. Chem. 98, 1851 (1994).
- ⁵²B. O. Roos, in *Lecture Notes in Quantum Chemistry*, Lecture Notes in Chemistry (Springer-Verlag, Berlin, 1992).
- ⁵³B. O. Roos, in *Lecture Notes in Quantum Chemistry II*, Lecture Notes in Chemistry (Springer-Verlag, Berlin, 1994), Vol. 64.
- ⁵⁴S. Yamanaka, M. Okumura, K. Yamaguchi, and K. Hirao, Chem. Phys. Lett. 225, 213 (1994).
- ⁵⁵C. Pisani, R. Dovesi, and C. Roetti, *Hartree–Fock Ab Initio Treatment of Crystalline Systems*, Lecture Notes in Chemistry (Springer-Verlag, Berlin, 1988), Vol. 48.
- ⁵⁶C. Pisani in *Quantum-Mechanical Ab-Initio Calculation of the Properties* of Crystalline Materials, Lecture Notes in Chemistry (Springer-Verlag, Berlin, 1996).
- ⁵⁷R. Dovesi, V. R. Saunders, C. Roetti, M. Causà, N. M. Harrison, R. Orlando, and E. Aprà, CRYSTAL95 User's Manual, University of Trino, Trino, 1996.
- ⁵⁸ M. Nishino, S. Yamanaka, Y. Yoshioka, and K. Yamaguchi, J. Phys. Chem. A **101**, 705 (1997).
- ⁵⁹Y. Takano, T. Soda, Y. Kitagawa, Y. Yoshioka, and K. Yamaguchi, Chem. Phys. Lett. **301**, 309 (1999).
- ⁶⁰ A. Rajca, S. Rajca, and S. R. Desai, J. Chem. Soc. Chem. Commun. 1957 (1995).
- ⁶¹A. Rajca and S. Rajca, J. Am. Chem. Soc. 118, 8121 (1996).
- ⁶²A. Rajca, S. Rajca, and S. R. Desai, J. Am. Chem. Soc. 117, 806 (1995).
- ⁶³A. Rajca, K. Lu, and S. Rajca, J. Am. Chem. Soc. **119**, 10335 (1997).
- ⁶⁴A. Rajca and S. Rajca, J. Chem. Soc., Perkin Trans. 1, 1077 (1998).
- ⁶⁵ A. Rajca, J. Wongsriratankul, S. Rajca, and R. Cerny, Angew. Chem. Int. Ed. Engl. **37**, 1229 (1998).
- ⁶⁶L. Salem, *Electrons in Chemical Reactions: First Principles* (Wiley, New York, 1982), Chap. 7.

- ⁶⁷K. Yamaguchi, Chem. Phys. Lett. **30**, 288 (1975).
- ⁶⁸K. Yamaguchi, Chem. Phys. Lett. **34**, 434 (1975).
- ⁶⁹ K. Yamaguchi, S. Yamanaka, M. Nishino, Y. Takano, Y. Kitagawa, H. Nagao, and Y. Yoshioka, Theor. Chem. Acc. **102**, 328 (1999), and references therein.
- ⁷⁰K. Yamaguchi and H. Fukutome, Prog. Theor. Phys. 54, 1599 (1975).
- ⁷¹K. Yamaguchi, Int. J. Quantum Chem. 18, 101 (1980).
- ⁷²S. Yamanaka, T. Kawakami, S. Yamada, H. Nagao, M. Nakano, and K. Yamaguchi, Chem. Phys. Lett. **240**, 268 (1995).
- ⁷³K. Yamaguchi and T. Fueno, Chem. Phys. **19**, 35 (1977).
- ⁷⁴K. Yamaguchi, Chem. Phys. 29, 117 (1978).
- ⁷⁵ J. P. Predew, A. Savin, and K. Burke, Phys. Rev. A 51, 4531 (1995).
- ⁷⁶P. W. Anderson, Solid State Phys. **14**, 99 (1963).
- ⁷⁷ K. Yamaguchi, H. Fukui, and T. Fueno, Chem. Lett. 625 (1986).
- ⁷⁸ K. Yamaguchi, T. Tsunekawa, Y. Toyoda, and T. Fueno, Chem. Phys. Lett. **143**, 371 (1988).
- ⁷⁹S. Yamanaka, T. Kawakami, H. Nagao, and K. Yamaguchi, Chem. Phys. Lett. 231, 25 (1994).
- ⁸⁰ GAUSSIAN 94, M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, Gaussian, Inc., Pittsburgh PA, 1995.
- ⁸¹A. D. Becke, Phys. Rev. A 38, 3098 (1988).
- ⁸²A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).
- ⁸³C. Lee, W. Yang, and R. G. Parr, Phys. Rev. B 37, 785 (1988).
- ⁸⁴R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys. 54, 724 (1971); W. J. Hehre and J. A. Pople, *ibid.* 56, 4233 (1972).
- ⁸⁵W. J. Hehre, R. Ditchfield, and J. A. Pople, J. Chem. Phys. **56**, 2257 (1972); P. C. Hariharan and J. A. Pople, Theor. Chim. Acta **28**, 213 (1973); J. D. Dill and J. A. Pople, J. Chem. Phys. **62**, 2921 (1975).
- ⁸⁶T. Kawakami, S. Yamanaka, Y. Takano, Y. Yoshioka, and K. Yamaguchi, Bull. Chem. Soc. Jpn. **71**, 2097 (1998).
- ⁸⁷ See EPAPS Document No. E-JCPSA6-113-308029 for the optimized geometrical of a radical group and a benzene ring for low- and high-spin states of *m*-phenylene molecules **1–6** by UBLYP/4-31G (listed in Table SI). This document may be retrieved via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html) or from ftp.air.org in the directory /epaps/. See the EPAPS homepage for more information.
- ⁸⁸ Total energies for the low- and high-spin states and energy gaps of 1–6 by UBLYP, UHF and UB3LYP methods are listed in Table SII of EPAPS (see Ref. 87).
- ⁸⁹Energy levels and splitting widths of singly occupied molecular orbitals for high-spin states of 1–5 by UBLYP, UHF, and UB3LYP methods are listed in Table SIII of EPAPS (see Ref. 87).
- 90 K. Yamaguchi and T. Fueno, Chem. Phys. Lett. 159, 465 (1989).
- 91 Total energies, total angular momentum and effective exchange integrals for polycarbene oligomers linked with *m*-phenylene bridges **8** by UHF, UB3LYP, and UBLYP methods are listed in Table SIV of EPAPS (see Ref. 87).
- 92 U. von Barth and L. Hedin, J. Phys. C 5, 1629 (1972).
- ⁹³S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. 58, 1200 (1980).
- ⁹⁴J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
- ⁹⁵J. P. Perdew, Phys. Rev. B **33**, 8822 (1986); **34**, 7406 (1986).
- ⁹⁶J. P. Perdew and Y. Wang, Phys. Rev. B **33**, 8800 (1986); **40**, 3399 (1989); **45**, 13 244 (1992).
- ⁹⁷ J. P. Pewdew, in *Electronic Structure of Solids 1991*, edited by P. Ziesche and H. Eschrig (Akademie-Verlag, Berlin, 1991), pp. 11–20.
- ⁹⁸ J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396 (1997).
- ⁹⁹ A. W. Bosman, H. M. Janssen, and E. W. Meijer, Chem. Rev. **99**, 1665 (1999).
- ¹⁰⁰G. R. Newcome, E. He, and C. N. Moorefield, Chem. Rev. **99**, 1689 (1999).