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The Electronic Structure of the Heptafulvalene Trianion Radical—The Doublet Instability of the Hartree–Fock Solution and Related Phenomena

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The restricted Hartree–Fock (RHF) solution for the trianion radical of heptafulvalene, obtained using the open-shell SCF formalism of the Pariser–Parr–Pople method, is found to be doublet unstable at the conventional D_{2h} nuclear arrangement. We calculate the broken-symmetry charge-density wave (CDW) solution and examine its properties. It is shown that the proton hyperfine splittings for the trianion radical calculated from the CDW solution are in good agreement with the experimental values. Further, we briefly refer to the possibility of the lattice instability of the trianion radical from the fully-symmetrical D_{2h} to the C_{2v} nuclear arrangement.

Key words: Heptafulvalene trianion radical – Doublet instability of the HF solution.

1. Introduction

In recent years, the trianion radicals of conjugated hydrocarbons have been the subjects of experimental investigations, especially of the ESR studies [1–5]. Of the trianion radicals examined, the heptafulvalene trianion radical studied by Bauld and others [4] is of great interest. The ESR spectrum of this radical indicates that the unpaired spin density is not delocalized throughout the molecule, but it is localized essentially on a single seven-membered ring. A similar anomaly in spin-density distribution has already been observed by Sevilla and others [6] in the heptafulvalene monoanion radical.

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In a previous paper [7], we have investigated the origin of the anomalous spin-density distribution of the heptafulvalene monoanion radical by examining the doublet instability of the restricted Hartree–Fock (RHF) solution [8–10]. It has been shown that the RHF solution of the monoanion radical at the conventional D_{2h} nuclear arrangement is doublet unstable and the spin-density distribution obtained from the resulting broken-symmetry charge-density wave (CDW) solution is in good agreement with the experimental information [6].

In this paper, in order to explain the anomalous spin-density distribution of the heptafulvalene trianion radical, we examine the doublet instability of the RHF solution by using the open-shell SCF formalism of the Pariser–Parr–Pople MO method [11]. It will be shown that the RHF solution of the trianion radical also is doublet unstable and the proton hyperfine splittings calculated from the CDW solution are in good agreement with the experimental values. Further, we point out a distinct difference with regard to the distributions of the unpaired spin density and the ring charge density between the monoanion and trianion radicals. Finally, we briefly refer to the possibility of the lattice instability of the trianion radical from the fully-symmetrical D_{2h} to the C_{2v} nuclear arrangement.

2. The Doublet Stability Conditions

The doublet stability conditions of the RHF solutions for the open-shell case were formulated by Paldus and Čižek [8–10], which require that all the eigenvalues of the following eigenvalue problem are to be positive:

$$\begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix}\begin{pmatrix} D \\ D^* \end{pmatrix} = \lambda \begin{pmatrix} D \\ D^* \end{pmatrix} \tag{1}$$

where 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 configurations, respectively. The elements of the column matrix D are the mixing coefficients which give the weights with which the virtual RHF molecular orbitals are admixed to the occupied ones, and the asterisk superscript denotes the complex conjugates.

The eigenvector $d_{\min}$ of Eq. (1), corresponding to the lowest eigenvalue $\lambda_{\min}$, gives the direction of the steepest descent when $\lambda_{\min} < 0$, or the slowest ascent when $\lambda_{\min} > 0$, of the energy hypersurface of the energy functional at the point of the symmetry-adapted RHF solution.

When the elements of the matrices, A and B, are real, the eigenvalue problem given in Eq. (1) can be reduced to the following two eigenvalue problems:

$$\begin{aligned} (A+B)D_+ &= \lambda_+ D_+ \\ (A-B)D_- &= \lambda_- D_-. \end{aligned} \tag{2}$$

If $\lambda_+ < 0$ or $\lambda_- < 0$, a doublet instability occurs and a new HF solution is a real CDW solution or a complex CDW solution lower in energy than the conventional symmetry-adapted RHF solution, respectively.

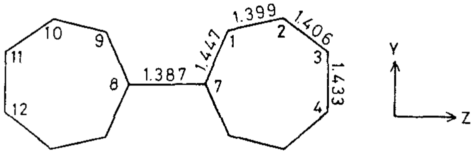


Fig. 1. The optimized C—C bond lengths (in Å unit) of the heptafulvalene trianion radical at the D_{2h} nuclear arrangement, the numberings of atomic positions, and the choice of molecular axes

3. Results and Discussion

3.1. *Doublet Instability of the* RHF *Solution*

The optimum nuclear arrangement of the trianion radical with the D_{2h} symmetry was calculated by using Longuet-Higgins and Pople's SCF MO method [11] in conjunction with the variable bond-length technique [12]. The RHF solution to which the stability conditions will be applied is the one corresponding to the molecular geometry thus optimized with respect to C—C bond length (Fig. 1).

The calculated lowest-lying eigenvalue $\lambda_{\min}$ and the symmetry of the corresponding eigenvector $d_{\min}$ are respectively -1.204 eV and b_{1u}. It is noted that this eigenvalue is obtained from the λ_+ subproblem of Eq. (2). Since for the trianion radical the direction of the steepest descent in the variational space of the energy functional is of b_{1u} symmetry, there appears broken-symmetry CDW solution having the C_{2v} spatial symmetry.

3.2. *Broken-symmetry* CDW *Solution*

The CDW solution of the trianion radical is treated according to the same procedure as used in a previous paper [7]. The electronic configurations which play an important role in the doublet instability of the RHF solution turn out to be those including the orbital jumps from the highest doubly occupied orbital ϕ_8 to the half-filled orbital ϕ_9 and from the next highest doubly occupied orbital ϕ_7 to the lowest vacant orbital ϕ_{10}. For obtaining the CDW solution we take into account only the two orbital jumps above. This approximate procedure is justified, for the eigenvalue $\lambda'_{\min}$ (-1.193 eV) thus obtained reproduces well the eigenvalue $\lambda_{\min}$ (-1.204 eV) obtained by including all the excited configurations. By using the mixing coefficients of the eigenvector $d'_{\min}$ corresponding to the eigenvalue $\lambda'_{\min}$, the new occupied molecular orbitals are formed as:

$$\begin{aligned} \psi_i &= \phi_i \qquad (i = 1-6) \\ \psi_7 &= \mu_1\phi_7 + \mu_2\phi_{10} \\ \psi_8 &= \nu_1\phi_8 + \nu_2\phi_9 \\ \psi_9 &= \nu_1\phi_9 - \nu_2\phi_8 \end{aligned} \tag{3}$$

and

$$\begin{aligned} \mu_1 &= \{1-(0.350\kappa)^2\}^{1/2}, \qquad \mu_2 = 0.350\kappa \\ \nu_1 &= \{1-(0.937\kappa)^2\}^{1/2}, \qquad \nu_2 = 0.937\kappa \end{aligned} \tag{4}$$

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

$$\begin{aligned}{}^2\Psi_{\mathrm{CDW}}(\kappa) = {} & \mu_1^2\nu_1^2\,{}^2\Psi_{\mathrm{RHF}}(B_{1g}) + \mu_1^2\nu_2^2\,{}^2\Psi_1(8\rightarrow 9; A_u) \\ & + \sqrt{2}\mu_1\mu_2\nu_1^2\,{}^2\Psi_1(7\rightarrow 10; A_u) + \mu_2^2\nu_1^2\,{}^2\Psi_2(7, 7\rightarrow 10, 10; B_{1g}) \\ & + \sqrt{2}\mu_1\mu_2\nu_2^2\,{}^2\Psi_2\,(7, 8\rightarrow 10, 9; B_{1g}) \\ & + \mu_2^2\nu_2^2\,{}^2\Psi_3(7, 7, 8\rightarrow 10, 10, 9; A_u) \qquad (5)\end{aligned}$$

where notations used are the same as those in a previous paper [7].

The CDW solution thus obtained comprises the configurations of B_{1g} and A_u symmetries. The symmetry-breaking components are the configurations of A_u symmetry, for the RHF ground state is of B_{1g} symmetry. Then the unnormalized symmetry-restored B_{1g} solution is obtained by the simple deletion of the configurations of A_u symmetry from the broken-symmetry CDW solution [13–15]. On the other hand, the unnormalized symmetry-restored A_u solution is obtained by deleting the configurations of B_{1g} symmetry.

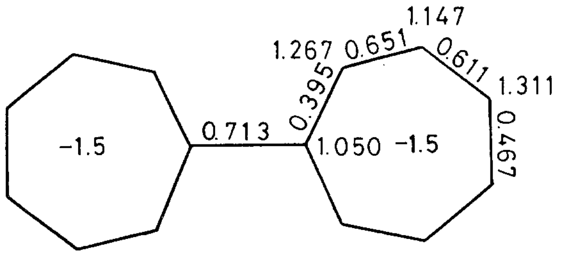
We examine the dependence of the energy expectation values of the broken-symmetry CDW solution and the symmetry-restored B_{1g} and A_u solutions on the mixing parameter κ. Then the stable broken-symmetry CDW solution is found at the κ value of 0.73 and the associated energy lowering from the symmetry-adapted RHF solution is calculated to be 0.359 eV. The energy minimum points for the symmetry-restored B_{1g} and A_u solutions are found at the κ values of 0.76 and 0.59 and the associated energy depressions from the symmetry-adapted RHF solutions are calculated to be 0.399 eV and 0.322 eV, respectively.

Thus, in the framework of the approximation used the symmetry-restored B_{1g} solution becomes the ground state. The symmetry-restored A_u solution corresponds to the lowest excited doublet state.

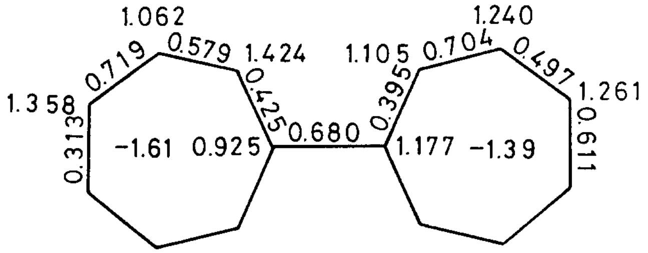
3.3. The Electron Density, Bond-order, and Unpaired Spin-density Distributions

We show in Fig. 2 the values of density matrix elements of the stable broken-symmetry CDW solution, together with those of the symmetry-adapted (D_{2h}) RHF solution. The distribution of the (negative) ring charges shown also in this figure indicates that the ring charges due to the symmetry-adapted RHF solution are equal in the two rings, while those due to the broken-symmetry CDW solution are unequal: one ring is more negative by −0.22 than the other ring. A similar unequality of ring charge is seen in the monoanion radical, the difference in charge between the two rings being −0.35 [7].

In Fig. 3 we show the dependence of the unpaired spin densities of the broken-symmetry CDW solution on the mixing parameter κ. It is found that the unpaired spin-density distribution of the stable CDW solution at $\kappa = 0.73$ is essentially localized on a single seven-membered ring. A similar phenomenon is also seen



Symmetry-adapted RHF solution (D_{2h})



Broken-symmetry CDW solution (C_{2v})

Fig. 2. The distributions of density matrix elements and ring charge densities of the usual symmetry-adapted RHF solution and the stable broken-symmetry CDW solution

in the monoanion radical [6, 7, 16]. However, there is a distinct difference with regard to the distributions of the unpaired spin density and the ring charge density between the monoanion and trianion radicals. In the monoanion radical, the unpaired spin density is localized on the seven-membered ring having a

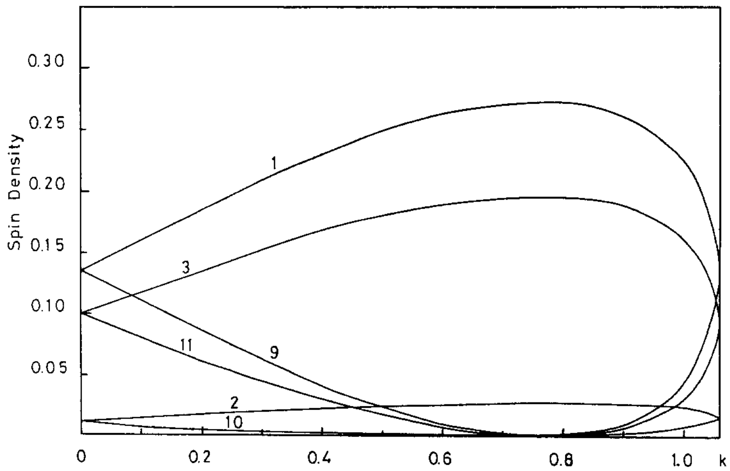


Fig. 3. The dependence of the unpaired spin densities of the broken-symmetry CDW solution on the mixing parameter κ. The spin densities on the carbon atoms 7 and 8 are zero

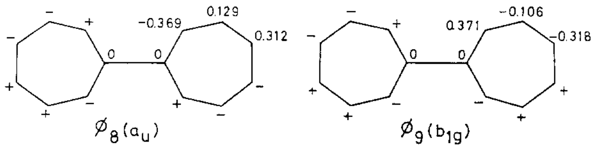


Fig. 4. The atomic-orbital coefficients of the usual symmetry-adapted RHF orbitals, ϕ_8 and ϕ_9, for the heptafulvalene trianion radical

larger negative charge (−0.67), while in the trianion radical it is localized on the ring having a smaller negative charge (−1.39, see Fig. 2). This difference will be explained by using Eq. (3) as follows: in the trianion radical, the occupied orbitals that are affected greatly by the appearance of the doublet instability are the doubly occupied orbital ψ_8 and the half-filled orbital ψ_9, whereas in the monoanion radical it is the half-filled orbital ψ_8 [7]. As shown in Fig. 4, the atomic-orbital coefficients for the RHF orbitals ϕ_8 and ϕ_9 are almost equal in absolute value and opposite on the respective carbon atoms. Thus, as the mixing parameter κ increases, orbitals ψ_8 and ψ_9 will be localized on the different seven-membered rings. Consequently, in the monoanion radical the unpaired spin density should be found on the seven-membered ring having a larger charge. On the other hand, in the trianion radical the unpaired spin density should be found on the ring having a smaller charge.

The detailed spin densities and the proton hyperfine splittings calculated assuming the stable broken-symmetry CDW solution of the trianion radical are listed in Table 1. The observed hyperfine splitting constant of 7.55 G is assigned to the proton attached to carbon atom 1, and that of 4.92 G is assigned to the proton attached to carbon atom 3. It is of interest to note that without invoking the

Table 1. Spin densities and proton hyperfine splittings of the heptafulvalene trianion radical

	Symmetry-breaking CDW solution (D_{2h} nuclear configuration)		Observed[a]
Atom	Spin density	Hyperfine splitting (G)[b]	Hyperfine splitting (G)
1	0.2734	6.82	7.55
2	0.0277	0.69	
3	0.1982	4.94	4.92
7	0	0	
8	0	0	
9	0.0003	0.01	
10	0.0001	0.00	
11	0.0004	0.01	

[a] Ref. [4].

[b] The hyperfine splittings a^H were calculated by using McConnell's relationship [24] with $|Q| = 24.94$ G.

lattice instability (i.e. the molecular-symmetry reduction), the observed proton hyperfine splittings can well be accounted for.

3.4. Lattice Instability

It is found that the stabilization energy due to the appearance of the stable broken-symmetry CDW solution is fairly small, but its density matrix elements are remarkably different from those for the symmetry-adapted RHF solution (see Fig. 2). Hence, it is expected that the stable broken-symmetry CDW solution is further stabilized by distorting the nuclear arrangement so that it may match up with the distribution of bond-order matrix elements of the broken-symmetry CDW solution [17–19]. Thus, it is predicted that the D_{2h} nuclear arrangement does not represent a minimum of the potential energy and a nuclear configuration with a lower symmetry (C_{2v}) is more stable. The lattice instability thus predicted for the heptafulvalene trianion radical is closely related with the pseudo-Jahn–Teller effect [20–23] as follows: in the RHF approximation, the ground state is of B_{1g} symmetry and the lowest excited doublet state is of A_u symmetry, and both the states are nearly degenerate, the energy difference being calculated to be 0.050 eV. It is therefore expected that the ground-state nuclear arrangement of the trianion radical would undergo a strong pseudo-Jahn–Teller distortion from the fully-symmetrical D_{2h} to the C_{2v} nuclear arrangement by the interaction with the lowest excited doublet state through the nuclear displacement of $b_{1u}(z)$ symmetry. On this point, we would like to discuss in detail elsewhere.

Finally, it is added that the trication radical of pentafulvalene is expected to experience a similar doublet instability of the RHF solution and exhibit an anomalous spin-density distribution similar to that of the pentafulvalene monocation radical [7, 16].

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