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A STUDY OF ELECTRONIC STRUCTURES OF SOME $C_9H_9^-$ CARBOANIONS

M. B. HUANG
Department of Modern Chemistry, University of Science and Technology of China, Hefei, Anhui, People's Republic of China

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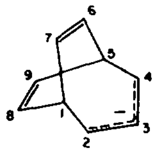
Abstract—The electronic structures of five $C_9H_9^-$ carboanions have been studied by *ab initio* STO-3G calculations, and some general conclusions on related $C_9H_9^-$ and $C_9H_9^+$ structures are presented. Large antibonding interactions in one occupied MO make barbaral-9-yl anion (**2**) unstable as its cationic counterpart (**8**). The proposed D_{9h}-symmetrical cation and D_{3h}-symmetrical anion (**3**) do not exist due to Jahn–Teller distortions. A study of the MO correlations confirms that the two tetracyclic anions with C_{2v} symmetry (**5** and **6**) are the results of the Jahn–Teller distortions of **3**. Anion **5** is identified as the proper intermediate of the Cope rearrangement of anion **2**.

The $C_9H_9^-$ potential energy surface, like its cationic counterpart, contains several theoretically interesting structures. We have been studying the following $C_9H_9^-$ structures: bicyclo[3.2.2]nona-3,6,8-trienyl anion (**1**), barbaral-9-yl anion (**2**), the proposed D_{3h}-symmetrical ion (**3**), cyclononatetraenyl anion (**4**), and two tetracyclic ions with C_{2v} symmetry (**5** and **6**).



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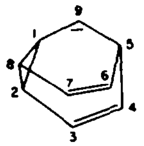

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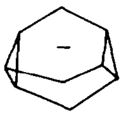

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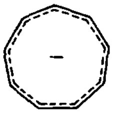

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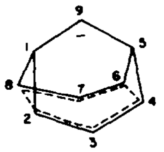

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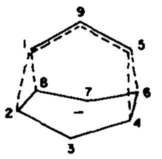

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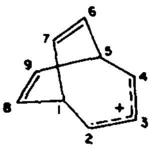

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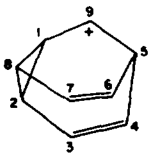

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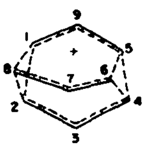

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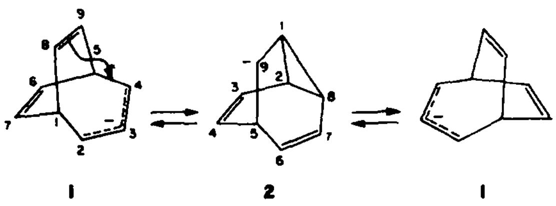
Experimentally observed degenerate rearrangement of **1** was proposed to use **2** as an intermediate, with $E_a = 22.5$ kcal/mol;[1–3] Grutzner and Winstein[1] suggested that the rearrangement of anion **1** into **2** proceeds through a mechanism: the symmetry-allowed distortatory cyclopropane openings and closures (Scheme 1). They also claimed:[1] "A more complex scheme must be written if the barbaralyl ion undergoes a Cope rearrangement before it reopens to the [3.2.2] ion. The relatively slow rearrangement of protonated barbaralone suggests that this additional feature does not play a role in the cation rearrangement but may be quite significant in the anion."

Recently we[4] systematically studied the above-mentioned six anions. Anions **1**,† **2**, **4**,‡ **5** and **6** were found as energy minima in both of the MINDO/3[10] and MNDO[17] energy surfaces. However, anion **3** was excluded as a stable structure by both the theoretical consideration and the analysis of the computational results. Ions **5** and **6** are actually the products of the Jahn–Teller distortions[7] of **3**. The following energy ordering was obtained: **4** < **1** < **2** < **5** < **6** (Fig. 1 in ref. 4). The relations **1** < **2** and **2** < **5**,**6** are in agreement with the experimental results about the two rearrangements.

Besides the calculations of the optimized geometries and the energy ordering, a careful analysis of the



Scheme 1.

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† The MINDO/3 and STO-3G *ab initio* SCF calculations for **1** had been performed by Grutzner and Jorgensen.[5]

‡ The MNDO calculations for **4** had been performed by Owamerali.[6]

electronic structures of these anions can give better understanding about stabilities and rearrangement mechanisms. This is the goal of our present paper.

The optimized geometries and the electronic structures of five $C_9H_9^+$ ions have been reported.[8,9] Three of them, the bicyclo[3.2.2]nona-3,6,8-trien-2-yl cation (7), the 9-barbaralyl cation (8) and the D_{3h}-symmetrical cation (9), have their anionic counterparts 1, 2 and 3 (3 does not exist[4]), respectively. In contrast to the anions, the [3.2.2] cation 7 is less stable than the barbaralyl cation 8 and rearranges to 8 through the same mechanism (Scheme 1), but it goes inversely. In the following analysis, the electronic structures of cations 7, 8, and 9 are needed for comparison.

Method of calculation. Ab initio STO-3G[11] SCF calculations using the MINDO/3 optimized geometries[4] gave the electronic structures. *Ab initio* SCF calculation with minimal basis set for anions usually gives positive MO energies to the HOMOs,[12] which is wrong. However, we assume that the problem with the STO-3G SCF calculation for anions affects the total energy and MO energy (absolute) values, but the general feature of MOs, the MO ordering and populations, are still reliable for the analysis of their electronic structures. Actually, STO-3G SCF calculations are still widely used for electronic structure analyses of relatively large anionic systems.[5,13]

RESULTS AND DISCUSSION

Cyclonoatetraenyl anion 4

Apparently anion 4 is an aromatic system due to the $4n+2$ rule, which is the reason why it is the most stable.[4]

The analysis of its electronic structure indicates that a D_{9h}-cationic structure (singlet) does not exist because the HOMOs of anion 4 are a pair of degenerate MOs and the removal of a pair of electrons from the HOMOs will result in the Jahn–Teller distortions of the molecular structure.

Bicyclo[3.2.2]*nona*-3,6,8-*trienyl anion* 1 *and barbaral*-9-*yl anion* 2

The STO-3G C—H group charges and overlap populations for the carbon frameworks of anions 1, 2, 5 and 6 are given in Fig. 1. Ion 1 (with C_{2v} symmetry) has charge (negative) concentrated in the allylic bridge as its cationic counterpart 7 (positive charge),[9] and as we presented in refs. 4 and 8, the geometries of 1 and 7 differ just in this part.

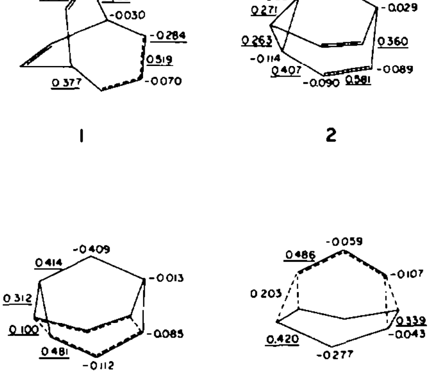

Fig. 1.

The electronic structures of anion 1 and cation 7 were previously studied by Grutzner and Jorgensen[5] and by ourselves,[9] respectively. Simple theory[14] predicted that anion 1 is bicycloaromatic and cation 7 antibicycloaromatic. However, neither stabilizing MO interaction in 1 nor destabilizing MO interaction in 7 could be identified. Some other explanations for the stability of 1 were sought.[5]

Anion 2 (with C_s symmetry) has charge concentrated in the cyclopropylcarbinyl part as its cationic counterpart 8.[9] The geometries of the charged parts of anion 2[4] and cation 8[8] are quite different (for details and explanations, see ref. 4), but the geometries of the 1,4-pentadiene parts (uncharged) are very similar.

The four frontier MOs of 8 and 2 are shown in Fig. 2 (**a** and **b**). The LUMO (No. 32) in 8 is related to the HOMO (No. 32) in 2. The 30th MO in 8 is related to the 31st MO in 2. Because the 31st MO of anion 2 shows bigger antibonding interaction between C_2 (C_8) and C_3 (C_7) (bigger coefficients on C_2 and C_8, but the same C_2—C_3 and C_8—C_7 bond lengths as in 8), this MO has been lifted in energy in anion 2. Therefore, anion 2 is destabilized, which is in agreement with the experimental result that 2 is less stable than 1.[1-3]

Apparently the 31st MO in 8 is related to the 30th in 2, and the 29th in 8 to the 29th in 2.

Structures 5 *and* 6. Our previous theoretical work[4] indicated that 5 and 6 are stable structures rather than transition states. The C—H group charges and overlap populations for the carbon frameworks of 5 and 6 shown in Fig. 1 are very different. Most of the charge is located on the inner part C_3—C_7—C_9 in both 5 and 6, but in 5 the biggest charge is located on C_9 as in anion 2 while in 6 the biggest charges are located on C_3 and C_7. The overlap populations on the two outer "rings" are also very different: small on C_2—C_8 and big on C_1—C_2 in 5 (with C_{2v} symmetry), while the inverse in 6 (C_{2v}).

Anions 5 and 6 have been considered[4] as the results of the Jahn–Teller distortions of a D_{3h} anionic structure (it does not exist) since the LUMOs of the D_{3h} *cationic* structure are a pair of degenerate MOs.[9,15] When the D_{3h} group goes to its subgroup C_{2v}, this degenerate level e′ will split into two non-degenerate levels $\mathbf{a}_1$ and $\mathbf{b}_2$.[16] By checking the electronic structures of 5 and 6, we found: the HOMO $8\mathbf{b}_2$ and LUMO $13\mathbf{a}_1$ in 5 and the HOMO $13\mathbf{a}_1$ and LUMO $8\mathbf{b}_2$ in 6.

The potential Cope rearrangement of anion 2 is supposed to proceed through an intermediate with C_{2v} symmetry. Since the candidates 6 and 5 have similar relative energies to 2 in our previous calculations,[4] an analysis of their electronic structures will help us identify the proper intermediate. Let us classify the MOs in anions 2, 5 and 6 with respect to the mirror plane containing C_1—C_9—C_4. Each of them has 32 occupied MOs. There are 20 symmetric MOs and 12 antisymmetric MOs in both 2 and 5, but 21 symmetric and 11 antisymmetric ones in 6. Therefore, the interconversion of 2 and 5 is a symmetry-allowed process, and we can conclude that the Cope rearrangement of 2 proceeds through 5 rather than 6. The charge distributions in 5 indicate that during the rearrangement, the biggest charge stays at C_9.

The frontier MOs (the 32nd, 31st, 30th and 29th) of 5

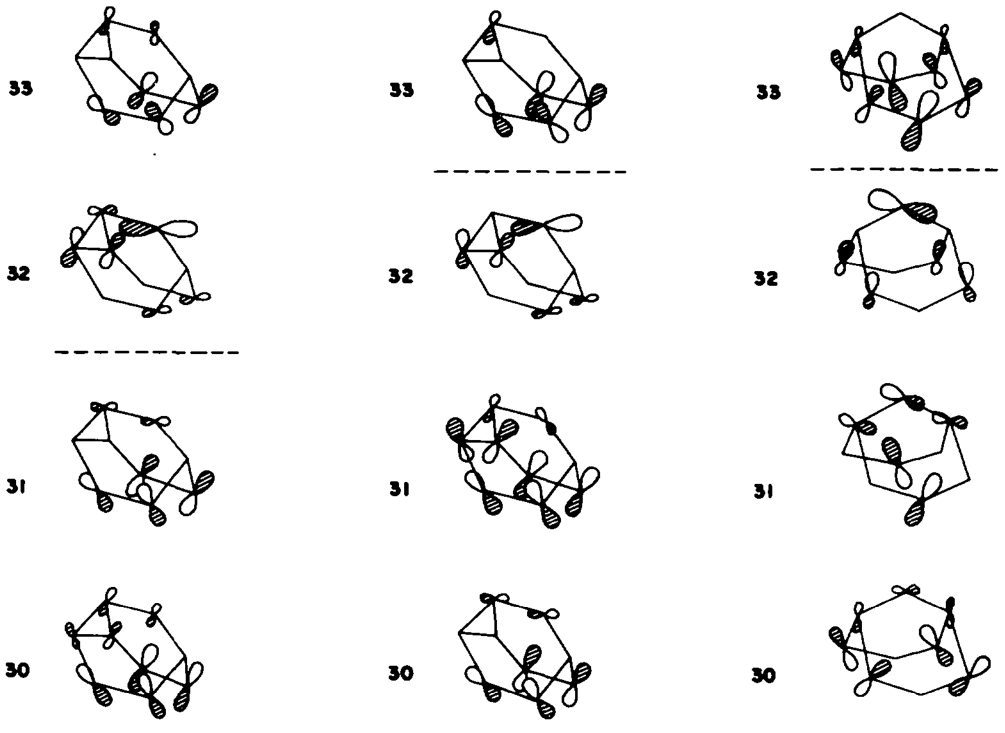

Fig. 2.

and **2** are shown in Fig. 2 (**b** and **c**). The correlations between the two sets of MOs are apparent.

CONCLUSIONS

Some general conclusions on the $C_9H_9^-$ and $C_9H_9^+$ structures can be drawn based on our calculation results (the optimized geometries and energy orderings) presented in refs. 8 and 4, and the theoretical analyses of their electronic structures presented in ref. 9 and this paper.

The anionic D_{9h} structure is a stable aromatic system, but the analysis of its electronic structure indicates that its cation counterpart (singlet) does not exist.

The barbaralyl and the [3.2.2] structures were found in both of the $C_9H_9^-$ and $C_9H_9^+$ energy surfaces. The optimized geometries of each pair of the positive and negative ions are different mainly in the charged parts (the cyclopropylcarbinyl part in barbaralyl ions and the allylic part in the [3.2.2] ions). In agreement with the experimental results on the rearrangements, the calculation results[4,8] indicated that the [3.2.2] ion is more stable than the barbaralyl ion in the anion case, and the inverse in the cation case. The electronic structure analysis indicates that big antibonding interaction in one occupied MO destabilizes the barbaralyl anion, which is the reason (or one of the reasons) why the energy order of these two structures is inversed in the anion case.

The D_{3h} structure exists in the cation case, but no D_{3h} structure (singlet) exists in the anion case, and two C_{2v} structures (**5** and **6**) exist in the anion case, but not in the cation case.[4] A study of the MO correlations confirmed that the two anionic C_{2v} structures are the products of the Jahn–Teller distortions of the proposed anionic D_{3h} structure.

The electronic structure analysis indicated that the intermediate of the Cope rearrangement of the barbaralyl anion is **5** rather than **6**.

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