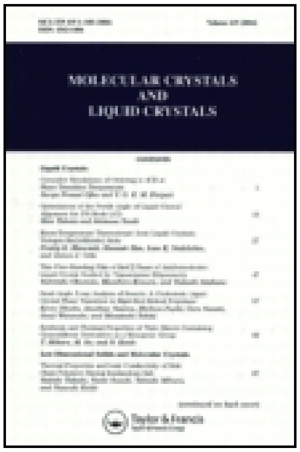

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Electronic Structures of Ions of M-Phenylenebis (Phenylmethylene)

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ELECTRONIC STRUCTURES OF IONS OF *M*-PHENYLENEBIS (PHENYLMETHYLENE)

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Abstract The electronic structures of a high spin molecule, *m*-phenylenebis (phenylmethylene) (*m*-PBPM) ion are studied with a semi-empirical model for n and π electrons using the unrestricted Hartree-Fock(UHF) and resonating Hartree-Fock(Res HF) approximations. The experimental results show that both the cation and anion have the quartet ground state. In the UHF approximation, the doped charge is always localized around a carbene as a spin density wave(SDW) polaron. The Res HF results show that the quartet state is more stabilized than the doublet state by about 0.1eV due to the quantum motion of the SDW polaron between the right and left carbenes. This is true even if the quantum fluctuations in phenylenes , the most significant energetically one are taken into account. The stabilization energy by the latter effect is about 2eV, that is, about three times as large as the ground state correlation energy in benzene.

INTRODUCTION

m-Polyphenylcarbene is one of the representative molecules which have high spin ground state in the neutral state[1-4] due to the dynamic spin polarization(DSP)[5,6] in the π system and intraatomic exchange interaction between n and π electrons on carbenes. These polycarbenes were at first predicted to have high spin ground state by N.Mataga[7]. *m*-Phenylenebis(phenylmethylene) (*m*-PBPM) has a quintet ground state in the neutral state[8,9]. The spin density (SD) structures of the quintet ground state are shown in Fig.1. The arrows above and below each carbene denote π and n spins, respectively. For their ions, the results of the experiments by the ESR and ENDOR [10,11] show that it has a quartet ground state in both the monocation and monoanion. Furthermore, in these ionic systems, the injected charge enters mainly on the π orbitals and the conformation changes from trans-cis to trans-trans by the ionizations.

In this paper, we use the n-π model in which π electrons in the phenylenes are treated by the Pariser-Parr-Pople(PPP) model and the π and n electrons on each carbene are approximated with a treatment like the Intermediate-Neglect-Differential-Overlap (INDO) model. Within this model, the electronic states of *m*-PBPM ions are calculated by the unrestricted Hartree-Fock(UHF) and resonating Hartree-Fock(Res HF)[12] approximations. The Res HF method is a method to treat quantum fluctuations resulting from large amplitude collective motions. The broken spin symmetries of the Res HF wavefunctions are restored by the approximate Löwdin spin projection[13].

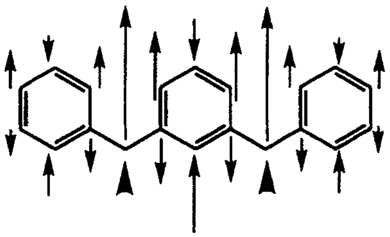

Fig.1 The SD structures of the quintet ground state of neutral *m*-PBPM

METHOD OF CALCULATIONS

The n-π model and its parametrizations will be published in detail elsewhere. The geometry of *m*-PBPM is fixed at a bond angle on each carbene of $\theta=140°$ [14] and the twisting angle between the carbene and the adjacent phenylene of $\phi=20.6°$. Two conformers, C_2 and C_{1h} are possible but the results are almost the same. So, we show only the results for C_2 conformer.

In the UHF calculations, the program with a direct optimization algorism[15] is used. The convergence condition is that the differences of the density matrices in consecutive iterations become smaller than 10^{-4}.

The Res HF method is as follows. The wavefunction is approximated by a superposition of non-orthogonal Slater determinants(S dets). And the configuration interaction(CI) coefficients and the orbitals in each S det are optimized simultaneously[16] with an efficient algorism. Each of S dets in the Res HF wavefunction, which is usually of broken symmetry, is generally expressed as a superposition of multiple excitations from each of the other S dets in it, due to the non-orthogonality. Therefore, if we start from appropriate S dets, the Res HF method can give the solution very close to the full CI one, by using small number of S dets. This is different from the multi-configurational self-consistent field(MCSCF) method, in which the trial wavefunction is usually defined as a superposition of one S det and the excited states generated from it, and the number of S dets is generally large. Especially, in the complete active space self-consistent field (CASSCF) method, the dimension of the active space will be too large to calculate in order to explain the electronic structures of large molecules such as *m*-PBPM enough.

m-PBPM has the C_2 or C_{1h} symmetry. As both C_2 and C_{1h} symmetry-groups have two real 1D irreducible representations(irreps), there are two kinds of the symmetry-adapted Res HF wavefunctions, | m , ±>. They are as follows.

$$|m,\pm\rangle = \sum_{k=1}^{m} C_k\big(|k\rangle \pm R(G)|k\rangle\big) \qquad (1)$$

where | k > is a base, that is, a S det of broken symmetry. G= C_2 or C_{1h} and R denotes the other element of the C_2 or C_{1h} symmetry except identity. When *m* S dets are used as bases and optimized without the spatial projection, we call the Res HF wavefunction | m ,0 >. In the followings, | m , ±> or | m ,0 > in the ion is also represented simply as the (m, ±) or (m,0) ion, respectively. In the Res HF calculation, the convergence condition is that the differences of the energy in consecutive iterations become smaller than 10^{-5} eV, except when otherwise is indicated.

Because a large amount of spin contaminations can be contained in the Res HF wavefunctions, the approximate Löwdin spin projection method[13] applied to the resultant Res HF wavefunctions. The spin projection operator used in this work avoids components from the two spin states adjacent to the one of interest.

With the model, parametrizations and spin projection operator described above, the SD structures of the neutral quintet ground state of *m*-PBPM in the spin projected UHF (PUHF) approximation well reproduce those in the experiment of the ENDOR[17].

RESULTS AND DISCUSSION

The Results of the Res HF Calculation Using UHF Solutions as Trial Bases

In this subsection, we introduce the results of the previous paper[18,19]. Here, we call the UHF and Res HF states the ^{5}S, ^{4}S, ^{3}S, and ^{2}S states if their Sz=2, 3/2,1, and 1/2, respectively. Furthermore, the spin projection operator always projects the states with Sz =3/2 and 1/2 onto the states with S=3/2 and 1/2, respectively, except when otherwise is indicated. The previous results are as follows.

(1) In the UHF approximation, the ^{4}S state is more stable than the ^{2}S state in both cation and anion though the ^{2}S-^{4}S energy gaps(D-Q gaps) are at most 20meV. But, after spin projection, the gap becomes 8meV and is very small in the cation and the ^{2}S state becomes more stable by 3meV in the anion.(Table I) The UHF ^{4}S and ^{2}S states are called $E_0(^4S)$ and $E_0(^2S)$, respectively.

(2) In the UHF approximation, the injected charge is always pinned on a carbene as a SDW polaron. The injected charge density(ICD) and SD structures of $E_0(^4S)$ and $E_0(^2S)$ anions are shown in Fig.2. In the ^{4}S state, the n spins on the right and left carbenes are

parallel to each other. Therefore, Two $E_0(^4S)$s with a SDW polaron pinned on the right and left carbenes, respectively, are of broken symmetry but degenerate to each other. In the ^2S state, the two n spins are antiparallel each other. Therefore, the two ^2S states with a SDW polaron pinned on the n(↓) and n(↑) carbenes, respectively, are not equivalent. The former is $E_0(^2S)$ and the latter state also exists as an UHF ^2S excited state which we call $E_1(^2S)$ in the following. $E_1(^2S)$ has a π (↑)-n(↓) carbene which gives the small n-π exchange energy gain. Therefore, $E_1(^2S)$ has higher energy than $E_0(^2S)$ by about 0.5eV. In the cation, the UHF solutions, $E_0(^4S)$, $E_0(^2S)$ and $E_1(^2S)$ are qualitatively similar to the cases in the anions as described above.

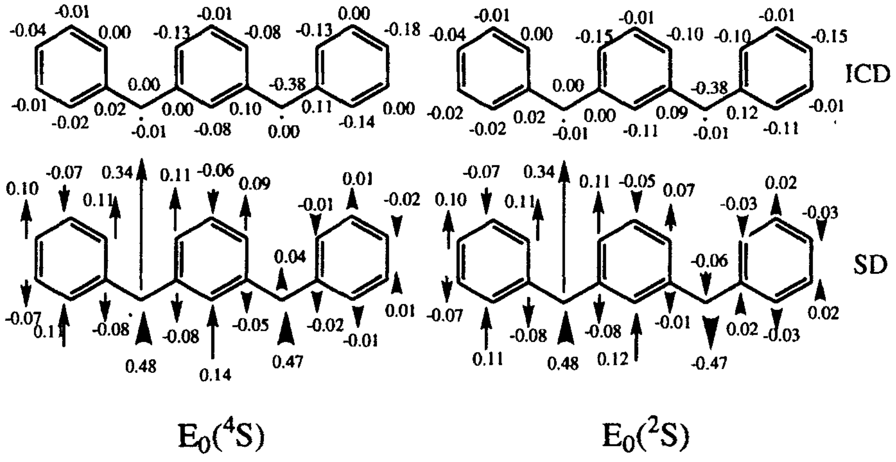

Fig.2 The ICD and SD structures of $E_0(^4S)$ and $E_0(^2S)$ anions

(3) The Res HF ^4S and ^2S (1,±) ions are calculated. The trial bases are $E_0(^4S)$ and $E_0(^2S)$, in the ^4S and ^2S states, respectively. From eq.(1), the (1,±) ions contain the effect of the quantum motion of a SDW polaron between the right and left carbenes. In the ^4S (^2S) state, | 1,- > (| 1,+ >) has lower energy than | 1,+ > (| 1,- >). From the spin projected Res HF(PRes HF) (1,±) - PUHF energy gaps, the stabilization energies of the quantum motion of a SDW polaron between the two carbenes are about 0.2eV and 30meV in the ^4S and ^2S states, respectively.(Table I) Therefore, the stabilization by the quantum motion of a SDW polaron between the two carbenes is much larger in the ^4S state than in the ^2S state. As a result of orbital optimization, the SDW polaron in the Res HF ^4S (1,-) base becomes broadened by the quantum motion of a SDW polaron. On the other hand, the Res HF ^2S (1,+) base is not modified by the optimization of the trial bases due to the approximate orthogonality between $E_0(^2S)$ and $R(C_2)E_0(^2S)$ by the

antiparallel n spins on the carbenes.

(4) The ^{2}S (2,0) ions are also calculated. The two trial bases are the UHF solutions, $E_0(^2S)$ and $E_1(^2S)$. The PRes HF ^{2}S (2,0) energies are lower than PRes HF ^{4}S (1,-) energies by 68meV and 17meV in the cation and anion, respectively. In both the Res HF ^{2}S (2,0) cation and anion, both of the two bases have a SDW polaron pinned on the $n(\downarrow)$ carbene though one of the two trial bases, $E_1(^2S)$, has it on the $n(\uparrow)$ carbene. Therefore, the resonance between the two bases does not show the quantum motion of a SDW polaron between the two carbenes. But, in the anion, π -SDs on the right phenylene are large in both the two bases and the DSPs there are out of phase between the two bases. Such large spin fluctuations in the right phenylene stabilize the ^{2}S (2,0) anion. The ^{2}S (2,0) cation is also stabilized by quantum fluctuations in the phenylenes. But, they are in a different manner from the ^{2}S (2,0) anion. The details will be published elsewhere. Therefore, the ^{2}S (2,0) ions are stabilized by the quantum fluctuations in the phenylenes. They are generated from the SDW polaron pinned on the same carbene.

Benzene and *m*-Phenylenebis(methylene) (*m*-PBM)

From the above result (4), the quantum fluctuations in the phenylenes are taken into account by the resonance among several S dets with a SDW polaron pinned on the same carbene. But, in the cases of less than eight S dets, as the number of S dets is larger, the Res HF energy becomes lower and does not seem to converge. Therefore, such method is not enough. In order to take the correlation more systematically, the Res HF method is applied to benzene with the PPP model.

In the Res HF calculation of benzene, one S det of broken symmetry is used as a base to be optimized with the spatial projection onto a irrep of the C_{6v} symmetry-group which benzene belongs to. We adopt a S det with a neutral soliton pair as the trial base of the neutral state. In the cation and anion, a S det with excess charge localized on a carbene is used as the trial base. As a result, by optimizing only one S det, its spatial projected state can explain 97.7% and 95% of the correlation energies in the neutral and ionic states, respectively. These correlation energies are 0.76eV and 0.64eV in the neutral and ionic states, respectively. The optimized base is of perfectly broken C_{6v} symmetry in both the neutral and ionic states. Therefore, the most significant correlation in benzene with the PPP model is the quantum motions of the charges and spins around the benzene ring. Because such charges and spins cannot be characterized definitely unlike the SDW polaron, we simply call this correlation the quantum fluctuations in the phenylene. In the Res HF method, the fluctuations can be generated by only one S det of complete broken symmetry.

Furthermore, we apply the Res HF method to *m*-PBM ^{4}S ions with the n-π model because *m*-PBM is an analogous molecule to *m*-PBPM small enough to yield exact solutions. To take the Res HF trial bases including the electron correlation in benzene enough, the Res HF wavefunctions of benzene are used. *m*-PBM has the C_{2v} symmetry that is lower than the C_{6v} symmetry of benzene. Therefore, to take the correlation in benzene described above, the symmetry related S dets in benzene are considered as independent variables. There are two possibilities in connecting two carbenes to the Res HF wavefunction of benzene. The one is to connect an ionic and neutral carbenes to neutral benzene. Another is to connect two neutral carbenes to ionic benzene. In the former case, Sz=0 in benzene and in this case, spin reversed S dets are also considered. Therefore, 2 × 12 independent S dets are prepared in the former case where 12 is the number of elements of the C_{6v} symmetry-group. In the latter case, $Sz \neq 0$ in benzene and spin reversed Sdets are not considered. Furthermore, the symmetry axis of *m*-PBM is also that of the benzene in it and both of the two carbenes are neutral. Because the S dets of *m*-PBM are optimized with the spatial projection onto an irrep of the C_{2v} symmetry-group in the Res HF calculation, $12 \div 2=6$ independent S dets are needed in the latter case. Thus $2 \times 12+6=30$ independent S dets of *m*-PBM are used as trial bases and the ^{4}S (30,-) ions are calculated. As a result, 99.17% of the correlation energy can be explained in both cation and anion. On the other hand, ^{4}S (1,-) ions which includes only the quantum motion of excess charge between the two carbene, can explain only 35% of it.

Significant Electron Correlation in *m*-PBPM Ions

From the results of *m*-PBM, we construct the trial bases of *m*-PBPM ions with a similar idea to the case of *m*-PBM. Concretely, *m*-PBPM is separated into three parts, right and left phenylmethylenes(PMs) and central *m*-PBM. And the Res HF method is applied to each of three parts with the trial bases prepared with a similar idea to the case of the ^{4}S *m*-PBM ions. After that, the S dets in the three parts are connected. The details will be published elsewhere. As a result, we calculate the Res HF (42,-) and (32,0) ions with Sz=3/2 and 1/2, respectively.

In Table I, the Res HF and PRes HF energies, and D-Q gaps of the ^{4}S (42,-), ^{2}S (32,0), ^{2}S (32,+) ions are shown. The D-Q gaps are those between the ^{4}S (42,-) and ^{2}S (32,+) ions. Due to difficulty of the calculation with large dimension, the value here in the Res HF (42,-) and (32,0) are stopped at 530th and 360th iterations, respectively. But each state converges in the order of 10^{-4}eV. The Res HF (32,+) ions are calculated by using the converged (32,0) bases as the trial bases and with the convergence condition of 10^{-4}eV. From Table I, the PRes HF ^{4}S (1,-) - ^{4}S (42,-) energy gaps are about 2eV in both the cation and anion. This is about three times larger than the correlation energies of benzene. The PRes HF ^{2}S (32,0) -(32,+) energy gaps are small and almost the same as the PE$_0$(^{2}S) - PRes HF ^{2}S (1,+) energy gaps. The ^{2}S (32,+) - ^{4}S (42,-) energy gaps are a little smaller than the ^{2}S (1,+) - ^{4}S (1,-) energy gaps in both cation and anion, but they can be regarded as the difference of the stabilization energy by the quantum motion of a SDW polaron between carbenes.

Table I Res HF and PRes HF energies and D-Q gaps

Charge	Sz	ψ	E_{res} (eV)	E_{pres} (eV)	Δ E(eV)
+1	3/2	UHF	-302.285	-302.400	0.008
		(1, -)	-302.506	-302.596	0.178
		(42, -)	-304.425	-304.470	0.116
	1/2	UHF	-302.266	-302.392	
		(1, +)	-302.266	-302.419	
		(32, 0)	-304.297	-304.328 -304.305 (S=3/2)	
		(32, +)	-304.297	-304.355	
-1	3/2	UHF	-313.344	-313.474	-0.003
		(1, -)	-313.579	-313.682	0.175
		(42, -)	-315.509	-315.563	0.148
	1/2	UHF	-313.334	-313.476	
		(1, +)	-313.334	-313.507	
		(32, 0)	-315.347	-315.382 -315.384 (S=3/2)	
		(32, +)	-315.347	-315.414	

In Table I, the results of the PRes HF ^{4}S (32,0) with Sz=1/2 are also listed. The D-Q gaps between the ^{2}S and ^{4}S (32,0) ions are only -23meV and +2meV in the cation and anion, respectively. The Res HF (32,0) states only contain the enough quantum fluctuations in the phenylenes and little effect of the quantum motion of the SDW polaron. Therefore, the quantum fluctuations in the phenylenes do not give the D-Q gaps. This fact supports that the origin of the D-Q gaps of *m*-PBPM ions is the difference of the stabilization energy by the quantum motion of the SDW polaron between carbenes. But more than 90% of the correlation energy is the stabilization energy by the quantum fluctuations in the phenylenes in the ^{4}S state. Similarity of the energy gaps between ^{2}S (32,+) - ^{4}S (42,-) and ^{2}S (1,+) - ^{4}S (1,-) suggests that the two kinds of electron correlation, the quantum motion of the SDW polaron and the quantum fluctuations in the phenylenes, are nearly independent.

The total ICD and SD structures of the ^{4}S (42,-) anion are similar to those of the ^{4}S (1,-) anion[18,19]. This may be because the effect of the quantum fluctuations in the phenylenes does not appear remarkably in the total ICDs and SDs, due to averaging the charges and spins around the phenylenes by their quantum motion there.

In conclusion, we make the n-π model which includes only π and n electrons.

Within this model, the electronic states of *m*-PBPM ions are investigated by the UHF and the Res HF method. As a result, the correlation energy of the quantum fluctuations in the phenylenes is about 2eV in both ^{2}S and ^{4}S ions. This is very large and about three times larger than the correlation energy of benzene. But the D-Q gaps are given almost by the difference of the stabilization energy by the quantum motion of a SDW polaron between the right and left carbenes, which is about a little more than 0.1eV. Therefore, *m*-PBPM ion has a ^{4}S ground state.

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