Tetrahedron Letters,Vol.24,No.11,pp 1179-1182,1983 0040-4039/83/111179-04$03.00/0
Printed in Great Britain

# THE GROUND-STATE ELECTRONIC STRUCTURE OF THE HEPTAFULVALENE TRIANION RADICAL

Azumao Toyota*
Department of Chemistry, Faculty of General Education, Yamagata University
Yamagata 990, Japan
Takeshi Nakajima
Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980, Japan

Abstract: The ground-state geometrical structure of the heptafulvalene trianion radical, calculated by using the semiempirical open-shell SCF MO method, is found to be of $C_{2v}$ symmetry. The proton hyperfine splittings of the radical obtained by assuming the $C_{2v}$ structure are in good agreement with the experimental data.

The ESR spectrum of the heptafulvalene trianion radical has been studied by Bauld et al.[1] They revealed that the unpaired spin density is not delocalized throughout the molecule, but it is localized essentially on a single seven-membered ring.

In view of the doublet instability of the restricted Hartree-Fock solution,[2] Toyota and Nakajima have examined the origin of the anomalous spin-density distribution of the trianion radical,[3] within the open-shell SCF formalism of the Pariser-Parr-Pople(PPP)-type MO method.[4-6] As a result, it is suggested that the ground-state nuclear arrangement of the trianion radical should undergo the second-order Jahn-Teller bond distortion[7] from the fully-symmetrical $D_{2h}$ to the $C_{2v}$ nuclear arrangement.

In this paper, we examine the energetically most favorable geometrical structure with respect to C-C bond lengths of the heptafulvalene trianion radical using the PPP-type SCF MO method in conjunction with the variable bond-length technique.[8]

Assuming the optimum $D_{2h}$ structure (Fig. 1) obtained previously[3] and using Longuet-Higgins and Pople's MO method,[4] we calculate the lower electronic states of the trianion radical. It turns out that the ground-state wave function is $\Phi_0 = |\phi_1 \bar{\phi}_1 \,.....\, \phi_8 \bar{\phi}_8 \phi_9|$ with the $B_{1g}$ symmetry and the lowest excited doublet state corresponding to a single MO transition $\phi_8 \rightarrow \phi_9$ is of $A_u$ symmetry, the energy separation between the two states being only 0.05 eV. Since both the states are nearly degenerate, the bond distortion of $B_{1u}$ (= $B_{1g} \times A_u$) symmetry should cause a strong vibronic interaction between them. Accordingly, the ground state of the trianion radical is expected to undergo the second-order Jahn-Teller distortion from the $D_{2h}$ to the $C_{2v}$ nuclear arrangement. This means that the conventional $D_{2h}$ nuclear arrangement does not represent a minimum but a saddle point of the potential energy surface of the system. Of the four types of bond distortion belonging to the $B_{1u}$ symmetry, the one actually effective for the molecular-symmetry reduction is given by examining the distribution of the transition density between the ground and the lowest excited doublet state.[9,10] The figures of the transition density $\phi_8\,\phi_9(B_{1u})$ over the molecular skeleton are shown in Fig. 1 (in italics).

We now calculate the geometrical structure with respect to C-C bond lengths of the trianion radical as follows: As a starting geometry for iterative PPP-type

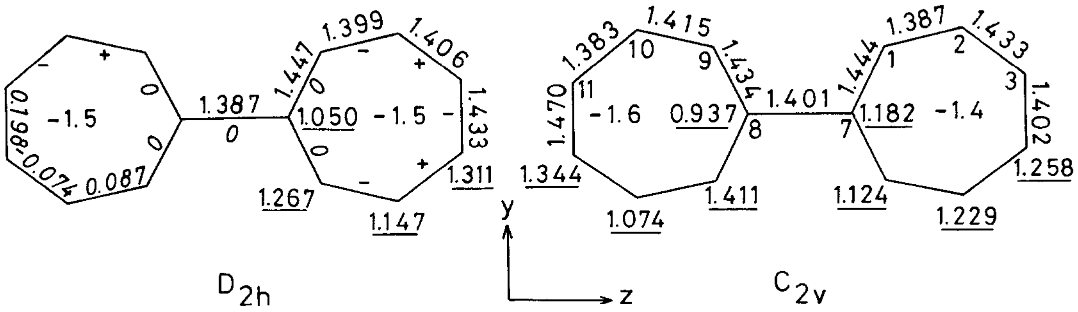

Fig. 1. The equilibrium bond lengths(Å), electron densities, and ring charges for the $D_{2h}$ and the $C_{2v}$ nuclear arrangement, the numberings of atomic positions, and the distribution of the nearest two-center components of transition density.

SCF MO calculation, we adopt a nuclear configuration in which C-C bond lengths are shortened or lengthened so that the set of displacement vectors may match up with the distribution of the transition density shown in Fig. 1. Then, self-consistency has been achieved at a set of C-C bond lengths corresponding to a lower symmetrical nuclear arrangement ($C_{2v}$). The stabilization energy, defined as the difference in total energy between the fully-symmetrical $D_{2h}$ and the reduced $C_{2v}$ molecular geometry,[10,11] is calculated to be 11.7 kcal mol$^{-1}$. The obtained equilibrium bond lengths, electron densities(underlined), and negative ring charges are also shown in Fig. 1.

In Table 1 we show the unpaired spin densities and the associated proton hyperfine splittings calculated by using McConnell's relationship[12] with $|Q|=$ 24.94 G. The values in the parentheses refer to those for the $D_{2h}$ nuclear arrangement. The spin densities on the carbon atoms 7 and 8 are zero by symmetry. It is revealed that in the $C_{2v}$ nuclear arrangement the unpaired spin density is essentially localized on the seven-membered ring having the smaller ring charge (-1.4). The observed splitting constant of 7.55 G is readily

Table 1. Spin densities and proton hyperfine splittings of the heptafulvalene trianion radical calculated by assuming the $C_{2v}$ nuclear arrangement

| Atom | Calculated<br>Spin density | <br>Hyperfine splitting(G) | Observed<br>Hyperfine splitting(G) |
|---|---|---|---|
| 1 | 0.2509(0.1375) | 6.25(3.43) | 7.55 |
| 2 | 0.0368(0.0113) | 0.92(0.28) | |
| 3 | 0.2115(0.1012) | 5.28(2.52) | 4.92 |
| 7 | 0(0) | 0(0) | |
| 8 | 0 | 0 | |
| 9 | 0.0005 | 0.01 | |
| 10 | 0.0000 | 0.00 | |
| 11 | 0.0003 | 0.01 | |

assigned to the proton attached to the carbon atom 1, and that of 4.92 G to the proton attached to the carbon atom 3. The theoretical values thus calculated by assuming the $C_{2v}$ nuclear arrangement are in good agreement with the experimental data.[1]

In conclusion, it can be said that the anomaly in spin-density distribution of the heptafulvalene trianion radical has its origin in the occurrence of the molecular-symmetry reduction, $D_{2h} \longrightarrow C_{2v}$, due to the second-order Jahn-Teller effect.

Finally, it is added that the trianion radical of 1.4-bis(cycloheptatrienylidene)-2,5-cyclohexadiene, [7.6.7]quinarene, is expected to undergo a similar molecular-symmetry reduction and exhibit an anomalous spin-density distribution similar to that of the heptafulvalene trianion radical.[13]

## References

1) N. L. Bauld, C. S. Chang, and J. H. Eilert, Tetrahedron Lett., 153 (1973).
2) J. Paldus and J. Cizek, Chem. Phys. Lett., 3, 1 (1969).
3) A. Toyota and T. Nakajima, Theoret. Chim. Acta (Berl.), 61, 505 (1982).
4) H. C. Longuet-Higgins and J. A. Pople, Proc. Phys. Soc. (London), A68, 591 (1955).
5) R. Pariser and R. G. Parr, J. Chem. Phys., 21, 446 (1953).
6) J. A. Pople, Trans. Faraday Soc., 49, 1357 (1953).
7) H. A. Jahn and E. Teller, Proc. Roy. Soc. (London), A161, 220 (1937).
8) H. Yamaguchi, T. Nakajima, and T. L. Kunii, Theoret. Chim. Acta (Berl.), 12, 349 (1968).
9) L. Salem, Chem. Phys. Lett., 3, 99 (1969).
10) T. Nakajima, A. Toyota, and S. Fujii, Bull. Chem. Soc. Japan, 45, 1022 (1972).
11) L. C. Snyder, J. Phys. Chem., 66, 2299 (1962).
12) H. M. McConnell, J. Chem. Phys., 24, 632, 764 (1956).
13) M. W. Murray and M. L. Kaplan, Tetrahedron Lett., 2903 (1965).

(Received in Japan 9 December 1982)