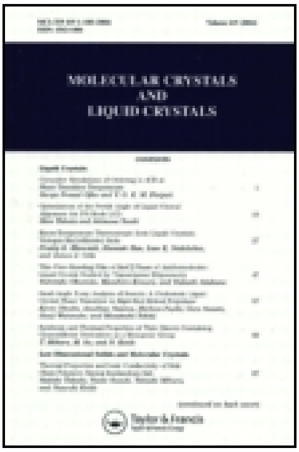

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Theoretical Study of Spin Alignment of Organic High-Spin Molecules in Terms of VB Description

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THEORETICAL STUDY OF SPIN ALIGNMENT OF ORGANIC HIGH-SPIN MOLECULES IN TERMS OF VB DESCRIPTION

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Abstract Spin alignment in organic high-spin molecules and their topological isomers with both unpaired π and σ electrons has been studied by the exact numerical solutions of the valence-bond Heisenberg Hamiltonian and of the UHF calculation of the generalized Hubbard Hamiltonian. In order to clarify the main path-way of the spin correlation, the spin configurations with large coefficients have been extracted from the eigenfunctions in the ground and low-lying excited states of the Heisenberg Hamiltonian. The contributions of their spin configurations to the total spin energy have been calculated. Using this procedure, important spin configurations (important path-way of exchange correlations) of the ground and low-lying excited states have been clarified. A similar treatment can be carried out by the generalized Hubbard Hamiltonian. Thus, the VB decompositions of UHF solutions of the generalized Hubbard model have been carried out using the total α spin and total β spin densities on each carbon site in the UHF total wavefunction. The VB picture so obtained is also qualitatively in agreement with the results of the valence-bond Heisenberg Hamiltonian. The detailed mechanism in the spin alignment has been discussed in terms of the VB description by these two model Hamiltonian approaches.

INTRODUCTION

High-spin polycarbenes, which are typical examples of organic high-spin systems, are very important in spite of their highly chemical reactivity, from the viewpoint of organic magnetism as well as spin ordering/spin control on the basis of the following reasons.[1] (i) One of the most prominent features of the high-spin polycarbenes is multielectron open shell systems in the ground or low-lying excited states which arise both from the degenerate delocalized π orbitals and from the σ dangling orbitals localized on the divalent carbon atoms. The latter orbitals are nearly degenerate with the highest half-filled π orbitals. (ii) The degeneracy of their π orbitals is governed by the particular connectivity of the π electron network, i.e., the topology of the π electron network. We have studied a series of high-spin polycarbenes as well as their π topological isomers, which have been designed by exploiting their π electron networks.[2] The π-topological isomers that we mean are molecules which have a difference only in the point of the topology of its π electron network (that is, there is a difference in the linked positions of its π bonds). We have already reported the spin alignment for these polycarbenes as studied by the UHF calculations based on the generalized Hubbard Hamiltonian[3] and by the valence-bond Heisenberg Hamiltonian[4] which has been applied to π-electron networks by Ovchinnikov[5] and Klein[6].

In the present work, we have carried out the decompositions of the eigenfunctions of the low-lying spin states, which have been obtained from the numerical diagonalization of the valence-bond Heisenberg Hamiltonian and from the UHF SCF calculations on the generalized Hubbard Hamiltonian. The main path-ways on the spin correlation and the important spin configurations with large coefficients for several low-lying spin states have been clarified, by using the decomposition. The detailed mechanism of the spin correlation and the role of the π-topology in the intramolecular spin alignment of organic high-spin systems are discussed from the theoretical viewpoint.

MODEL HAMILTONIAN AND VB DECOMPOSITION

Valence-bond Heisenberg Model

As a theoretical model which takes the spin correlation of many open-shell electrons in the polycarbenes into account, we have chosen the following valence-bond Heisenberg Hamiltonian[4,7]:

$$\mathcal{H} = -2\sum J_{ij}^{\mathrm{eff}} \boldsymbol{S}_i \cdot \boldsymbol{S}_j, \qquad (1)$$

where J_{ij}^{eff} is the effective exchange integral approximately given in the case of $U_{ii} >> T_{ij}$ by

$$J_{ij}^{\mathrm{eff}} = -2|T_{ij}|^2/U_{ii} + J_{ij}. \qquad (2)$$

We have estimated $J_{\pi\pi}^{\mathrm{eff}} = -1.5$ eV and $J_{\sigma\pi}^{\mathrm{eff}}/J_{\pi\pi}^{\mathrm{eff}} = -0.2$.[4] The valence-bond Hamiltonian has been solved by a numerical diagonalization of the matrix derived from the full basis set of the spin system $|S^z{}_1\ S^z{}_2\ S^z{}_3\ \ldots\ S^z{}_N>$, in which the subscripts denote the number of the carbon sites. In order to clarify which spin configurations are important, the coefficients of the basis vectors of the spin system have been examined for the eigenfunctions of the low-lying spin states. In addition, the Hamiltonian matrix in the sub-spin-space, which is derived using a limited number of the basis sets with the small number of node of spin correlation discussed later, was also solved by a numerical diagonalization. Using this procedure, the energetical contribution of each subspace to the total exchange energy has also been discussed.

Generalized Hubbard Model

As the other model Hamiltonian approach, unrestricted Hartree-Fock (UHF) calculations based on a generalized Hubbard model have been carried out, which give rather satisfactory and complementary descriptions for the spin structures of organic high-spin polycarbenes.

The generalized Hubbard model Hamiltonian[3,8,9] is given by

$$\mathcal{H} = -T \sum_{m,m',\sigma} a^{\dagger}{}_{m',\sigma}\, a_{m,\sigma} + (U/2)\sum_{m,\sigma} n_{m,-\sigma} n_{m,\sigma} - J\sum_{k,m}[S^z{}_k S^z{}_m + (S^+{}_k S^-{}_m + S^-{}_k S^+{}_m)], \ . \qquad (3)$$

with $n_{m,\sigma} = a^{\dagger}{}_{m,\sigma}\, a_{m,\sigma}$ and $\sigma = +1/2$. The subscripts m and k refer to the pπ and σ sites, respectively. T is the π

electron transfer integral between adjacent carbon sites, and U and J are the effective on-site Coulomb repulsion and the exchange integral between the s and π electrons at the divalent carbon atoms, respectively. In this calculation, these parameters have been taken as $U/T = 2.0$ and $J/T = 0.25$. The values have been shown to be most appropriate for a series of high-spin polycarbenes such as *m*-phenylen-bis(phenylmethylene). The resulting UHF total wavefunction is decomposed into VB components using the following procedure.

Valence-bond decomposition of UHF wavefunctions

The VB decompositions of the UHF solutions have been carried out using total α spin ($\rho_i(\alpha)$) and total β spin densities ($\rho_i(\beta)$) on each carbon site in the UHF wavefunction. Since we have used a second quantized representation in eq.(3), the antisymmetric property of the wavefunction, which is written as a Slater determinant, is taking into account. Moreover, the total occupation number (n_i) of the electrons in the pπ and σ orbitals on each i-th carbon site should be unity in the case of the neutral molecule without hetero atoms. These features lead to the following relationship between UHF total wavefunction $|\Psi\rangle$ written by a single Slater determinant and a VB basis $|\Phi_{VB}\rangle$ of its wavefunction.

$$n_i = \rho_i(\alpha) + \rho_i(\beta) = 1, \tag{4}$$

$$\langle\Phi_{VB}|\Psi\rangle = \sqrt{\rho_1(\alpha)\rho_2(\alpha)\rho_3(\beta)\cdots}, \tag{5}$$

where $|\Phi_{VB}\rangle = |\uparrow\uparrow\downarrow\cdots\rangle$. Therefore, we can easily decompose the UHF total wavefunction into the corresponding VB components in case of the Hubbard Hamiltonian of neutral molecules.

RESULTS AND DISCUSSION

Valence-bond Heisenberg Model Hamiltonian Approach

Figure 1 shows a series of polycarbenes with various spin-coupling units and the corresponding diagrammatic description, which has been theoretically studied in this study. In the diagrammatic description, a straight line

(——) denotes a antiferromagnetic interaction ($J_{\pi\pi}$) arising from the adjacent pπ - pπ overlap, and a broken line (----) a ferromagnetic one-center $\sigma\pi$ interaction ($J_{\sigma\pi}$) at the carbene site. In the present calculation, only the nearest-neighbor and one-center interactions are taking into account. The exact energy eigenvalues for these coupling units for the ground stats and the low-lying excited states, together with their total S values., which were obtained by the numerical diagonalization using the full basis sets of the spin system, are given in Table 1. The energy values are given in the units of $J = |J_{\pi\pi}|$. These predicted spin states are well in agreement with the experimental results of the corresponding polycarbenes, in which both the end carbons are substituted by phenyl(methylene) groups, as shown in the table. We have already reported a part of the results in Table 1 (energy separations and spin densities of some of molecules **1-3**,**4**, and **8**).[4] Klein also published similar results for **1** and **2**.[6]

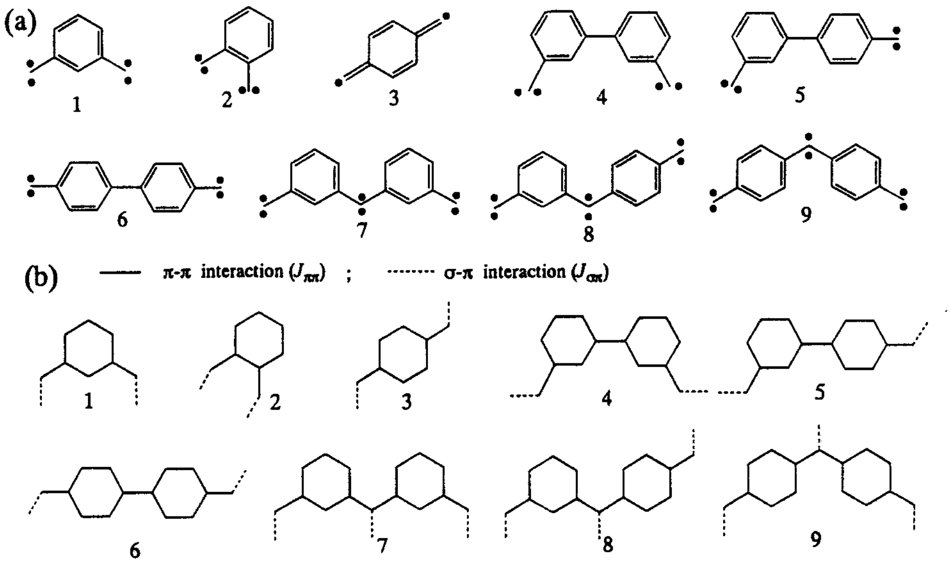


FIGURE 1 Several spin coupling units of high-spin polycarbenes and their topological isomers

Here, we define a node of spin correlation as follows. In the case of antiferromagnetic coupling bond (——), the spin configuration ↑——↓ is favorable from the energetical view point. Therefore, we define ↑——↓ as a nodeless spin configuration and the other spin configurations like ↑——↑ as spin configurations with a node. In the case of a ferromagnetic coupling bond (——), the definition is vice versa. The important spin configurations have been examined in the case of n = 0 - 6 (n: the number of the nodes of the spin correlation).

TABLE 1 Energy and spin states of the ground and low-lying excited states

	VB (Heisenberg $H = -2\Sigma J_{ij} S_i S_j$)		Experimental	
	G	1st EX.	G	1st EX.
1	-6.7946 (2)	-6.6823 (1)	2	–
2	-7.0988 (0)	-7.0718 (1)	–	–
3	-7.0682 (0)	-7.0430 (1)	0	1
4	-12.5974 (0)	-12.5744 (1)	0	1
5	-12.6013 (2)	-12.5311 (1)	2	–
6	-12.74701 (0)	-12.7227 (1)	0	1
7	-13.3612 (3)	-13.2830 (2)	3	–
8	-13.5444 (1)	-13.5037 (2)	1	2
9	-13.6456 (1)	-13.6012 (0)	–	–

The obtained important spin configurations of **1** and **3** are given in Figure 2. The energetical contributions to the total spin-exchange energy are given in the inserted tables in the figures. There exists only one nodeless spin configuration denoted by Φ_1 in **1**, which gives ca. 62% of the total spin-exchange energy of its ground state. The coefficient of Φ_1 in the ground state wavefunction is 0.6447, which is also very large compared with other configurations. This largest spin configuration agrees with that predicted by the simple VB picture. Thus, the alternant spin-up and spin-down network (pseudo π-spin density wave) is formed in the π electron network. In the case of **3**, there exist two equivalent nodeless spin configurations, Φ_{1+} and Φ_{1-}, in the ground state. These nodeless spin configurations also have the largest coefficients in the ground state wavefunction. It should be noted that in the spin singlet (S=0) ground state of **3**, there always exist a pair of the equivalent configurations denoted by suffix + and -.

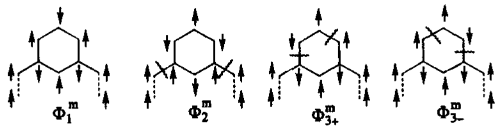
As shown in the tables inserted, the energetical contributions arising from the noded spin configurations are smaller than those of the nodeless ones. In addition, when the number of the nodes increase, the energy contribution of their spin configurations decrease as expected from the energetical point of view.

FIGURE 2 Energetical contributions and the several spin configuratons with large coefficients of **1** and **3**

—— ; Node of the Spin Correlation

(a)

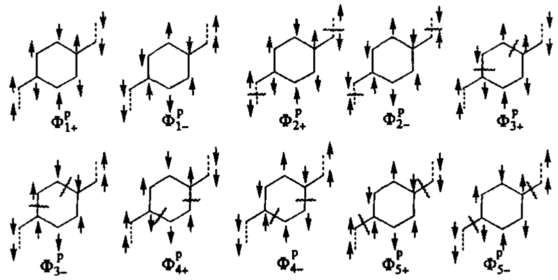
Exact Solution	n = 0 (1)	n ≤ 2 (4)	n ≤ 3 (18)	n ≤ 4 (41)
-6.795 *J*	-4.200 *J*	-4.932 *J*	-6.309 *J*	-6.499 *J*



$$|\Psi_G^m> = -0.6447\Phi_1^m + 0.1372\Phi_2^m + 0.2568(\Phi_{3+}^m + \Phi_{3-}^m) + \cdots$$

(b)

Exact Solution	n = 0 (2)	n ≤ 2 (10)	n ≤ 3 (54)	n ≤ 4 (122)
-7.068 *J*	-4.200 *J*	-4.932 *J*	-6.446 *J*	-6.742 *J*



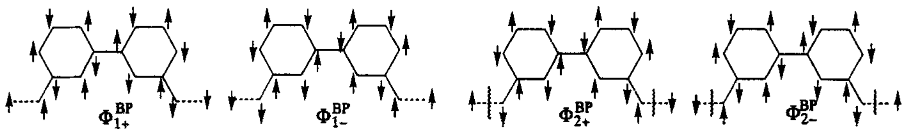
$$|\Psi_G> = -0.3232(\Phi_{1+}^p - \Phi_{1-}^p) + 0.2355(\Phi_{2+}^p - \Phi_{2-}^p) + 0.1611(\Phi_{3+}^p - \Phi_{3-}^p) + 0.1611(\Phi_{4+}^p - \Phi_{4-}^p) + 0.0668(\Phi_{5+}^p - \Phi_{5-}^p) + \cdots$$

Several important spin configurations in the ground (S=0) and low-lying first excited states (S=1) of **4** are shown in Figure 3. In the spin singlet (S=0) ground state, there exist a pair of the equivalent configurations, similar to the case of **3**. The nodeless spin configurations, Φ_{1+} and Φ_{1-}, also plays the main contributions to the wavefunction in the ground state, in agreement with the simple VB picture. On the other hand, these nodeless configurations give no contribution in the first excited state. The spin configurations, Φ^{EX}_{1+} and Φ^{EX}_{1-}, with only one node given in Figure 3(b) make the main contributions in the excited triplet state, and the other configurations with one node of the spin correlation are not contained. On the contrary, the spin configurations with only one node play no contribution in the singlet ground state, as easily expected from the symmetrical properties of the alternant hydrocarbons. In cases of **3** and **4**, the coefficients of the dominant configurations are not so large compared with that of **1**, which is a ground state high-spin (S=2) molecule. This small coefficients of the dominant configurations leads to a small energy difference between the ground state and the excited spin states of **3** and **4** (see Table 1). This finding gives a theoretical interpratation of the low-lying triplet excited states of the dicarbenes with the spin coupling units corresponding to **3** and **4**.

(a) Ground State (S=0)

----- ; Node of the Spin Correlation

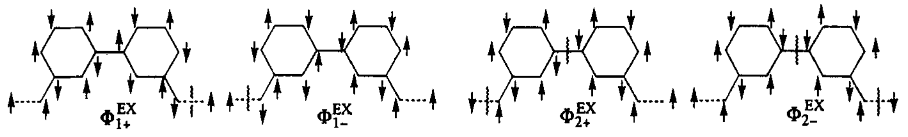
Exact Solution	n = 0 (2)	n ≤ 2 (18)	n ≤ 3 (108)	n ≤ 5 (1242)
-12.597 *J*	-7.700 *J*	-8.936 *J*	-10.598 *J*	-11.596 *J*



$|\Psi_G^{BP}\rangle = -0.2216(\Phi_{1+}^{BP} - \Phi_{1-}^{BP}) + 0.1084(\Phi_{2+}^{BP} - \Phi_{2-}^{BP}) + \cdots$

(b) First Excited State (S=1)

Exact Solution	n = 0 (0)	n = 1 (2)	n ≤ 2 (22)	n ≤ 3 (94)	n ≤ 4 (328)
-12.574 *J*	—	-7.500 *J*	-8.047 *J*	-9.120 *J*	-10.551 *J*



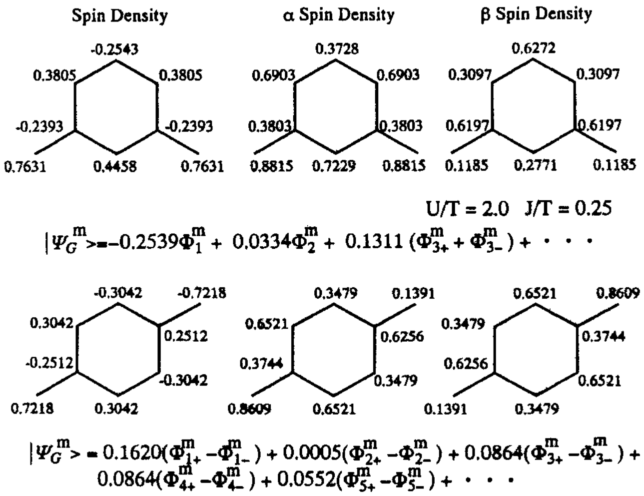
$|\Psi_G^{EX}\rangle = -0.2151(\Phi_{1+}^{EX} - \Phi_{1-}^{EX}) + 0.0941(\Phi_{2+}^{EX} - \Phi_{2-}^{EX}) + \cdots$

FIGURE 3 Energetical contributions (see text) and the several spin configuratons with large coefficients of 4

We have also examined other molecules shown in Figure 1 using the same procedure. The results are similar to those described above. Thus, the high spin molecules, **5** and **7**, have large coefficients of the nodeless spin configurations corresponding to the simple VB structure in its ground state. In their topological isomers, **6**, **8**, and **9**, the coefficients of the dominant configurations are not so large, leading to the low-lying higher spin excited states above the ground states. The procedures used in this paper in order to clarify the main path-way of the exchange spin correlations in molecules can be easily extended to other Hamiltonians. For example, in the next section we describe the results of the calculation based on the already-mentioned VB decomposition of UHF wavefunctions.

VB Decomposition Approach based on Generalized Hubbard Hamiltonian

In this paper, the results of **1** and **3** are briefly described. As mentioned above, the present VB decomposition method is easily applicable to the Hartree-Fock wavefunctions of other Hamiltonians. Figure 4 shows the total α and β spin densities and the ordinary spin densities, which correspond the deference between the total α and β spin densities. The coefficients of each VB component, $<\Phi_{VB}|\Psi>$, in the total wavefunction have been calculated by eq. (5) shown in the



$$|\Psi_G^m> = -0.2539\Phi_1^m + 0.0334\Phi_2^m + 0.1311\,(\Phi_{3+}^m + \Phi_{3-}^m) + \cdot\cdot\cdot$$

$$|\Psi_G^m> = 0.1620(\Phi_{1+}^m - \Phi_{1-}^m) + 0.0005(\Phi_{2+}^m - \Phi_{2-}^m) + 0.0864(\Phi_{3+}^m - \Phi_{3-}^m) + 0.0864(\Phi_{4+}^m - \Phi_{4-}^m) + 0.0552(\Phi_{5+}^m - \Phi_{5-}^m) + \cdot\cdot\cdot$$

FIGURE 4 VB decompositions of the total UHF wavefunctions of **1** and **2**

Figure 4. Here, we chose the same VB components, as given in Figure 2, in order to compare the results with those of Figure 2. In both cases of **1** and **3**, the spin configurations predicted by a simple VB picture (pseudo π-spin density wave state) are the largest components, in agreement with the results of the valence-bond Heisenberg Hamiltonian approach although the coefficients are smaller. Most of other important spin configurations also agree with the results of the Heisenberg Hamiltonian approach. These results show that the simple VB decomposition procedure used in this paper also gives a qualitative estimation of the VB components in the Hartree-Fock wavefunctions and is useful for the discussion of the spin alignment of organic high-spin molecules and their topological isomers, since the procedure is easily applicable to the actual large molecules.

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REFERENCES

1. J. S. Miller and D. A. Dougherty eds., Proceedings of the Symposium on Ferromagnetic and High-Spin Molecular Based Materials, 197th ACS Meeting, Dallas USA (1989); Mol. Cryst. Liq. Cryst., 176, 1-562 (1989).
2. Y. Teki et al., Mol. Cryst. Liq. Cryst., 232, 261 (1993); ibid., 232, 271 (1993).
3. Y. Teki et al., Chem. Phys. Lett., 141, 201 (1987).
4. Y. Teki et al., Chem. Phys. Lett., 142, 181 (1987).
5. A. A. Ovchinnikov, Theor. Chim. Acta. (Berl.), 47, 297 (1978).
6. S. A. Alexander and D. J. Klein, J. Am. Chem. Soc., 110, 3401 (1988).
7. J. A. R. Coope, Chem. Phys. Lett., 1, 77 (1967).
8. J. Hubbard, Proc. Roy. Soc., 276A, 238 (1963); R. M. White, Quantum Theory of Magnetism, Springer p.139 (1983).
9. K. Nasu, Phys. Rev., B33, 330 (1986).