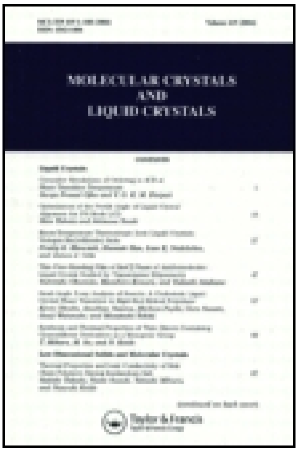

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Role of the Spin Correlation and Weakly Interacting Model for the Spin Alignment in Organic High-Spin Molecules

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ROLE OF THE SPIN CORRELATION AND WEAKLY INTERACTING MODEL FOR THE SPIN ALIGNMENT IN ORGANIC HIGH-SPIN MOLECULES

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Abstract In order to clarify the role of the electron-spin correlation and that of the topology in the π electron network, a typical organic high-spin molecule, its topological isomer, and a model compound of organic ferrimagnets have been investigated in terms of the spin density distributions. It is shown that the pseudo π-SDW (spin density wave) governed by the topological nature plays important role in the stabilization of the high-spin ground state. It is also clarified that the existence of a node in the π-SDW is essential for the formation of the low-lying high-spin excited states of the topological isomer. The relationship is also derived, which predicts the spin density distributions of the ground and low-lying excited states formed by a weak interaction between two high-spin units. This relationship gives rationale for the formation of the excited triplet state of the topological isomer and for the spin density distribution characterized by an unusually large negative spin polarization in the model for the organic ferrimagnets.

INTRODUCTION

Organic high-spin polycarbenes are interesting as suitable models for organic magnetic materials[1] and as ideal model compounds for studying the mechanism of the spin alignment and spin coupling in organic systems.[1-3] One of the most prominent features of the polycarbenes is multi-electron open shell systems which arise from degenerate delocalized π orbitals and from σ dangling orbitals at divalent carbons.[3] The spin correlation among the unpaired spins via the delocalized π orbitals is most important in order to understand the spin alignment and to predict the ground and low-lying excited spin states. The aim of this paper is to clarify the physical picture of the spin alignment in organic high-spin molecules and their topological isomers.

In this work, we have studied the electronic structures of three model compounds, an organic high-spin molecule and its topological isomer, biphenyl-n,n'-bis(phenylmethylene) (I: n,n'=3,4'; II: n,n'=3,3'), and a model compound of organic ferrimagnets, III, in terms of the spin density distributions. Their intramolecular spin alignment and the role of spin correlation among the unpaired π and σ spins are investigated also theoretically by two model Hamiltonian approaches and a weakly-interacting model described.

GROUND AND LOW-LYING EXCITED SPIN STATES

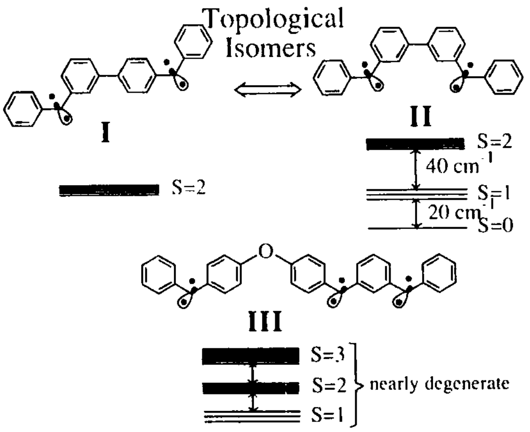


FIGURE 1 Model compounds studied in this work.

The model compounds and their spin states determined by our ESR experiments are shown in Figure 1. Molecule I has the high-spin quintet (S=2) ground state.[4] In contrast, its topological isomer II has the low-spin singlet (S=0) ground state with low-lying higher spin states (S=1 and S=2).[5] The model compound of organic ferrimagnets, III has the low-spin triplet (S=1) ground state with low-lying higher-spin states (S=2 and S=3).[6] The spin density distributions of the high-spin (S=2) ground state of I, the low-lying excited state (S=1) of II, and the low-spin triplet (S=1) ground state of III have been determined experimentally by single-crystal ENDOR spectroscopy.

EXPERIMENTAL

The synthetic work of the diazo precursors of I - III will be published elsewhere. Each diazo precursor was diluted in a host single crystal of benzophenone-d_{10}. The polycarbenes were generated at 2 - 4 K by the photolysis of the corresponding diazo precursors using the 405 nm light from an XBO 500W high-pressure mercury lamp. All the ESR and ENDOR experiments were carried out with a Bruker ESP300/350 spectrometer equipped with an Oxford variable temperature controller ESR910. The spectra of the low-lying excited state of II were observed under the thermal excitation of these excited energy levels. Other spectra were measured at ca. 2 - 4 K.

THEORETICAL

In addition to the experimental work, we have calculated the spin density distributions and the electronic states of I - III using model Hamiltonian approaches. In what follows, these model Hamiltonian approaches are briefly described.

(i) **Weakly Interacting Multiplet-Multiplet Model**

Using a model described below, we deals with the ground and the low-lying excited states which are formed by a magnetically weak interaction between two high-spin units as shown in Figure 2. The treatment is expected to be appropriate for the composite molecule such as III, which two high-spin moieties are connected each other with the oxygen-atom bridge having a closed-shell pπ orbital. This model is also good approximation for II, in which two high-spin molecules are connected each other at the carbon positions where the unpaired π orbitals (π-SOMOs) have a node on the RHF one-electron molecular orbital or the simple Hückel molecular orbital. Thus, molecule II corresponds to the disjoint case in the disjoint-nondisjoint theory by Borden and Davidson.[7]

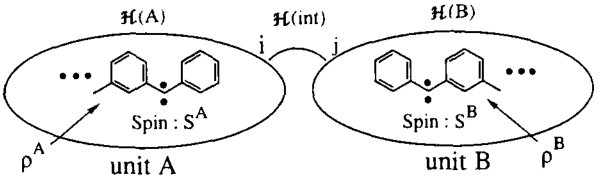


FIGURE 2 Weakly interacting multiplet-multiplet model.

The whole Hamiltonian for the system consisting of weakly interacting two units A and B with spins S^A and S^B, respectively, may be written as

$$\mathcal{H} = \mathcal{H}(A) + \mathcal{H}(B) + \mathcal{H}(\mathrm{int}), \qquad \mathcal{H}(\mathrm{int}) << \mathcal{H}(A),\ \mathcal{H}(B), \tag{1}$$

where the first (second) term is the electronic Hamiltonian consisting of both orbital parts and spin parts for the unit A(B) and the third term that for interaction. We assume the interaction term as a following Heisenberg exchange type

$$\mathcal{H}(\mathrm{int}) = -2J_{ij}^{\mathrm{eff}}\, s_i^A \cdot s_j^B. \tag{2}$$

This term arises from the effective exchange through the chemical bond (molecule II) or the superexchange interaction (molecule III). The s_i^A (s_j^B) is the spin operator of the π electron spin on the carbon site i (j) belonging to the unit A(B). The relation, $\mathcal{H}$(int) << $\mathcal{H}$(A), $\mathcal{H}$(B), is reasonable for III, since the superexchange interaction through the closed-shell pπ oxygen atomic orbital is usually small in magnitude compared with the electronic Hamiltonian, $\mathcal{H}$(A) or $\mathcal{H}$(B). As discussed latter, this relation is also valid for the disjoint type's molecules, such as molecule II. Under this condition (weak-interacting limit), we derived the following relationship for the spin densities of the whole molecule with the total spin S. The spin density ρ_i^A on the carbon site i in the interacting A unit of the whole molecule can be expressed in terms of the corresponding spin density ρ_{i0}^A in the isolated A unit molecule with the spin S^A and of the Clebsch-Gordan coefficient $C(S^A S^B S;\ m_A\ M\text{-}m_A)$:

$$\rho_i^A(S, M) = (1/S^A)\rho_{i0}^A \sum_{m_A} m_A C(S^A S^B S;\ m_A\ M\text{-}m_A)^2, \tag{3}$$

TABLE I Relationship of spin densities between resultant spin (S) and two constituent spins (S^A, S^B)

(i) S^A=S^B=1 (homo-spin system)

S=2		S=1		S=0	
unit A	unit B	unit A	unit B	unit A	unit B
ρ_i^A	ρ_i^B	$\frac{1}{2}\rho_i^A$	$\frac{1}{2}\rho_i^B$	0	0

(ii) S^A=2, S^B=1 (hetero-spin system)

S=3		S=2		S=1	
unit A	unit B	unit A	unit B	unit A	unit B
ρ_i^A	ρ_i^B	$\frac{5}{6}\rho_i^A$	$\frac{1}{3}\rho_i^B$	$\frac{3}{4}\rho_i^A$	$-\frac{1}{2}\rho_i^B$

where $S=S^A+S^B$, S^A+S^B-1, ..., $|S^A-S^B|$. Similar expression holds also for the unit B. Table I shows the relationship derived from Eq. (3) in the case of $S^A= S^B = 1$ (homo-spin system) and of S^A=2 and S^B=1 (hetero-spin system) which are the cases for II and III, respectively. We can, therefore, calculate the spin densities in the whole molecule from those of the isolated unit moieties. In this weak-interacting limit, we can also derive the energy relation among the ground and the low-lying excited spin states formed from the interacting two high-spin units, as given by

$$\mathcal{H} = E^A + E^B - J_{ex} [S(S+1) - S^A(S^A+1) - S^B(S^B+1)] \,. \tag{4}$$

The effective exchange interaction J_{ex} is expressed in terms of the spin densities, ρ_{i0}^A and ρ_{j0}^B, on the connecting sites i and j in Figure 2, and the effective exchange integral J_{ij}^{eff} in equation (2) is in the following;

$$J_{ex}= J_{ij}^{eff}\, \rho_{i0}^A \cdot \rho_{j0}^B/(4S^AS^B). \tag{5}$$

This equation corresponds to a generalization of the relation given by McConnell[8] to the arbitrary spins, S^A and S^B and to the intramolecular case.

(ii) Generalized Hubbard Model[4a,9]

As a theoretical approach clarifying the physical picture of the intramolecular spin alignment and calculating the spin density distribution of the high-spin ground state, we have adopted the UHF calculation using a generalized Hubbard model.[4a,9] The generalized Hubbard model is expressed by

$$\mathcal{H} = -T \sum a^+_{m'\sigma} a_{m\sigma} + (1/2)U \sum n_{m-\sigma} n_{m\sigma} - J \sum [S^z_k S^z_m + (S^+_k S^-_m + S^-_k S^+_m)/2] \,, \tag{6}$$

where a^+ and a are the creation and annihilation operators, respectively, and $n_{m\sigma} = a^+_{m\sigma} a_{m\sigma}$. T stands for 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 σ and π electrons at the divalent carbon atoms, respectively. We have taken these parameters as $U/T = 2.0$ and $J/T = 0.25$, the values of which we have shown to be most appropriate for a series of high-spin polycarbenes.[4a] The spin densities of the quintet ground state of I and those of the ground states of the isolated unit moieties of II and III were calculated by this approach.

(iii) Heisenberg Valence-Bond Hamiltonian Approach[10]

As an improved theoretical approach taking the spin correlation of many open-shell electrons into account, we have calculated the numerical exact solution of the valence-bond Hamiltonian[10]:

$$\mathcal{H} = -2\Sigma J_{ij}^{eff} s_i \cdot s_j, \qquad (7)$$

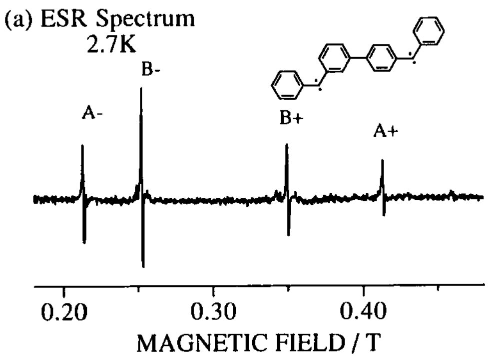
where J_{ij}^{eff} is the effective exchange integral approximately given by

$$J_{ij}^{eff} = -2|T_{ij}|^2/U + J_{ij}. \qquad (8)$$

The effective exchange integrals are estimated to be $J_{\pi\pi}^{eff} = -1.5$ eV and $J_{\sigma\pi}^{eff}/J_{\pi\pi}^{eff} = -0.2$.[10a] This model Hamiltonian has been solved by an exact numerical diagonalization of the matrix derived from the full basis set of the spin system $|s^z_1\ s^z_2\ s^z_3\ \ldots\ s^z_N\rangle$, in which the subscript denotes carbon sites.

RESULTS AND DISCUSSION

(A) Spin Density Distribution and Spin Alignment of Molecule I



(b) ^{1}H-ENDOR Spectrum

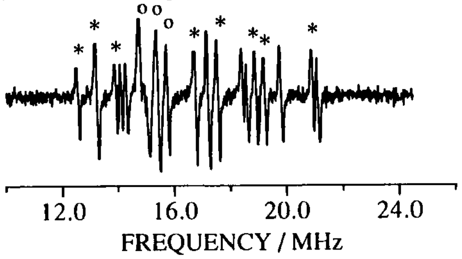


FIGURE 3 Typical ESR and ^{1}H-ENDOR Spectra of I. The external magnetic field is along the *b* axis.

Figures 3 (a) and 3(b) show a typical ESR and ^{1}H-ENDOR spectra of the quintet ground state of molecule I. The ENDOR spectrum was observed by monitoring the B+ ESR transition (Ms= 0↔+1). The eight signals labeled by the asterisk are due to the protons of the central biphenyl group. All the ^{1}H-hyperfine tensors were determined from the analysis of the angular dependence of their ENDOR frequencies in the three crystallographic planes, *ab*, *bc*, and *ca*, of benzophenone host single crystals. The π spin densities on the carbon atoms adjacent to the hydrogen atoms were obtained from the isotropic terms A_F's of their hyperfine tensors with the help of McConnell's equation $A_{Fi}=Q\rho_i^{\pi}/2S$ (Q= -66.9 MHz). Their

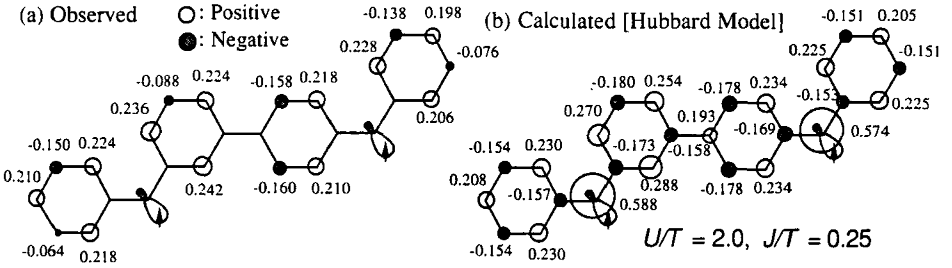


FIGURE 4 Spin density distributions in the quintet ground state of I.

observed π spin densities and the theoretical values based on the UHF Hubbard model are given in Figures 4(a) and 4(b), respectively. The spin densities on the carbon atoms without circles could not be obtained in this experiment, since they have no neighboring protons.

These spin density distributions give the following physical picture for the intramolecular spin alignment of the quintet ground state of I. As shown in Figure 5, the unpaired π electrons are distributed over the carbon skeleton with alternating the sign of the spin density from carbon to carbon, thus forming the up-and-down spin network of the π spin. We define this up-and-down network as the pseudo π-spin density wave (pseudo π-SDW), since in infinite systems the spin network forms a spin density wave.[4a] On the other hand, the two unpaired π spins in the localized σ dangling orbitals become parallel to each other as a results of the ferromagnetic coupling to the unpaired π spins at each divalent carbon site, because the one-center exchange integral J in Eq. (6) on the same carbon site is usually ferromagnetic. The π spin densities at both divalent carbon sites have the same positive sign in I, leading to the quintet ground state. Thus, this picture shows that the spin alignment in I is predominantly determined by the pseudo π-SDW formed according to the topology of its π electron network.

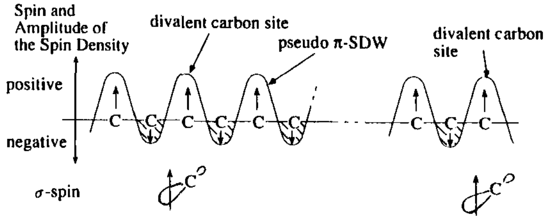


FIGURE 5 Formation of pseudo π-SDW and spin alignment.

(B) Spin Correlation and Spin Alignment of the Low-Lying Triplet Excited State of Molecule II

As shown in Figure 1, molecule II has the low-spin (S=0) ground state with the low-lying higher-spin excited states (S=1 and S=2).[5] This molecule has four unpaired spins in the nearly degenerate nonbonding π and σ orbitals as well as I. The difference in their ground-state spin multiplicities between I and II indicates that the pathway of the intramolecular spin correlation among their unpaired spins is different with each other. As mentioned above, the pseudo π-SDW can be formed with the same signs of the spin densities at the two divalent carbon sites in I. In contrast, molecule II is expected to have different signs in a pathway of the spin correlation, according to the topology of its π electron network, although the net spin density can not be detected in the singlet ground state. This is the reason why II has the low-spin ground state, in contrast to its topological isomer I.

Clarifying the spin density distribution of the low-lying excited states as well as the ground state is also important in order to understand the intramolecular spin correlation among the unpaired spins. These low-lying high-spin excited states are of great interest in connection with the molecular magnetism. Therefore, we measured the ENDOR spectra for the low-lying triplet state of II. Figure 6(a) shows a typical ESR spectrum observed at 34 K. A ^{1}H-ENDOR spectrum in Figure 6(b) was observed for the thermally excited triplet state at 15K by monitoring the T+ ESR transition (Ms= $0 \leftrightarrow +1$). In order to determine the π and σ spin densities at the divalent carbons, we also measured ^{13}C-ENDOR spectra from the compound ^{13}C-labeled at the divalent carbons.

The observed spin densities are given in Figure 7(a), which are determined from the analysis of the angular dependence of the observed ENDOR frequencies. According to the relationship in Table I(i) based on the weakly interacting model, the spin densities ρ_i's of the low-lying triplet (S=1) state of II are expected to be one-half of those of the isolated diphenylmethylene unit moieties. The

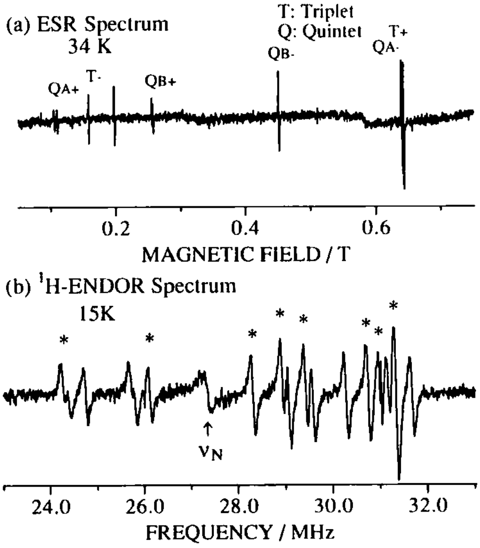


FIGURE 6 Typical ESR and ^{1}H-ENDOR spectra of II. The external magnetic filed is along the *a* axis.

spin density distribution in Figure 7(b) was calculated using this relationship. This calculation well interprets the observed spin density distribution. The observed and calculated spin density distributions show that the pseudo π-SDW is formed within each moiety. As a results of these, the central two carbon sites of the biphenyl group should have the same negative sign. This violates the formation of the pseudo π-SDW in the whole molecule. The existence of this node, which leads to the loss of the spin exchange-correlation energy, makes the observed triplet state to be an excited state above the spin-less ground state.

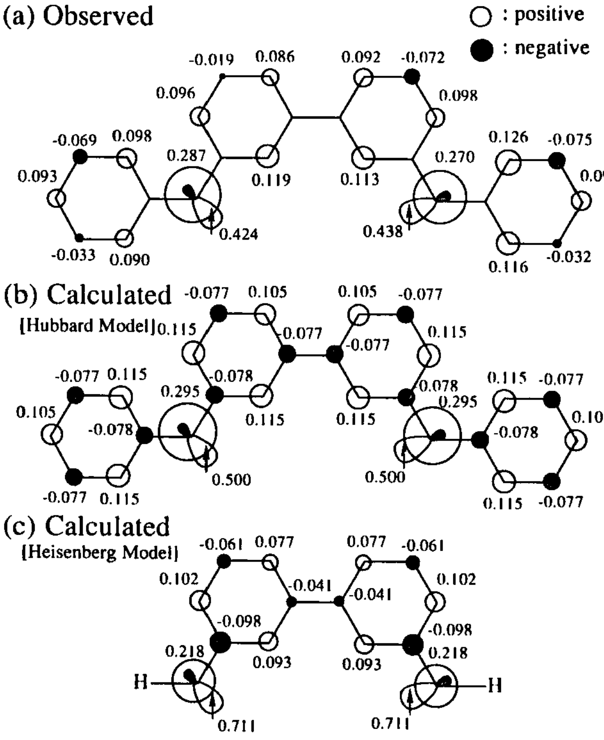


FIGURE 7 Spin density distributions in the low-lying triplet excited state of II.

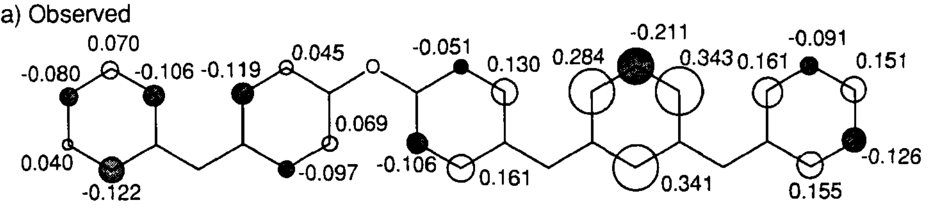
The exchange-correlation energy through the π bond between the bridged carbons can be roughly estimated by the expectation value of the interacting Hamiltonian (2). Apart from a factor of S^2, the value is given by J_{ex} in Eq. (5), which relates the magnitude to the product of the spin densities at bridge positions i and j. Thus, the small spin densities on the bridge carbon sites leads to the weak-interaction between unit moieties. In the case of the molecules such as II which two high-spin moieties are connected at the disjoint[7] position, the effective exchange interaction is expected to be weak, since the spin densities at the bridged carbon sites is small in magnitude. This is the reason why the weakly interacting model can be applicable to II. The magnitude of the spin coupling in II was estimated to be ca. 20 cm^{-1} using the observed spin densities of the diphenylmethylene[11] and $J_{ij}^{eff}=J_{\pi\pi}^{eff}=-1.5$ eV in Eq. (8). The magnitude is comparable to the observed energy difference between the singlet and the triplet states ($\Delta E_{ST}=2J_{ex}=20$ cm^{-1}) in Figure 1.

Figure 7(c) shows the spin density distribution calculated by the valence-bond Heisenberg Hamiltonian approach where we replaced the end phenyl groups of II with the hydrogen atoms to reduce the size of the Hamiltonian matrix. This calculation also provides the results similar to Figure 7(b) without using the weakly interacting model. Although this model is the limiting case of $U >> T$ in the Hubbard model, the spin correlation among the π and σ spins is exactly taken into account within the model Hamiltonian, leading to the correct ordering of the ground and the low-lying excited states.[10a]

(C) Spin Density Distribution of the Ferrimagnetic Triplet ground State of Molecule III

Molecule III is a model compound of organic ferrimagnets in which the triplet diphenylmethylene and the quintet m-phenylenebis(phenylmethylene) are antiferromagnetically coupled to each other (hetero-spin system), forming the low-spin (S=1) ground state with low-lying higher-spin excited states as shown in Figure 1. The spin density distribution of the low-spin ground state determined by our ^{1}H-ENDOR experiment is given in Figure 8(a). This observed spin density distribution shows that the triplet diphenylmethylene moiety possesses unusually large negative π-spin polarization. Thus, the negative spin densities larger than the positive ones have been detected in this triplet moiety, indicating the spin inversion of this moiety by the antiferromagnetic coupling to the quintet m-phenylenebis(phenylmetylene) moiety. This

(a) Observed



(b) Calculated

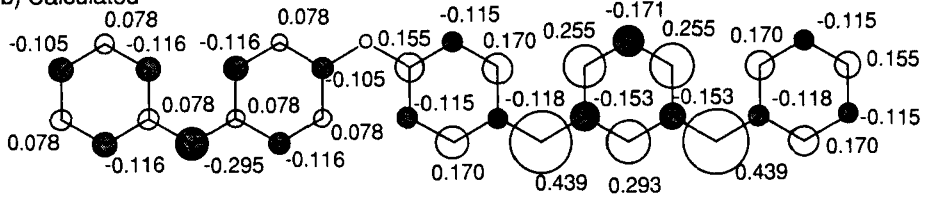


FIGURE 8 Spin density distributions in the triplet ground state of III.

spin inversion is characteristic of the organic ferrimagnetic spin system. The magnitudes of the negative spin densities amount to about one-half of the positive ones of the isolated triplet diphenylmethylene molecule itself, and those of the spin densities in the quintet moiety ca. 20 % smaller than those of the isolated quintet m-phenylenebis(phenylmethylene) itself. These characteristic signs and magnitudes of the spin densities are also well interpreted by the relationship for S=1 in Table I(ii), as shown in Figure 8(b).

ACKNOWLEDGEMENT

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    The spin densities in Table VI in this paper are normalized to be unity per the molecule. Since, in our formalism, the spin densities are normalized to unity per one unpaired electron, the doubled spin densities should be used in Eq. (5), i.e., $\rho = -0.0381 \times 2$ for the connecting carbon sites in II.