Bull. Chem. Soc. Jpn., **69**, 3443—3450 (1996)

Through-Bond and Through-Space Interactions of Organic Radicals Coupled by *m*-Phenylene

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(Received June 6, 1996)

Through-bond and through-space magnetic interactions in tricarbene and its related triradicals coupled through *m*-phenylene units are discussed with a semiempirical molecular orbital method including configuration interactions (PM3-CI method). The high-spin (HS) and low-spin (LS) states have quite similar geometries, but the methylene bridging angle is larger in the HS states. The HS states of these lie well below the corresponding LS states, except for one which contains nitroxide and aminiumyl radicals. Instability of the HS state of the heteroatomic system is a consequence of significant mixing between NBMOs and benzene e_{1g}-type orbitals, which can be explained in terms of simple perturbation theory. The energy difference between the HS and LS states is not explicitly influenced by the conformation of the molecules examined. This shows that such conformations have little effect on the magnetic properties in possible polymer ferromagnets which contain *m*-phenylene coupling units, as far as the second nearest neighbor interaction.

Design and synthesis of molecular ferromagnets have been extensively discussed from both theoretical and experimental points of view.[1—7] Organic ferromagnets can be classified into two main groups. One of them is composed of extended arrays of stable organic radicals such as nitroxide. The first organic ferromagnet is a crystal of 2-(4-nitrophenyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-yloxyl 3-oxide reported by Kinoshita et al.[8] which shows a Curie temperature (T_c) of 0.6 K. Moreover, similar nitroxide-based organic ferromagnets have been prepared and characterized by Rassat et al.[9] and Nogami et al.[10] These organic ferromagnetic crystals show a low T_c in the vicinity of 1 K.

Another main group of organic ferromagnets consists of polymer-based radicals,[11] although no real ferromagnet has yet appeared from this group. A total spin quantum number S much larger than 1/2 has been realized in such systems,[12—17] and the magnitude of the effective exchange integral (J) is expected to be larger than that of nitroxide-based molecular crystals. Thus, polymer ferromagnets can exhibit potentially a higher T_c value. This is the reason why polymer ferromagnets have attracted theoretical and experimental interests as a main group for high-T_c organic ferromagnets.

Following Mataga's proposal[11] for preparing organic ferromagnets based on magnetic interactions through an *m*-phenylene coupler, synthesis and characterization have been carried out along this strategy.[12—27] A large amount of work for *m*-phenylene structures has shown that an *m*-phenylene coupler is generally effective for the realization of high-spin (HS) states in organic molecules. Although this type of polymer ferromagnets has not yet been realized, strong spin–spin interactions from the topological π-conjugated network have been well-established.

It seems difficult to synthesize polymer ferromagnets with a large number of repeating units, because *intermolecular* through-space magnetic interactions, which are in general antiferromagnetic, are significant in larger polymeric systems. For example, 1,3,5-trisubstituted hexacarbenes **1** and **2** (indicated in Scheme 1), which are expected to be a ground state of $S=6$, can take various conformations. Iwamura and co-workers[15] confirmed **1** and **2** as a ground state of $S=6$, and X-ray structural analysis of **1** by Furukawa et al.[16] showed that there is no possibility of *intramolecular* through-space magnetic interactions. However, if the distance between two triplet methylene centers is short, the alignment of spins might be partially antiferromagnetic. In fact, Iwamura's group[27] reported recently that *m*-phenylene-connected nonacarbene which is predicted to have a ground state of $S=9$ shows $S=7$ in its ground state,due to partial cross-linking within a molecule.

In this article, we examine in detail the second-nearest neighbor magnetic interactions between organic radicals coupled through *m*-phenylene units, as indicated by the dotted boxes in Scheme 1. In order to design polymer ferromagnets, we need to know *intramolecular* through-space as well as through-bond magnetic interactions. Although there have been a large number of theoretical studies on spin preference in organic ferromagnets,[28—37] our theoretical knowledge on the second-nearest neighbor magnetic interactions through *m*-phenylene couplers is still incomplete. Our theoretical interests include also ionic molecular systems[35d,35f,36,37] for the realization of organic ferromagnets. We thus per-

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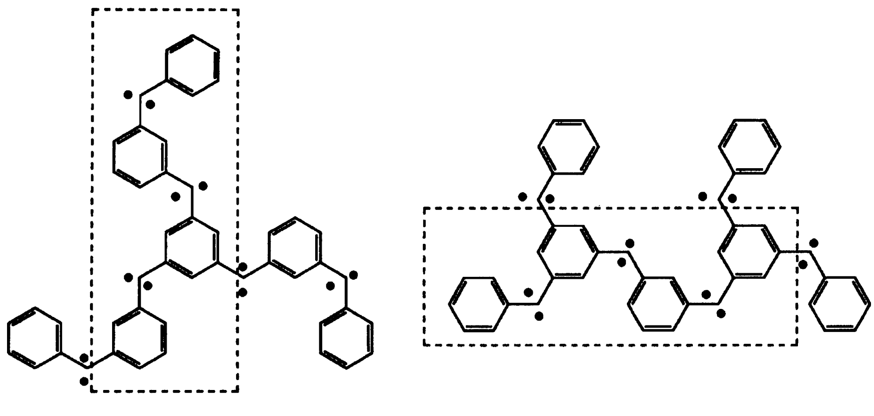


1 **2**

Scheme 1.

formed molecular orbital (MO) calculations in various conformations of tricarbene, 3,3′-bis(phenylmethylene)diphenylmethylene, indicated below in **3a** and its related triradicals, **3b**—**3e** of Scheme 2. These systems include typical stable organic radicals such as methylene, methyl, aminiumyl, and nitroxide in their structures.

Computational Details

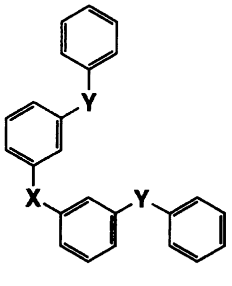
We used a semiempirical MO method, due to the sizes of these extended molecular systems. In a subtle problem such as Jahn–Teller distortion, it has been pointed out that UHF energies are not reliable for comparison of relative stability among various electronic states with different amounts of spin contamination.[38] Thus, we calculated the geometries and energies of **3**'s using the restricted open-shell Hartree–Fock (ROHF) method. We used the PM3 parametrization in the MOPAC semiempirical program.[39] Since MOPAC cannot calculate a molecule which has a spin multiplicity higher than 6, we rewrote its source program in order to calculate the septet state for the HS state of tricarbene **3a**.

The labels of atoms and important internal coordinates of **3**'s are shown in Fig. 1. The geometry of these molecules can be typically represented by a dihedral angle, ϕ, defined as X_2–X_1–C_1–C_2. Prior to an analysis of the electronic structures of these as a function of ϕ, partial geometry optimization was carried out under the restrictions shown below:

(1) Bridging angles θ_1 and θ_2 in Fig. 1 were optimized using a standard energy-gradient method.

(2) The starting structures were assumed to be planar within C_{2v} symmetry: Dihedral angle ϕ was taken as 180°.

(3) The bond lengths and angles of the benzene rings were fixed as standard ones (C–C = 1.40 Å, C–H = 1.08 Å, C–C–C and C–C–H = 120°). The other bond lengths (X_1–X_2, Y_1–Y_2, Y_3–Y_4, X_1–C_1, X_1–C_1', Y_1–C_4, Y_1–C_4', Y_3–C_3, and Y_3–C_3') were optimized.



(X, Y) = $(\mathrm{C}^{\bullet\bullet}, \mathrm{C}^{\bullet\bullet})$ **3a**

= $(\mathrm{C}^{\bullet}\text{—H}, \mathrm{C}^{\bullet\bullet})$ **3b**

= $(\mathrm{N}^{\bullet+}\text{—H}, \mathrm{N}^{\bullet+}\text{—H})$ **3c**

= $(\mathrm{N}^{\bullet}\text{—O}, \mathrm{N}^{\bullet}\text{—O})$ **3d**

= $(\mathrm{N}^{\bullet+}\text{—H}, \mathrm{N}^{\bullet}\text{—O})$ **3e**

Scheme 2.

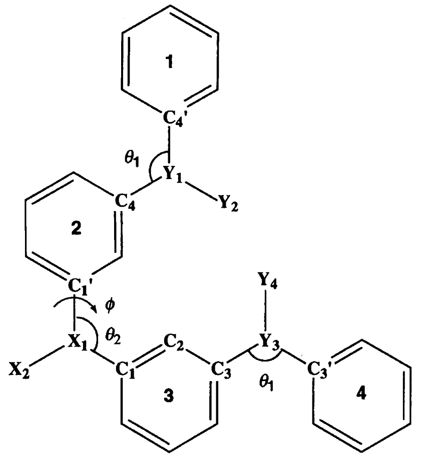
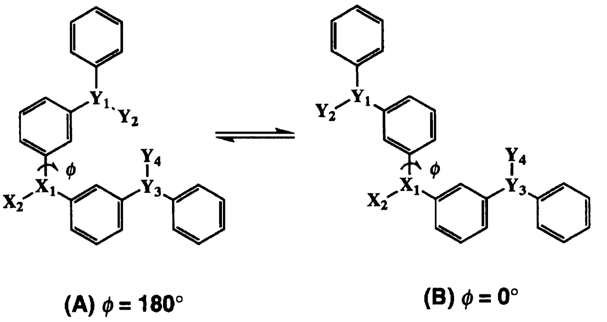


Fig. 1. Atomic numbering and important internal coordinates of **3**'s. X_2, Y_2, and Y_4 are not present in **3a** (see Scheme 2).

The geometries for the HS and low-spin (LS) states of **3**'s were optimized separately. These HS electronic states are not degenerate because all the nonbonding molecular orbitals (NBMOs), associated with an *m*-phenylene skeleton, are occupied by a single electron in the HS states. Thus, the HS skates are described well within the framework of the ROHF method. On the other hand, we need to calculate the LS states using a limited configuration interaction method (PM3-CI), because these molecules have nearly degenerate NBMOs and thus it is difficult to describe these LS states by a single configuration. After geometry optimization, UHF calculations were carried out in order to look at the spin density distribution of the HS states of these molecules.

Results and Discussion

Scheme 3 shows two planar conformations, (A) and (B) which are defined by dihedral angle ϕ. Optimized geomet-



Scheme 3.

rical parameters of **3a**—**3e** with conformation (A) are given in Table 1. Important bond angles of the bridging methylene centers are about 148° for the high-spin septet state of **3a** with planar geometry (A). On the other hand, the bridging angles in the corresponding low-spin triplet state are about 143°. This is consistent qualitatively with the observation that singlet methylene has a smaller bond angle than triplet methylene.[40)]

Higuchi[41)] reported a probable methylene angle to be 144—150° for triplet diphenylmethylene and nearly 140° for quintet *m*-phenylenebis(phenylmethylene). Moreover, Hutchison et al.[42)] estimated the bridging angle for diphenylmethylene as 154° and 148° in Refs. 42a and 42b, respectively. Optimized bridging angles, θ_1 and θ_2 for the methylene centers in **3a** are qualitatively consistent with these values. The bridging angles of methyl, aminiumyl, and nitroxide radical centers are in the range of 136—144°. These angles are probably pushed apart slightly, due to planarity constraint, but are clearly smaller than that of high-spin methylene.

After geometry optimization, we looked at the correlation between dihedral angle ϕ and the magnetic properties of **3a**—**3e**. As can be seen from Scheme 3, intramolecular through-space interactions, due to $Y_1 \cdots Y_3$ and $Y_2 \cdots Y_4$ nonbonded contacts, are expected to be stronger with increasing ϕ and maxima at $\phi = 180°$. If the through-space interactions are large enough, the energy difference between HS and LS states will depend strongly on ϕ, because such interactions stabilize LS states in general. We therefore calculated the total energies of the HS and LS states for **3a**—**3e** from 0° to 180° of ϕ for every 30°.

Figure 2 shows the relative energies of the HS and LS states as a function of torsion angle ϕ. $\Delta = E_{\mathrm{LS}} - E_{\mathrm{HS}}$, where E_{LS} is the total energy of the lowest-lying LS state and E_{HS} signifies that of the HS state. That is, Δ corresponds to the energy difference of septet–triplet for **3a**, sextet–doublet for **3b**, and quartet–doublet for **3c**, **3d**, and **3e**. When $\Delta > 0$, the HS state is most stable. We found from Fig. 2 that molecular conformation has little effect on the energy differences between the HS and LS states. We can therefore conclude that the through-space interactions mentioned above are not so strong. The HS state is more stable than the lowest-ly-

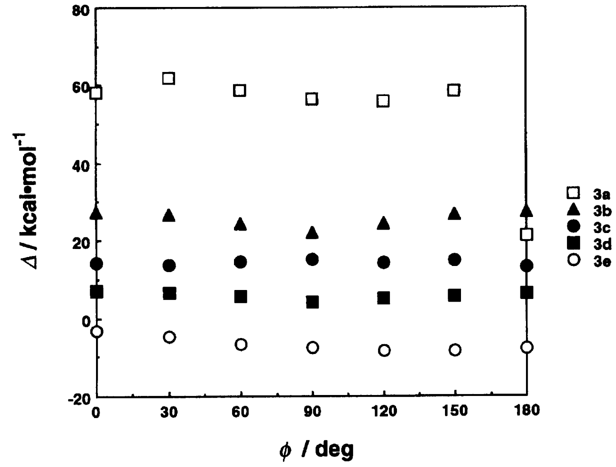
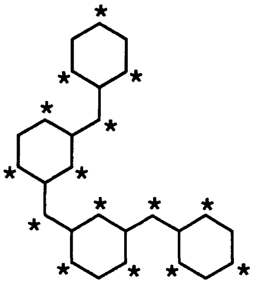


Fig. 2. Energy splitting between HS and lowest-lying LS states of **3a**—**3e** as a function of torsion angle ϕ. A positive value of $\Delta (= E_{\mathrm{LS}} - E_{\mathrm{HS}})$ means that a HS state is stable compared with the corresponding LS states.

Table 1. Optimized Parameters of the Conformation (A) Employing the ROHF Method at the PM3 Level of Approximation[a)]

		3a	3b	3c	3d	3e
Bond length	X_1–X_2		1.11	1.00	1.27	1.00
			1.11	1.00	1.28	1.00
	X_1–C_1	1.39	1.43	1.41	1.48	1.40
		1.41	1.43	1.42	1.45	1.41
	Y_1–Y_2			1.00	1.27	1.26
				1.42	1.45	1.40
	Y_1–C_4	1.39	1.39	1.44	1.48	1.46
		1.41	1.41	1.40	1.47	1.44
	Y_1–C_4'	1.40	1.40	1.39	1.49	1.49
		1.41	1.41	1.39	1.47	1.39
Bond angle	θ_1	147.5	147.6	141.0	136.5	136.9
		142.6	142.6	142.1	136.8	141.0
	θ_2	147.6	140.8	143.5	137.0	141.9
		142.7	140.7	143.0	137.2	143.5

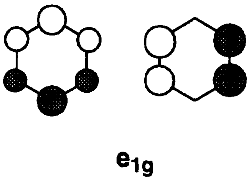
a) Upper and lower lines are associated with the high-spin and low-spin states, respectively.



Scheme 4.

ing LS state in **3a**—**3d**. This is clearly due to the well-established through-bond ferromagnetic interactions which appear from topological degeneracy of homoatomic systems coupled through an *m*-phenylene unit.[11—27] The through-space $Y_1 \cdots Y_3$ interaction in the LS triplet state of **3a** will be discussed later in this article.

On the other hand, in **3e** the LS state is more stable than the HS state. There are a few examples[43] in which *m*-phenylene does not work as a ferromagnetic coupler; **3e** is probably such an example. Let us now look at Hückel frontier orbitals to consider this. It is important to note that in these systems the conjugated atoms are alternately labeled as starred and unstarred, such that no two atoms of the same label are directly linked. Figure 3 indicates NBMO-type orbitals of **3a** or **3b**, **3c**, and **3e**. Those of **3d** are omitted in this illustration. In carbon-based systems, **3a** and **3b**, the NBMOs are threefold degenerate within the framework of the Hückel method, due to their topological property given by an *m*-phenylene coupling unit. The amplitude of these frontier orbitals is localized well just on the "starred" atoms indicated in Scheme 4. This is the most important characteristic of the NBMOs for alternant hydrocarbons. Therefore these MOs have nonbonding energy of 0, due to the nearest-neighbor approximation used in the Hückel method; as a consequence, they are threefold degenerate. This is nearly so at any higher-levels of theory.



Scheme 5.

However, as also shown in Fig. 3, in heteroatomic sys-

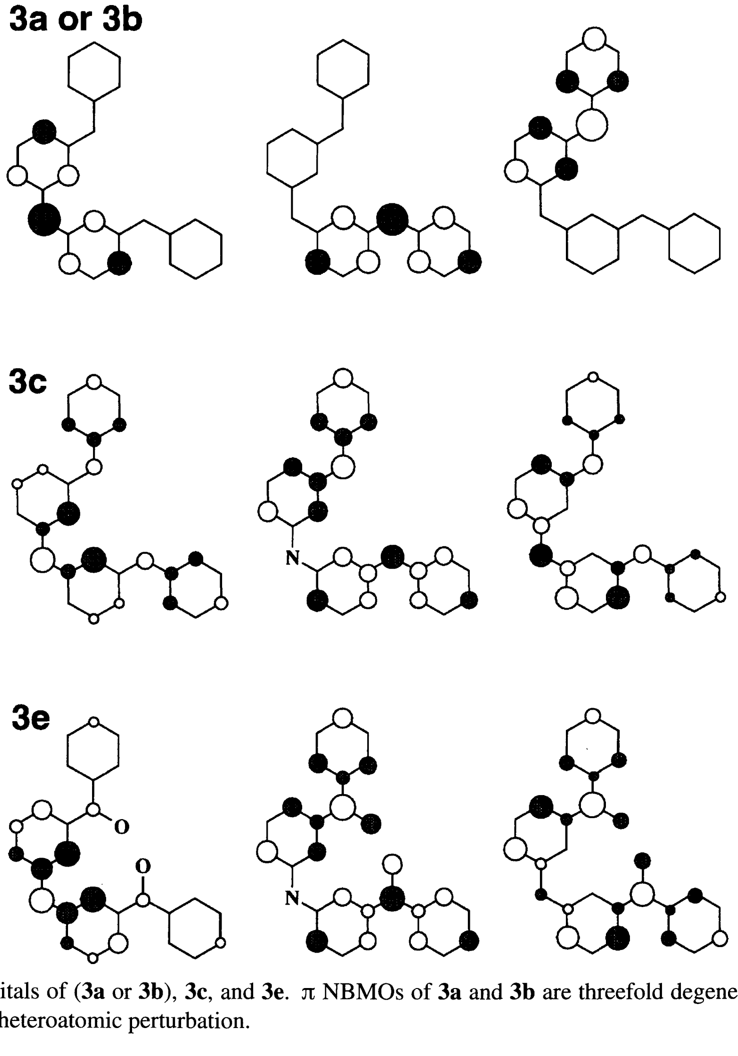


Fig. 3. Hückel frontier orbitals of (**3a** or **3b**), **3c**, and **3e**. π NBMOs of **3a** and **3b** are threefold degenerate, but the degeneracy is lifted in **3c** and **3e**, due to heteroatomic perturbation.

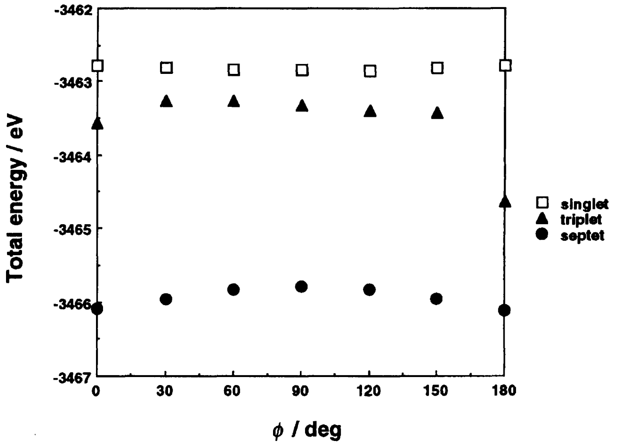
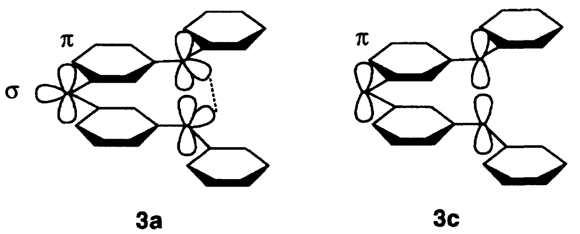


Fig. 4. Total energies of the septet, triplet, and singlet states of **3a** as a function of ϕ.

tems, **3c** and **3e**, the NBMOs are mixed significantly with e_{1g}-type orbitals of benzene indicated in Scheme 5. This is an important consequence of one kind of intramolecular perturbation,[44] i.e., heteroatomic perturbation. There are thus non-negligible orbital coefficients on the unstarred atoms, although they are not so large. As a result, the degeneracy of the NBMOs is removed in these heteroatomic systems, and their orbital energies are not equal to zero. The energy splitting of the three frontier orbitals in **3c**, **3d**, and **3e** is 0.12β, 0.10β, and 0.17β, respectively. The ground state doublet in **3e** can be explained by this large energy splitting, in terms of simple perturbation theory. Since the energy variation as a function of ϕ is small in **3e**, as shown in Fig. 2, we think that the intramolecular through-space interaction, especially coming from the O···O nonbonded contact, is not so strong.

In earlier papers, Tyutyulkov et al.[45] and our group[46] have indicated theoretically that the NBMO nature of an *m*-phenylene coupling unit is appropriate for the localization of electrons and is therefore important for the realization of HS states in polymer systems. However, when there is a perturbation such as a charge-transfer interaction in heteroatomic systems, the NBMOs are mixed with other MOs and the topological degeneracy is consequently removed.[46b] High-spin states can become unstable by this intramolecular perturbation.

We next consider the stability of the HS state over the LS states specifically for **3a**. We calculated the total energies of the three kinds of spin states in **3a**, i.e., septet, triplet, and singlet states. We used a limited CI method to calculate the LS triplet and singlet states, whereas the ROHF method was applied to the HS septet state, as mentioned above in the method of calculation. In this CI methodology, the LS triplet and singlet states are described as a linear combination of several triplet and singlet states, respectively. Among several LS (triplet and singlet) states, we consider just the lowest LS state in this article. The total energies of the septet, triplet, and singlet states of **3a** are shown as a function of dihedral angle ϕ in Fig. 4. Those of the septet and singlet states are nearly constant, whereas that of the triplet state is decreased very much at $\phi = 180°$, in which the distance between Y_1 and Y_3 is approximately 6.5 Å. Since each methylene center has a directional in-plane σ orbital which accommodates a radical spin, the $Y_1 \cdots Y_3$ nonbonded interaction is not completely negligible, as indicated by the dotted line in Scheme 6. In the LS triplet state of **3a**, the nonbonded methylene centers are therefore antiferromagnetically coupled by the through-space pσ–pσ interactions. This coupling is clearly strong in conformation (A) with $\phi = 180°$.



3a **3c**

Scheme 6.

This situation is quite different in the LS doublet states of **3c** and **3d** because these triradicals have just unpaired π spins and the through-space pπ–pπ interactions are much weaker than the through-space pσ–pσ interactions in **3a**. Thus, the LS doublet states of **3c** and **3d** are not stabilized at $\phi = 180°$. In fact, the doublet-energy curves of **3c** and **3d** are flat (not reported here). On the other hand, the LS triplet state of **3a** is greatly stabilized at $\phi = 180°$, as shown in Fig. 4, because the through-space pσ–pσ interaction is maximum in this conformation. However, the septet state is 21.1 kcal mol^{-1} more stable than the LS triplet state in **3a** even at $\phi = 180°$, and we can conclude again that the through-space interactions mentioned above are not so strong compared with the well-established through-bond ferromagnetic interactions in an *m*-phenylene coupler.

Let us next look at spin density distribution. Figure 5 shows the total and π-spin densities of the HS states of **3a**—**3d** calculated with the UHF method. The π-spin densities are indicated by bracket in this illustration. Note that the π-spin distribution of **3a** is very similar to that of **3b**. As expected, π-spin densities are largely delocalized on the π-conjugated systems; on the other hand, σ-spin densities are localized well on the methylene centers in **3a** and **3b**. It is now clear that spin polarization derives mainly from the π-spin delocalization over the molecules.

However, as seen in Fig. 3, the π-type NBMOs are localized well on the starred atoms in **3a** and **3b**, so that this delocalized π-spin density does not necessarily mean mobile spins. In fact, extended Hückel band calculations in Ref. 46c have shown that both the π- and σ-bands of poly(*m*-phenylcarbene) are extremely narrow, 0.1—0.2 eV. Consequently we can conclude that the π electrons of **3a** and **3b**'s polymer would not contribute to electrical conduction. It is therefore an apt analogy when the π–σ interaction in these systems is compared with the well-known s–d interaction in metals. A typical bandwidth of an s band in metals is 10 eV in contrast to d bands, and s electrons contribute greatly to electrical

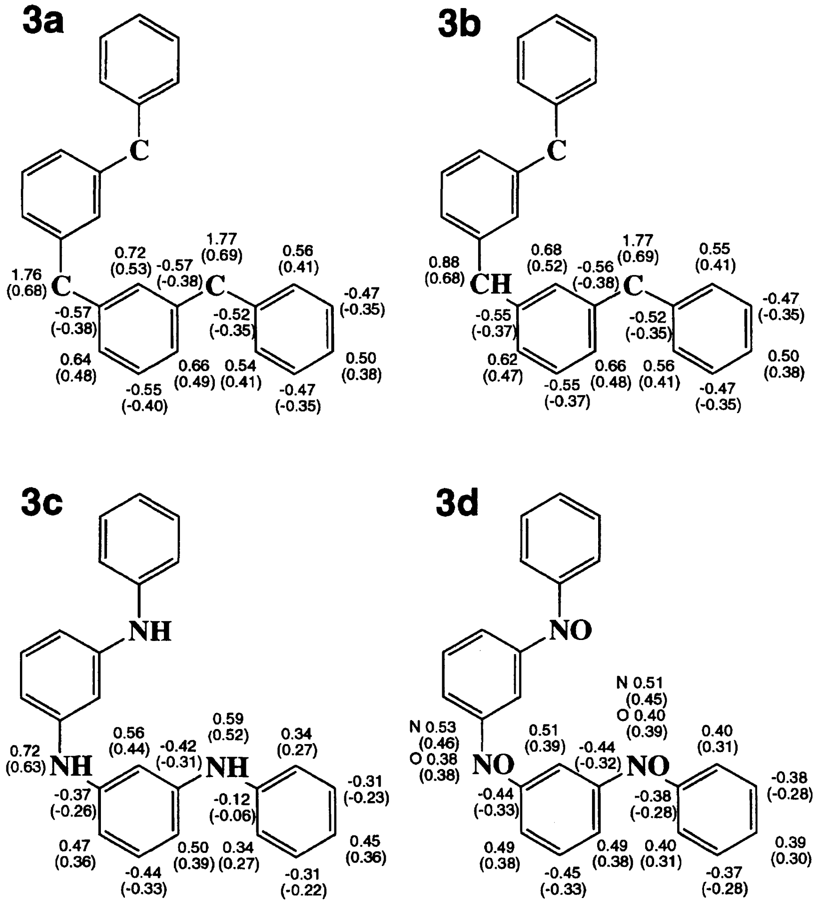


Fig. 5. Spin densities of the HS states of **3a**—3d. The quartet state of **3e** is unstable compared to the corresponding doublet state.

conduction of metals.

Finally we would like to consider contributions of through-bond and through-space interactions to Hartree–Fock total energy in the HS state of **3a**. Using the zero-differential-overlap (ZDO) approximation, the exchange interactions among up- (α-) spins can be proportional to α-spin density product, $\rho^{\alpha}_r\rho^{\alpha}_t$, as shown in Eq. 1:

$$\begin{aligned} -\sum_{i,j} K^{\alpha}_{ij} &= -\sum_{i,j}\sum_{r,s,t,u} C^{\alpha}_{ir}C^{\alpha}_{is}C^{\alpha}_{jt}C^{\alpha}_{ju}(rs|tu) \\ &\cong -\sum_{i,j}\sum_{r,t} C^{\alpha}_{ir}C^{\alpha}_{ir}C^{\alpha}_{jt}C^{\alpha}_{jt}(rr|tt) \\ &= -\sum_{r,t}\rho^{\alpha}_r\rho^{\alpha}_t(rr|tt), \qquad (1) \end{aligned}$$

where i and j are labels of MO; r,s,t, and u labels of atomic orbitals; $(rr|tt)$ is the Coulomb repulsion integral.[47] Equation 1 is dependent on the through-space exchange interactions among X_1, Y_1, and Y_3 because in **3a** there appear large α-spin densities on these bridging methylene centers, as we saw in Fig. 5.

Let us pay attention to the two planar conformations (A) and (B) indicated in Scheme 3. When ϕ is changed from 180° to 0°, the intramolecular through-space interaction from the $Y_1(C^{\bullet\bullet})\cdots Y_3(C^{\bullet\bullet})$ nonbonded contact is considered to be weakened very much. Accordingly the exchange interaction should destabilize the Hartree–Fock total energy for the HS state of **3a** when ϕ is changed from 180° to 0°. However, our calculational results do not show this; the total energies of the HS states of the two planar conformations are nearly equal. We can therefore conclude that in the HS state of **3a** the through-space interaction is almost negligible compared with the through-bond interactions, as regards the second-nearest neighbor interaction coupled by *m*-phenylene. On the other hand, the LS triplet state of **3a** is largely dependent on ϕ, as discussed above.

Conclusions

We have investigated the electronic and magnetic structures of tricarbene **3a** and its related triradicals, especially for conformational dependence on through-bond and through-space magnetic interactions. Three kinds of conclusions can be drawn from this study. The first conclusion is on the electronic ground states of **3a**—**3e**. HS ground states were confirmed by the PM3-CI method in **3a**—**3d**, but not in **3e**. In particular, the HS septet state of **3a** lies 21.1 kcal mol^{-1} below the most stable LS triplet state.

The second conclusion is about the structural dependence on the stability of the HS states of **3a**—**3d**. Even if the dihedral angle ϕ is changed, these HS states are always more stable than the corresponding LS states, because the through-bond interactions are predominant in these systems coupled by an *m*-phenylene unit. Through-space interaction appears to have less influence on the stability of the HS state of these.

The third is about the instability of the HS state of a heteroatomic system, **3e**. This system is one of exceptions to the rule that *m*-phenylene always works as a robust ferromagnetic coupler. We have discussed the origin of this exception by analyzing Hückel MOs from the viewpoint of simple perturbation theory. The instability of the HS state of **3e** is probably caused by heteroatomic perturbation, not by the through-space interactions coming from the $Y_1 \cdots Y_3$ or $Y_2 \cdots Y_4$ contact. In this heteroatomic system, the NBMOs are found to be mixed significantly with e_{1g}-type orbitals of benzene, due to a perturbation effect. As a consequence, the degeneracy of the NBMOs is lifted in this heteroatomic system, and its HS state is destabilized.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture. Thanks are also due to the JSPS Program for Research for the Future. Numerical calculations were carried out at the Data Processing Center and the Supercomputer Laboratory of the Institute for Chemical Research, Kyoto University.

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