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ELECTRONIC STRUCTURE OF IONS OF M-PHENYLENEBIS(PHENYL-METHYLENE)

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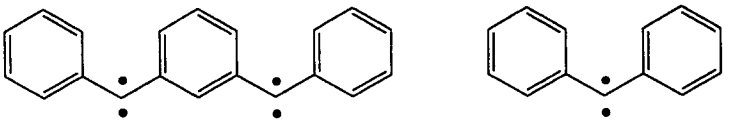
ABSTRACT The electronic structure of an ionized high spin molecule, m-phenylenebis(phenyl-methylene), is studied with a semi-empirical model for π and n electrons using the unrestricted Hartree-Fock (UHF) and resonating HF (Res HF) approximations. The injected hole or electron is in the π system and the calculated spin multiplicity of the ground state is the quartet, which is consistent with the experiments. In the UHF approximation, it makes a spin density wave (SDW) polaron localized around a carbene site. The Res HF approximation shows that quantum motion of the SDW polaron between the carbene sites and quantum fluctuations of its spins more stabilize the quartet state.

INTRODUCTION

It is well known that spin structures of neutral radicals of conjugated hydrocarbons are governed by the dynamic spin polarization (DSP) effect producing alternating spin density correlations. The total spin of the ground state can be easily predicted from the topology of the molecule, and many kinds of high spin molecules have been designed using the DSP effect to realize a ferromagnetic coupling among permanent spin moments. Ionic states of such molecules, however, have not been well understood yet. What total spins are realized? What kinds of electron correlation are important? These questions recently attract some interest in the field of molecular magnetism. The problem is similar to that in doped Mott insulators such as copper oxides.

Meta-phenyl carbene oligomers are representative neutral radicals which have high spin ground states.[1] The π and n electrons at a carbene site make a $S = 1$ spin state owing to the Hund's coupling and the spins at different carbene sites couple ferromagnetically via an alternating SDW in phenyl rings. A few years ago, experiments were reported on the ions of m-phenylenebis(phenyl-methylene) (m-



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PBPM) (I).[2-4] It has been found that the injected electron or hole is in the π system and the spin multiplicity of the ground state is the quartet (Q), i.e., the high spin state.

In this paper, we make a semi-empirical model for the m-phenyl carbene oligomers and calculate the electronic structure of the ions of m-PBPM. Using the UHF and Res.HF approximations,[5,6] we verify the above experimental results and understand why the ground states of the ions have the high spin. The Res HF approximation is expected to incorporate effects of electron correlation appearing as large quantum fluctuations. The details of our results will be published elsewhere.

SEMI-EMPIRICAL MODEL FOR π AND n ELECTRONS

Our model Hamiltonian treats only π and n electrons. It is PPP like and includes the Hund's coupling at the carbene sites and the π-n mixing caused by the non-planer structure due to a steric hindrance. (Fig.1)

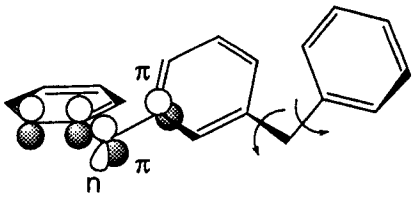

Fig.1 n and π orbitals in m-PBPM

The nearest neighbor π-π transfer integrals in phenylenes are -2.39eV, the same as the value in the benzene. The π-π and π-n transfer integrals between the carbene and the adjacent sites, where the bonds are rotated by $\phi = \pm 20.6°$, are given by $\beta_{\pi\pi} = -2.24$eV and $\beta_{\pi n} = -0.78$eV, respectively. We note the two adjacent π-n transfers have opposite signs. The intraatomic Coulomb repulsion is the semi-empirical value of 11.13eV and the interatomic Coulomb repulsion follows

the Ohno formula that can explain the observed spin density in diphenyl-methylene.[7] The Coulomb integrals for the π AOs in phenyl rings are given by $U_\pi = -I_p$ where I_p is the ionization potential of the carbon. The Coulomb integrals for the π and n AOs of carbene sites are given by $U_\pi^C = U_p^C$ and $U_n^C = U_p^C \sin^2(\chi/2) + U_s^C \cos^2(\chi/2)$, where χ is the hybridization angle that is related to the bond angle at the carbene as $\cos\theta = (\cos\chi - 1)/(\cos\chi + 3)$. $U_p^C = -20.68$eV and $U_s^C = -28.01$eV are the Coulomb integrals of 2p and 2s AOs in the carbon atom with the core charge of $Z = 2$ given in the INDO model.[8] The intraatomic exchange integrals $\langle \pi n|\pi n\rangle$ at the carbene sites are estimated from the INDO values of $\langle sp|sp\rangle$ and $\langle xy|xy\rangle$ by $\langle xy|xy\rangle \sin^2(\chi/2) + \langle sp|sp\rangle \cos^2(\chi/2)$. Because U_n^C depends on the carbene bond angle, an increase of electron density in the n orbital will decrease the bond angle if the geometries are optimized. Our Hamiltonian and parametrization well reproduces the spin density of the neutral diphenyl-methylene.

RESULTS AND DISCUSSION

Is the excess charge injected into the π or n system?

First, we study the ionic states of diphenyl-methylene (II). Fig.2 schematically shows UHF molecular orbital (MO) levels for the *neutral* triplet carbene. The HOMO is the nonbonding π orbital with the energy ϵ_π, and the 2nd-HOMO is the n orbital with the energy ϵ_n. Thus, an injected hole will be always in the π system. On the other hand, the energies of the corresponding unoccupied orbitals of the opposite spin, $\overline{\epsilon_\pi} = \epsilon_\pi + \langle \pi\pi|\pi\pi\rangle + \langle \pi n|\pi n\rangle$ for π and $\overline{\epsilon_n} = \epsilon_n + \langle nn|nn\rangle + \langle \pi n|\pi n\rangle$ for n, depends on the bond angle of the carbene and the degree of the delocalization of

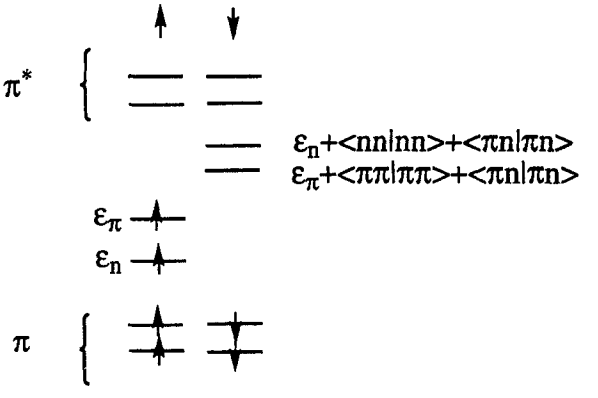

Fig.2 Schematic UHF MO energies of the triplet diphenyl-carbene

the π and n orbitals. If the bond angle and the extension of the π orbital are large, $\epsilon_\pi - \epsilon_n$ and $\langle\pi\pi|\pi\pi\rangle - \langle nn|nn\rangle$ are small, respectively, and the excess electron will be added to the π system. Otherwise, it will be added to the n one.

In the case of diphyenyl-carbene with the bond angle of 140° at the carbene[9], our calculation shows that either the hole or electron is injected into the π system. However, if the bond angle somehow becomes as small as 120°, the electron is injected into the n system. The excess charge in the π makes the the π-system almost singlet resulting in the very small spin density on the phenyl rings(< 0.01). In contrast, the excess electron in the n system does not change the SDW in the π system very much but will make the carbene bond angle considerably smaller.

SDW polaron

Now we study the ionic states of m-PBPM. According to the signs of the rotations avoiding the steric hindrance, it has C_2 or C_{1h} symmetry. We present here the results for the C_2 conformer. Those for the C_{1h} one are almost the same.

Table I shows the UHF energies of $S_Z = 3/2$ and $S_Z = 1/2$ states. We regard them as Q and doublet (D) states, respectively. States of $S_Z > 3/2$ have much higher energies (> 1eV for the cation and > 2eV for the anion). In both the cation and anion, the Q is lower than the D by $0.01 \sim 0.02eV$, which is consistent with the experiment of $\Delta E^{exp}_{D-Q} >> 1cm^{-1}$ and the INDO-UHF results of $\Delta E^{INDO}_{D-Q} =$ 0.075eV for the cation and 0.050eV for the anion. The π-n mixing is important to obtain the observed Q < D in the UHF approximation. However, we will see

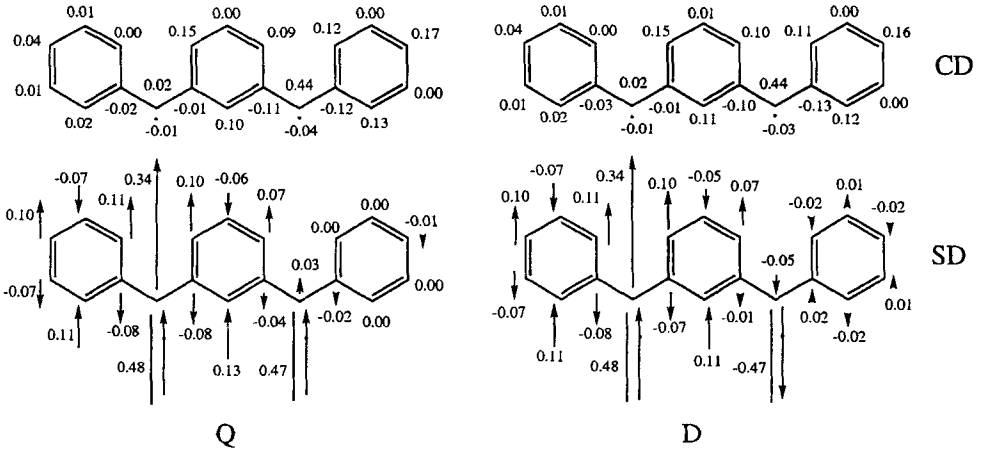

Fig.3 Calculated CDs and SDs of the Q and D cations in the UHF approximation

	S	UHF	PUHF	Res HF	
				$N_S = 2$	$N_S = 4$
Cation	3/2	0	-0.1150	-0.4709	-0.8461
	1/2	0.0196	-0.1066	-0.3782	-0.7288
	ΔE	0.0196	0.0084	0.0927	0.1173
Anion	3/2	0	-0.1294	-0.4816	-0.8802
	1/2	0.0102	-0.1320	-0.3543	-0.7320
	ΔE	0.0102	-0.0026	0.1373	0.1482

Table I. UHF, PUHF and Res HF energies of the ionic states (eV).

in the next section that an electron correlation makes the D-Q gap much larger. Figure 3 shows the calculated UHF charge and spin densities (CD and SD) for the Q and D. The injected charge is in the π system and localized around one of the carbene sites. Thus, the hole or electron makes a SDW polaron ($P^{\pm}$) similar to the spin bag in the antiferromagnetic Mott insulators.[10] UHF calculation with geometry optimization shows that the carbene bond angle does not change more than 2^{o} by ionization. Therefore, the $P^{\pm}$ has almost purely electronic character. A small charge density wave (CDW) like polarization is induced around the $P^{\pm}$. The similar CD and SD structures for the anion and cation mean that the violation of the alternancy symmetry due to the π-n mixing is small in the UHF approximation.

The HF states are schematically written as $|\pi_L n_L; \pi_R n_R\rangle = |\uparrow\uparrow; 0\uparrow\rangle$ for the Q and $|\uparrow\uparrow; 0\downarrow\rangle$ for the D. There exist local minimum solutions $|0\uparrow; \uparrow\downarrow\rangle$ and $|0\uparrow; \downarrow\uparrow\rangle$ for $S_Z = 1/2$. These states have about 0.4eV higher energies because of the less exchange coupling at the carbene site where π and n electrons have opposite spins.

Quantum Motion of the SDW polaron

$P^{\pm}$ can make quantum motion between the two carbene sites. The quantum fluctuations due to the motion can be expressed by superposing $|\uparrow\uparrow; 0\uparrow\rangle$ and $|0\uparrow; \uparrow\uparrow\rangle$ for the Q and superposing $|\uparrow\uparrow; 0\downarrow\rangle$ and $|0\uparrow; \uparrow\downarrow\rangle$ for the D. Since $|\uparrow\uparrow; 0\uparrow\rangle$ and $|0\uparrow; \uparrow\uparrow\rangle$ are degenerate, the energy gain due to the resonance in the Q is expected to be large. Since $|0\uparrow; \uparrow\downarrow\rangle$ has a higher energy than $|\uparrow\uparrow; 0\downarrow\rangle$, the energy gain due to the resonance in the D is expected to be small. Thus the exact D-Q gap will be larger than the UHF one. We study the effects of the quantum fluctuations using the Res HF method[5] which in general approximates a many body wave function by superposing non-orthogonal Slater determinants (S-dets) as $\sum_i^{N_S} |u_i\rangle C_i$. Both of C_i's and the orbitals in $|u_i\rangle$'s are optimized by a direct minimization method.[6]

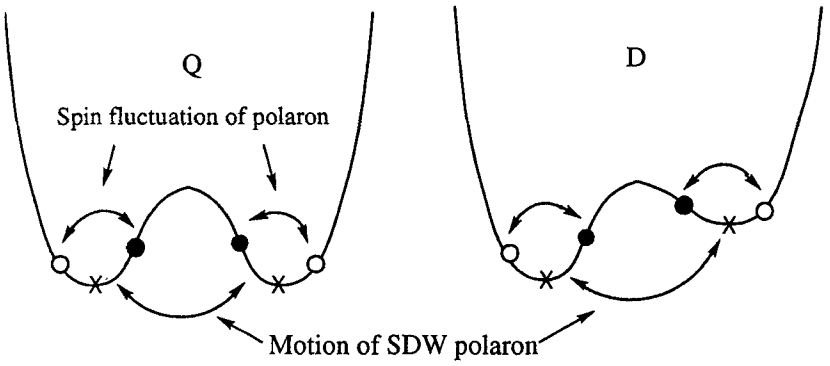

Fig.4 Schematic illustration of the Res HF states for Q and D

Table I also shows the Res HF and spin projected UHF (PUHF) energies of the lowest Q and D. In the Res HF calculations we remove $S = 5/2$ and $7/2$ contaminations from the $S_Z = 3/2$ state, and $S = 3/2$ and $5/2$ ones from the $S_Z = 1/2$ state by the partial Löwdin spin projection after the orbital optimization. The spin projection is almost complete for the cation and the Q anion, but some high spin contamination ($S > 7/2$) remains in the D anion in the Res HF calculations. The second column of Table I shows that the correlation energies incorporated by the PUHF approximation are similar(0.12 $\sim$ 0.14eV) for the Q and D states. However, since the UHF D-Q gaps are small, the order of the D and Q energies is changed for the anion in the PUHF approximation. In the Res HF calculation with $N_S = 2$ S-dets, it is unexpectedly found that, the polarons in the two optimized S-dets are localized in the same side for both Q and D. The electron correlation incorporated in this level is a spin fluctuation, mainly spin inversions in the terminal phenylene next to the carbene where $P^{\pm}$ is presented, as seen in the left S det in Fig.6. In the Res HF calculation with four S-dets, the quantum motion of $P^{\pm}$ between the two carbenes is also incorporated and the D-Q gap becomes considerably larger than the UHF one.

Figure 4 illustrates the above quantum fluctuations. The line shows a schematic HF variational energy surface. The minima of the surfaces ($\times$) represent UHF solutions of $P^{\pm}$ at two carbene sites. If the S-det is resonated with some other S-dets, the optimum position of the S-det is deviated to a ($\circ$) position. Spin fluctuation brings the ($\circ$) point to another point ($\bullet$). The resonance between the two valleys represents the quantum motion of the $P^{\pm}$ between the two carbenes.

We show in Fig.5 the CD and SD of the Res HF Q state of the cation with four S dets. The SD is smaller than the UHF one especially in the DSP in phenylenes.

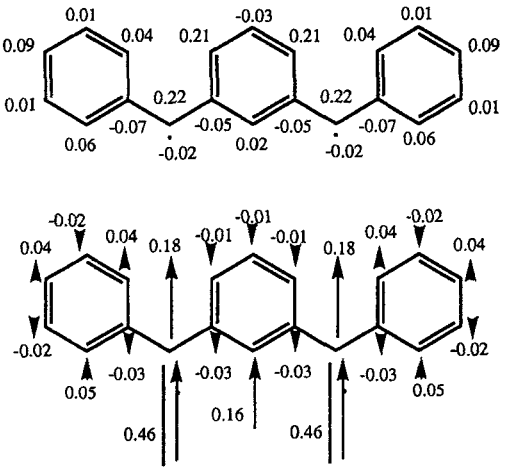

Fig. 5 Total CD and SD of the Q cation calculated by the Res HF approximation

This may be checked in future experiments. Figure 6 shows the CD and SD of the two spin projected S-dets in the Res HF wave function with four S dets for the Q cation. The other two S-dets are generated by their C_2 rotation. We note that the SDW polaron in the Res HF Q state is less localized on a carbene than in the UHF polaron.

The D-Q gap for the anion is larger than that for the cation, which may be understood as follows. The excess charge in the n system less destroys the DSP than that in the π system. So, the larger the probability of the excess charge in the n system, the larger is the D-Q gap. As mentioned in the preceding subsection $\overline{\epsilon_\pi} - \overline{\epsilon_n} = \epsilon_\pi - \epsilon_n + (\langle\pi\pi|\pi\pi\rangle - \langle nn|nn\rangle)$ is smaller than $\epsilon_\pi - \epsilon_n$ because $\langle\pi\pi|\pi\pi\rangle < \langle nn|nn\rangle$ in

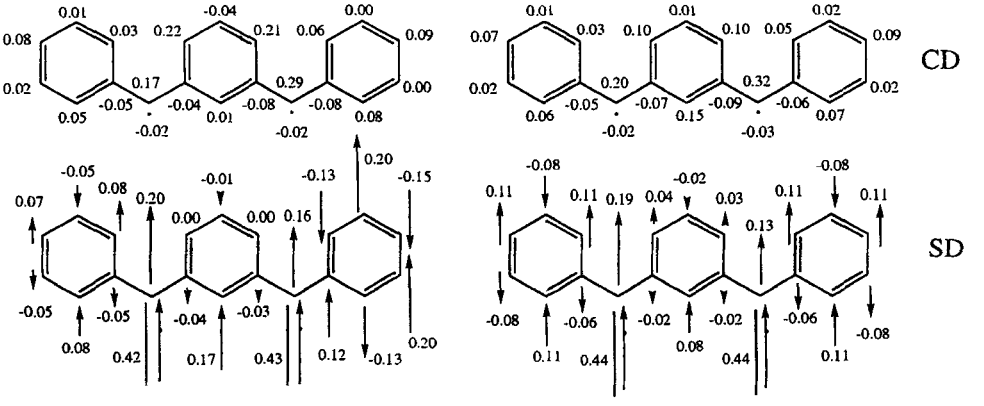

Fig.6 CD and SD of the two non-equivalent S-dets of the Res HF for the Q cation.

usual. Therefore, the probability to find the excess electron in the n orbital in the anion due to a quantum fluctuation will be larger than that to find the hole in the n orbital in the cation. Consequently, the D-Q gap of the anion is larger than that of the cation.

As for the Q, the B state of the C_2 symmetry is lower than the A. The resonance energy, which is due to the quantum motion of the SDW polaron between the two carbene sites, is 0.1845eV for the cation and 0.2394eV for the anion. The energy of the B $\rightarrow$ A transition will be in this order. It therefore may be observed in the IR region.

In conclusion, we have made a study on the electronic structure of the ions of m-PBPM. Either the hole or electron is injected into the π system and makes a SDW polaron. It makes quantum motion between the two carbene sites and spin fluctuations on a carbene site. These quantum fluctuations more stabilize the high spin state. The present theory can be checked experimentally by investigating the spin structure in the Q state and the energy gaps between the D and Q states.

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