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The Electronic Structure of the Fulvalene Trication Radical. A Localization of the Unpaired Electron

Azumao TOYOTA*,† and Takeshi NAKAJIMA
†*Department of Chemistry, Faculty of General Education, Yamagata University, Yamagata 990*
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980
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The restricted Hartree-Fock (RHF) solution for the trication radical of fulvalene, obtained by using the open-shell SCF formalism of the Pariser-Parr-Pople-type MO method, is found to be doublet unstable at the conventional D_{2h} nuclear arrangement. We calculate the broken-symmetry charge-density wave solution lower in energy than the usual symmetry-adapted RHF solution and examine its properties. It is predicted that the unpaired electron should be localized on the single five-membered ring having a smaller positive charge. Finally, on the basis of the second-order Jahn-Teller effect, we examine the molecular-symmetry reduction of the trication radical from the fully-symmetrical D_{2h} to the C_{2v} nuclear arrangement.

On the basis of the doublet instability of the restricted Hartree-Fock (RHF) solution,[1,2] we have examined the origin of the anomalous phenomena that in the monoanion and trianion radicals of heptafulvalene the unpaired electron is localized on a single seven-membered ring.[3,4] It has been shown that the RHF solutions for the anion radicals, obtained by using the open-shell SCF formalism of the Pariser-Parr-Pople (PPP) type MO method, are doublet unstable at the conventional D_{2h} nuclear arrangement and the spin-density distributions obtained from the resulting broken-symmetry charge-density wave (CDW) solutions are in good agreement with the experimental ones.[5,6]

The monoanion radical of fulvalene has recently been prepared by Davies *et al.*[7,8] The spin-density distribution of this radical is of interest in connection with that of the heptafulvalene monoanion radical. In order to obtain information about the behavior of unpaired electron, they have made the ESR studies of the radical and it is revealed that the unpaired electron is delocalized over the entire molecule, showing a sharp contrast to the situation observed with the heptafulvalene monoanon radical.[3]

Although neither the monocation nor the trication radical of fulvalene has so far been prepared, both of the radicals are of great interest from theoretical and experimental points of view, because our previous research suggests that the localization of unpaired electron similar to those in the heptafulvalene monoanion and trianion radicals should occur: As to the monocation radical, we have partly studied the problem in view of the doublet instability of the RHF solution at the conventional D_{2h} nuclear arrangement.[5]

In this paper, we investigate the behavior of unpaired electron and the distribution of charge density in the trication radical of fulvalene by examining the instability of the RHF solution and by using the second-order Jahn-Teller theory. On the basis of the results obtained, we point out a distinct difference with regard to the distributions of the unpaired spin density and the ring charge density between the monocation and trication radicals.

Theoretical

The Stability Conditions of the RHF Solution. The stability conditions of the RHF solution for the open-shell case were formulated by Paldus and Cizek.[1,2] Since the conditions are well discussed in several literatures, we give here only the outline of the theory.

Using the usual real molecular orbitals, the question of whether the RHF solution is doublet stable or not resolves itself into the solution of the lowest-lying eigenvalue of the following two eigenvalue problems:

$$(A+B)D_+ = \lambda_+ D_+,$$
$$(A-B)D_- = \lambda_- D_-. \qquad (1)$$

That is, if $\lambda_+<0$ or $\lambda_-<0$, a doublet instability occurs in the usual symmetry-adapted RHF solution and a new RHF solution becomes a real CDW solution or a complex CDW solution, respectively.

In Eq. 1, elements of the square matrices, A and B, represent the configuration interactions between spin unflip singly excited configurations and those between the RHF ground state and spin unflip bi-excited states, respectively. The elements of the column matrix D_+ or D_- are the mixing coefficients which give the weights with which the virtual RHF molecular orbitals are admixed to the occupied ones. If the occupied and virtual orbitals belong to different irreducible representations, the symmetry properties of the new orbitals are broken (see Eq. 2): The molecular orbitals do not transform according to the irreducible representations of the molecular point group and, as a result, the new HF solution becomes the so-called broken-symmetry CDW solution.

Results and Discussion

The Broken-symmetry CDW Solution and Its Properties. The optimum nuclear arrangement of the trication radical with the D_{2h} symmetry was

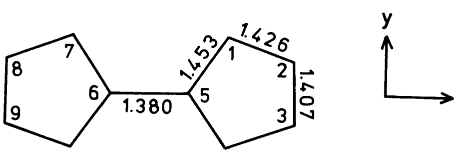

Fig. 1. The optimized bond lengths (in Å) of the fulvalene trication radical at the D_{2h} nuclear arrangement, the numberings of atomic positions, and the choice of molecular axes.

calculated by using Longuet-Higgins and Pople's MO method[9] in conjunction with the variable bond-length technique.[10] The RHF solution to which the stability conditions will be applied is the one corresponding to the molecular geometry thus optimized with respect to carbon nuclear arrangement (Fig. 1).

It turns out that the lowest-lying eigenvalue $\lambda_{\min}$, obtained from the λ_+ subproblem of Eq. 1, is -1.227 eV and the electronic configurations that play an important role in the RHF instability are those including the orbital jumps from the highest doubly occupied orbital ϕ_3 (b_{3u}) to the next lowest vacant orbital ϕ_6 (b_{2g}) and from the singly occupied orbital ϕ_4 (a_u) to the lowest vacant orbital ϕ_5 (b_{1g}). As noted above, since the eigenvector $d_{\min}$ is of b_{1u} symmetry, a new HF solution becomes a real CDW solution having the C_{2v} spatial symmetry.

Let us now treat the CDW solution according to the same procedure as used in a previous paper.[5] For obtaining the CDW solution we take into account only the two orbital jumps above. This approximate procedure is justified, for the eigenvalue $\lambda'_{\min}$ (-1.130 eV) thus obtained reproduces well the eigenvalue $\lambda_{\min}$(-1.227eV) obtained by including all the singly excited configurations. By using the mixing coefficients of the eigenvector $d'_{\min}$ corresponding to the eigenvalue $\lambda'_{\min}$ the new occupied orbitals are formed as:

$$\begin{aligned} \varphi_i &= \phi_i \, (i=1,2), \\ \varphi_3 &= \mu_1\phi_3 + \mu_2\phi_6, \\ \varphi_4 &= \nu_1\phi_4 + \nu_2\phi_5, \end{aligned} \tag{2}$$

and

$$\begin{aligned} \mu_1 &= \{1-(0.3135k)^2\}^{1/2}, \quad \mu_2 = -0.3135\,k \\ \nu_1 &= \{1-(0.9496k)^2\}^{1/2}, \quad \nu_2 = 0.9496\,k \end{aligned} \tag{3}$$

where k is the dimensionless mixing parameter, which indicates the degree of deformation of the CDW solution from the symmetry-adapted RHF solution. Using the molecular orbitals above, we can write the CDW solution as:

$$\begin{aligned} {}^2\Psi_{\mathrm{CDW}}(k) &= \mu_1{}^2\nu_1{}^2\,{}^2\Psi_{\mathrm{RHF}}(\mathrm{A_u}) + \mu_1{}^2\nu_2{}^2\,{}^2\Psi_1(\mathrm{B_{1g}}: 4\rightarrow5) \\ &+\sqrt{2}\,\mu_1\mu_2\nu_1\,{}^2\Psi_1(\mathrm{B_{1g}}: 3\rightarrow6) + \mu_2{}^2\nu_1{}^2\,{}^2\Psi_2(\mathrm{A_u}: 3,3\rightarrow6,6) \\ &+\sqrt{2}\,\mu_1\mu_2\nu_2\,{}^2\Psi_2(\mathrm{A_u}: 3,4\rightarrow6,5) \\ &+ \mu_2{}^2\nu_2{}^2\,{}^2\Psi_3(\mathrm{B_{1g}}: 3,3,4\rightarrow6,6,5), \end{aligned} \tag{4}$$

where notations used are the same as those in a previous paper.[5] It is seen that the CDW solution comprises the configurations of A_u and B_{1g} symmetries. Evidently, the symmetry-breaking components are the configurations of B_{1g} symmetry, for the RHF ground state is of A_u symmetry.

We now examine the dependence of the energy expectation value of the broken-symmetry CDW solution on the mixing parameter k. The result shows that the energy minimum point, *i.e.*, the stable CDW solution, is found at $k=0.66$, the energy lowering from the symmetry-adapted RHF solution being calculated to be 0.249 eV.

In Fig. 2 are shown the dependence of the electron densities and bond orders of the CDW solution on k. It is seen that the electron densities at 1 and 7, 2 and 8, and 5 and 6 and the bond orders between 1—5 and 6—7, 1—2 and 7—8, and 2—3 and 8—9 become separated as k increases. Included in Table 1 are the detailed values of electron density and bond order of the symmetry-adapted RHF and stable CDW solutions. It is found that there is a notable difference in the distribution of the density matrix elements between the two solutions: If we take the electron densities of the RHF solution as the reference values, a charge-density alternation can be seen along the longer molecular axis(z) in the electron-density distribution of the CDW solution. As to the

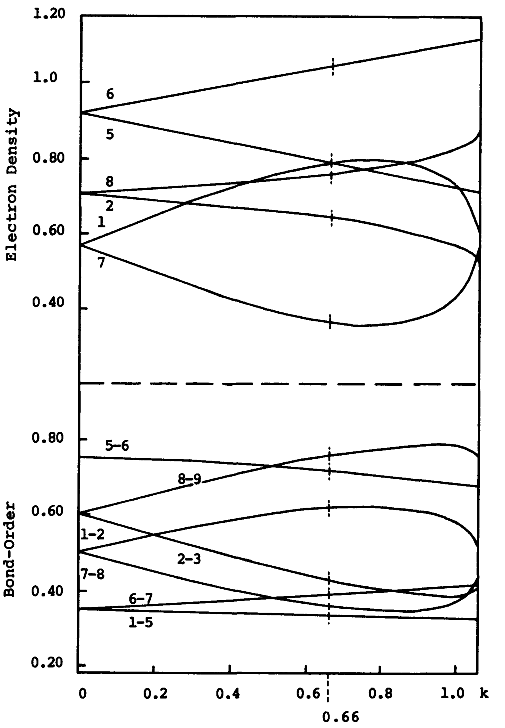

Fig. 2. The dependence of the electron densities and bond orders of the broken-symmetry CDW solution on the mixing parameter k.

Table 1. Electron densities bond orders of the fulvalene trication radical

	RHF solution	CDW solution	RHF solution
	(C$_{2v}$ molecular geometry)		(D$_{2h}$ molecular geometry)
Atom	Electron density		
1	0.750	0.791	0.579
7	0.410	0.374	
2	0.671	0.649	0.710
8	0.758	0.765	
5	0.779	0.796	0.921
6	1.043	1.048	
Bond	Bond order		
1-2	0.628	0.624	0.504
7-8	0.360	0.366	
2-3	0.424	0.438	0.607
8-9	0.752	0.763	
1-5	0.351	0.347	0.361
6-7	0.434	0.396	
5-6	0.693	0.726	0.753

distribution of bond orders, a similar behavior can be seen.[11] It is noted that the positive ring charges of the broken-symmetry CDW solution are unequal: The charge of the left-hand ring is 1.676(e) and that of the other ring is 1.324.

In Fig. 3 is depicted the dependence of the unpaired spin densities of the broken-symmetry CDW solution on k. This shows that the unpaired spin densities of the stable CDW solution (k=0.66) are localized essentially on a single five-membered ring. It is remarked that such a localization of the unpaired electron has also been found out theoretically in the monocation radical of fulvalene.[5] However there is a distinct difference with regard to the distributions of the unpaired spin density and the ring charge density between the trication and monocation radicals. In the latter, the unpaired spin density is localized in the five-membered ring having a larger positive charge, while in the former it is localized in the ring having a smaller positive charge. This difference will be explained by using Eq. 2 as follows. In the trication radical, the occupied orbital that is affected greatly by the appearance of the doublet instability is the singly occupied orbital ψ_4, whereas in the monocation radical such orbitals are the doubly occupied orbital ψ_4 and the singly occupied orbital $\psi_5(=\nu_1\phi_5-\nu_2\phi_4)$. As shown in Fig. 4, the atomic-orbital coefficients for the symmetry-adapted RHF orbitals, ϕ_4 and ϕ_5, are almost equal in absolute value and opposite on the respective carbon atoms. Thus, as k increases, orbitals ψ_4 and ψ_5 will be localized in the different five-membered rings. Consequently, in the trication radical the unpaired electron is localized in the ring having a smaller positive charge, while in the monocation radical it is localized in the ring having a larger positive charge.

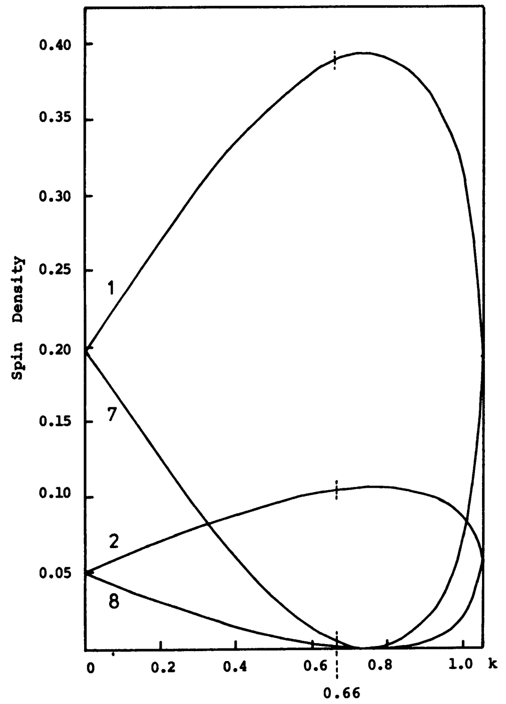

Fig. 3. The dependence of the unpaired spin densities of the broken-symmetry CDW solution on the mixing parameter k. The spin densities on the carbon atoms 5 and 6 are zero by symmetry.

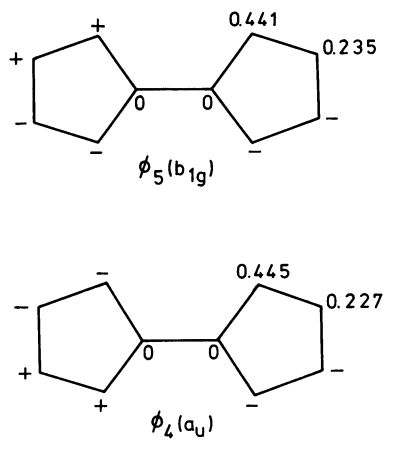

Fig. 4. The atomic-orbital coefficients of the usual symmetry-adapted RHF orbitals, ϕ_4 and ϕ_5, for the fulvalene trication radical.

Table 2. Spin densities and proton hyperfine splittings of the fulvalene trication radical

Atom	Broken-symmetry CDW solution (D_{2h} molecular geometry)		Symmetry-adapted RHF solution (C_{2v} molecular geometry)	
	Spin density	Hyperfine splitting/G[a]	Spin density	Hyperfine splitting/G
1	0.3887	8.16	0.3559	7.47
2	0.1054	2.21	0.1235	2.59
5	0	0	0	0
6	0	0	0	0
7	0.0050	0.11	0.0174	0.36
8	0.0009	0.02	0.0032	0.07

a) 1 G=10^{-4} T.

The detailed spin densities of the stable CDW solution are listed in Table 2, together with the proton hyperfine splittings calculated by using McConnell's relationship[12] with $|Q|$=21 G (1G=10^{-4}T). It is predicted that the proton hfs constant on the carbon atom 1 is greater than that on the carbon atom 2.

It has thus been shown that the distribution of the density matrix elements inherent in the stable CDW solution is lower in symmetry than that of the nuclear arrangement used. Such an effect has been recognized in the theory of chemical reaction as the electron-cloud preceding.[13] Since it is known that such a preceding behavior of electron cloud brings about the change in nuclear configuration from unstable to stable one, we may expect that the broken-symmetry CDW solution is further stabilized by relaxation of the nuclear framework such that it may match up with the symmetry of the CDW solution.[14] This implies that a lattice instability similar to the second-order Jahn-Teller effect[15] may occur, as is very often the case.

The Second-order Jahn-Teller Effect. From the above argument, it is suggested that the trication radical may undergo the second-order Jahn-Teller distortion.[15] In order to elucidate this problem, we examine the lower electronic states of the trication radical by assuming the optimized D_{2h} molecular geometry (Fig. 1). It turns out that the ground state is of A_u symmetry and the lowest excited doublet state corresponding to a single MO transition $\phi_4(a_u)\rightarrow\phi_5(b_{1g})$ is of B_{1g} symmetry, the energy separation between the two states being only 0.03 eV. Since both the states are nearly degenerate, the nuclear deformation of $B_{1u}(A_u \times B_{1g})$ symmetry should cause a strong vibronic interaction between them. Accordingly, we can expect that the ground state of the trication radical would undergo the second-order Jahn-Teller distortion from the D_{2h} to the C_{2v} nuclear arrangement. Of the three types of C–C bond distortion belonging to the B_{1u} symmetry, the one actually effective for the molecular-symmetry reduction can be given by examining the distribution of the transition density ρ between the ground and the lowest excited doublet state.[16-18] The nearest two-center components of the transition density, $\phi_4\phi_5$, are shown in Fig. 5.

We now calculate the geometrical structure with respect to C–C bond lengths of the trication radical as follows: As a starting geometry for iterative PPP-type SCF MO calculation, we adopt a nuclear configuration in which C–C bond lengths are distorted so that the set of displacement vectors may match up with the distribution of the transition density shown in Fig. 5. Then, self-consistency has been achieved at a set of C–C bond lengths corresponding to a lower symmetrical nuclear arrangement (C_{2v}). The obtained bond lengths and ring charges for the C_{2v} nuclear arrangement are shown in Fig. 5. Here, the stabilization energy, defined as the difference in total energy between the fully-symmetrical D_{2h} and the reduced C_{2v} molecular geometry,[16,17,19] is calculated to be 0.403 eV. In Table 1 are summarized the electron densities and bond orders for comparision with those of the broken-symmetry CDW solution. Moreover, the unpaired spin densities and the associated proton hfs constants calculated by assuming the C_{2v} nuclear arrangement are listed in Table 2. It is clear from Tables 1 and 2 that the density matrix elements of the symmetry-adapted RHF solution corresponding to the C_{2v} nuclear arrangement show a striking resemblance to those of the stable broken-symmetry CDW solution and the unpaired electron is confined to the single five-membered ring having a ring charge of 1.38 (see Fig. 5). It is further proved that the present symmetry-adapted RHF solution (C_{2v}) is lower in energy than the stable CDW solution by 0.154 eV. From these aspects, it can be said that the broken-symmetry CDW solution is realized in the C_{2v} nuclear arrangement, becoming to be symmetry adapted.

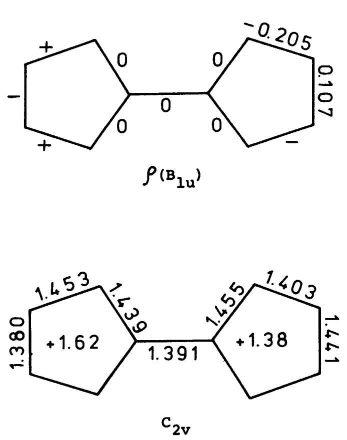

Fig. 5. The distribution of the nearest two-center components of transition density ρ and the optimized bond lengths (in Å) and ring charges at the C_{2v} nuclear arrangement.

The Ion Radicals of Fulvalene and Heptafulvalene. In connection with the fulvalene trication radical, it is noted that the RHF solution for the trianion radical, as well as that for the monoanion radical, is doublet stable ($\lambda_{min}=0.619$ eV) at the optimum nuclear arrangement with the D_{2h} symmetry. This shows a sharp contrast to the cases of the trication and monocation radicals. The explanation for this distinct difference between the anion radicals and the cation radicals of fulvalene can be given qualitatively as follows. From the stability conditions of the RHF solution, it is seen that the occurrence of the RHF instability depends on the magnitudes of energy separation between the RHF ground state and the singly excited doublet configurations. In fulvalene with the D_{2h} symmetry, the highest two occupied orbitals are nearly degenerate (in the HMO approximation those orbitals are accidentally degenerate). For the monocation and trication radicals, which are formed respectively by taking off one and three electrons from those orbitals, the RHF ground states are nearly degenerate with the respective lowest singly excited configurations. For this reason, the RHF solutions turn out to be doublet unstable. While, for the monoanion and trianion radicals the lowest singly excited configurations are well separated from the respective RHF ground states, so that the RHF solutions turn out to be doublet stable. In this connection, we also refer to the characteristic features of the RHF instabilities found in the ion radicals of heptafulvalene.[5,6] In heptafulvalene, the situation of the orbital pattern is quite different from that in fulvalene: The molecular orbitals that are accidentally degenerate in the HMO approximation are the lowest two unoccupied orbitals. Hence, for the monoanion and trianion radicals, which are formed respectively by adding the extra one and three electrons to those orbitals, the RHF ground states turn out to be nearly degenerate with the respective lowest singly excited configurations, resulting in the occurrence of the doublet instabilities in the RHF solutions. In cases of the monocation and trication radicals, the RHF solutions turn out to be double stable since the lowest singly excited configurations in question are well separated from the respective RHF ground states. Therefore, the origin of the instabilities of the RHF solutions and related phenomena, especially the anomalies in the spin-density distributions in the ion radicals of fulvalene systems, can be ascribed to the near degeneracy of the highest two occupied or the lowest two unoccupied orbitals inherent in the respective fulvalene systems.

Concluding Remarks. In the framework of the HF approximation, we have been concerned with the problem of the localization of unpaired electron in the fulvalene trication radical. The results of the present calculations based on the RHF instability and the second-order Jahn-Teller theory show that the ground-state geometrical structure of the trication should be of C_{2v} symmetry and in the stable nuclear arrangement the unpaired electron is localized essentially on the single five-membered ring having a smaller positive charge. It has also been demonstrated that the occurrence of the RHF instability provides useful information about the type of wave function and the symmetry of nuclear framework. Especially, the resulting broken-symmetry CDW solution is shown to give a good account of the mechanism how the localization of unpaired electron occurs.

It is noted that the trication radical of 2,5-bis(2,4-cyclopentadien-1-ylidene)-1,4-cyclohexadiene, [5.6.5]quinarene, is expected to undergo a molecular symmetry reduction ($D_{2h} \rightarrow C_{2v}$) and exhibit an anomalous spin-density distribution similar to that of the fulvalene trication radical.

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