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The CNDO/2 Study of Barbararyl Cation and Its Isomeric $C_9H_9{}^+$ Systems

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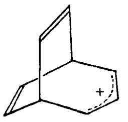
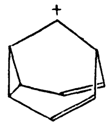
The geometrical and electronic structures of $C_9H_9{}^+$ systems have been studied applying CNDO-2 method. The calculated results are used to discuss the stabilities of the structures for $C_9H_9{}^+$ system and their electronic states. It is suggested that the carbonium ion which has a D_{3h} symmetry (IV) enjoys much stabilization energy, whereas bicyclo[3.2.2]nonatrienyl cation (I) is less stable than IV. The stability of IV can be explained by unusual delocalization of its electrons over the molecule.

A considerable amount of attention has been recently focussed on $C_9H_9{}^+$ systems such as bicyclo[3.2.2]-nonatrienyl (I), 9-barbararyl (II) and bishomotropylium (III) cations.[2-5] The direct observation of II and III by NMR at low temperature was recently reported by Winstein and his co-workers.[4b] On the other hand, based on the results of deuterium scrambling reaction, Schleyer[3] has proposed the presence of the reaction intermediate species (or the transition state) as presented in IV, which undergoes effective threefold symmetrization.


(I)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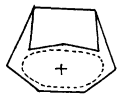
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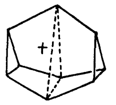
(IV)

The approach using molecular orbital calculations is helpful in investigating the stabilities and the electronic states of these systems. Although experiences with semiempirical molecular orbital methods suggest that they are capable of yielding very satisfactory geometrical data, it seems to be almost impossible to apply semiempirical MO method to $C_9H_9{}^+$ systems because of their large number of internal degrees of freedom ($3N-6$).

We have succeeded in carrying out the complete MO treatment for IV and I by considering the appropriate symmetry properties. First of all, all the bond angles and the bond lengths for the symmetrical structure (IV) were varied, and the most stable symmetrical structure was obtained. After that, the energy change by the possible deformations was examined. As a result, the calculated potential energy surface clearly indicates that the structure IV represents an energy minimum.

For the structure at the energy minimum, a population analysis[6] was carried out. The electron densities and the overlap populations demonstrated unusual delocalization in the structure IV. The similar MO treatment for I was carried out, even though much computing time was required due to the large number of internal degrees of freedom compared with the case of IV. The energy minimum obtained for I was much higher than that for IV, as expected from the theory of "bicycloaromaticity" proposed by Goldstein,[3a,3b] indicating I to be bicycloantiaromatic.

Method of Calculation

Our treatment is fundamentally composed of the following two steps; 1) the determination of the most stable structure by minimizing the molecular energy with respect to internal coordinates, 2) the estimation of the electron densities and the overlap populations in the structure of energy minimum.

The method of calculation employed in this study is CNDO-2 by Pople and Segal.[7] The model initially chosen has a D_{3h} symmetry [IV] as depicted in Fig. 1.

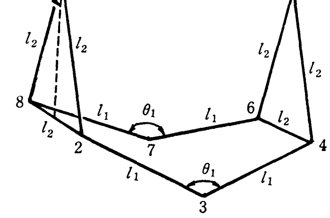

Fig. 1. Geometrical parameters for IV.

In the D_{3h} symmetrical structure, variable geometrical parameters are the bond lengths, $l_1(C_2C_3=C_3C_4=C_6C_7=C_7V_8=C_1C_9=C_9C_5)$, $l_2(C_1C_2=C_2C_8=C_8C_1=C_4C_5=C_5C_6=C_6C_4)$ and the bond angle $\theta_1(\angle C_2C_3C_4=\angle C_1C_9C_5=\angle C_8C_7C_6)$. The bond angle θ_2 is also a geometrical parameter to whose change, however, molecular energy is fairly insensitive. A bond length of 1.09 Å assumed for all C–H bonds. The calculation was

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[2] W. von E. Doering, B. M. Ferrier, E. T. Fossel, J. H. Hartenstein, M. Jones, Jr., G. Klumpp, R. M. Rubin, and M. Saunders, *Tetrahedron*, **23**, 3943 (1967).

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[4] a) P. von R. Schleyer, J. J. Harper, G. L. Dunn, V. J. Di Pasquo, and J. R. E. Hoober, *ibid.*, **89**, 698 (1967). b) P. von R. Schleyer and R. E. Leone, *ibid.*, **90**, 4164 (1968). c) J. C. Barborak, J. Daub, D. M. Follweiser, and P. von R. Schleyer, *ibid.*, **91**, 7760 (1969). d) J. C. Barborak and P. von R. Schleyer, *ibid.*, **92**, 3184 (1969).

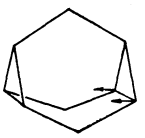
[5] a) P. Ahlberg, D. L. Harris, and S. Winstein, *ibid.*, **92**, 2146 (1970). b) P. Ahlberg, D. L. Harris, and S. Winstein, *ibid.*, **92**, 4454 (1970).

[6] R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1935).

[7] J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).

organized as follows. The bond length l_1 was first calculated by minimizing the molecular energy, assuming $l_2=1.54$ Å and $\theta_1=\theta_2=120°$. Using the calculated value for l_1(1.40 Å), the value of 115° for θ_1 was obtained, and then with these value of l_1 and θ_1, the bond length l_2 was calculated. With the new values for θ_1 and l_2, l_1 was recalculated. This process was repeated until an absolute minimum in energy with respect to l_1, l_2 and θ_1 was obtained. Fixing the final values for l_1, l_2 and θ_1, the best bond angle θ_2 was obtained.

Thus, after the most stable symmetrical structure was obtained by changing all the bond lengths and the bond angles, the change of the molecular energy with respect to several possible deformations was examined. All the bond angles and bond lengths were varied independently or simultaneously as shown in the examples below.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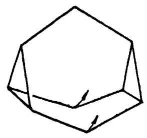
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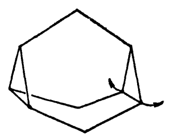

C

A similar treatment of bicyclo[3.2.2]nonatrienyl cation (I) was carried out. In this case, main geometrical parameters are the bond angles θ_1, θ_2, θ_3 and θ_4 as shown in Fig. 2. The coordinates of C_6, C_7, C_8 and C_9 was first calculated for changes in θ_1 and θ_2, assuming $\theta_3=120°$, $C_2C_3=C_3C_4=1.40$Å, $C_1C_2=C_4C_5=C_1C_7=C_1C_8=C_5C_6=C_5C_9=1.52$ Å and $C_6C_7=C_8C_9=1.34$Å according to the literature.[8] The coordinates for the protons H_2, H_3, H_4, H_6, H_7, H_8 and H_9 are calculated on the assumption that they lie in each corresponding plane and the C_1H_1 and the C_5H_5 bonds are at equal angles from the other bonds at C_1 and C_5, respectively. Using θ_1 and θ_2 obtained from the first computation (both 70°), the bond angles θ_3 and θ_4 were varied and determined by minimizing the molecular energy. This process was repeated until the energy minimum was obtained with respect to θ_1, θ_2, θ_3 and θ_4. Finally, using this set of bond angles, the changes in the molecular energy were tested by varying each bond length. In the present calculations the angles were calculated to within 1° and the bond lengths within 0.01 Å, respectively.

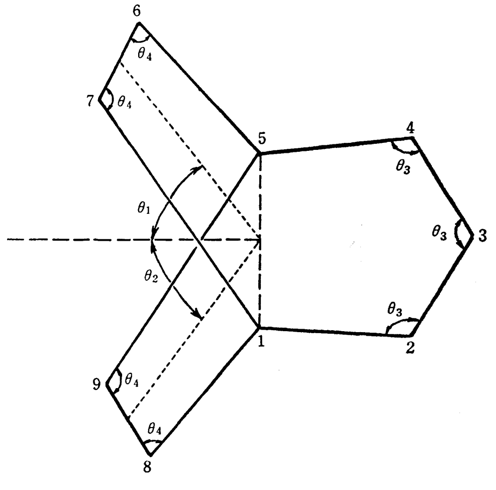


Fig. 2. Geometrical parameters for I.

The electron densities and the overlap populations for the structure (IV) and (I) were calculated and presented in Fig. 3 and 4, respectively.

Results and Discussion

From the calculation for (IV) changing all the geometrical parameters, the molecular energy for the most stable symmetrical structures was calculated to be −70.0733 a.u. In this structure, the bond lengths $l_1=1.41$ Å, $l_2=1.52$ Å and the bond angles $\theta_1=115°$ and $\theta_2=120°$. Any small geometrical deformation did not lower the energy of the symmetrical structure. It is clear that the structure IV is at least one of the minima on the potential energy surface. The electronic densities and the overlap populations for this structure are shown in Fig. 3. The positive charge was delocalized over all the carbon atoms as might be expected. An important aspect for this D_{3h} symmetrical structure is that the overlap populations for l_1 correspond to that for an aromatic bond, since the value of 0.924 for l_1 is comparable to that of benzene (0.960), whereas the value of 0.604 for l_2 is smaller than that of a typical sp^3 C–C bond, 0.704, which is obtained for the C–C bond in neopentane. Accordingly, the electronic state of IV could be visualized in (IV′). It is immediately obvious from this representation that IV is stabilized by cyclopropylcarbinyl resonance. There are six equivalent cyclopropylcarbinyl fragments, $C_8C_2C_1C_9$, $C_1C_8C_2C_3$, $C_2C_1C_8C_7$, $C_4C_5C_6C_7$, $C_5C_6C_4C_3$ and $C_6C_4C_5C_9$, as is seen in IV′. In other words, IV is a highly homoconjugated system.

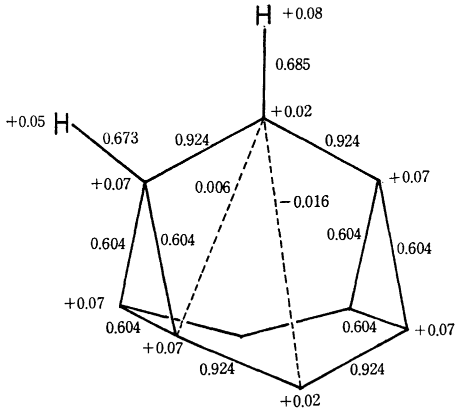
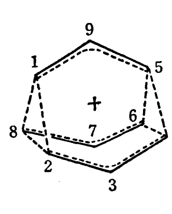


Fig. 3. The electronic charges and the overlap populations for IV.



(IV′)

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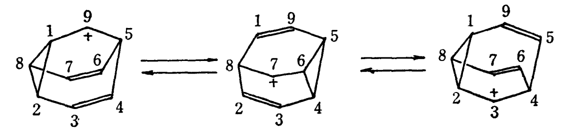
[8] J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967).

The prediction of much stability in IV supports the observation by Schleyer *et al.*4c) that deuterium distributed almost exclusively between C_3, C_7 and C_9 in the solvolysis of 9-D-barbararyl tosylate. In the study of the direct observation of II by NMR, Winstein and his coworkers5b) suggested a facile divinylcyclopropylcarbinyl-divinylcyclopropylcarbinyl rearrangement as given in the following mechanism, with which Schleyer *et al.* also agreed in their recent paper.4b) According to the present calculation, this rearrangement can be facilitated through the symmetrical intermediate IV′.



IIa IIb IIc

The calculation of the energy of the species derived from IV by simultaneous large deformations (A, B and C) might approach that for II. The computations were attempted several times, but a lower molecular energy was not obtained. As an attempt to find an energy minimum of II on the potential surface seemed to consume too much time, a laborious complete treatment was not carried out.

A similar theoretical treatment for another $C_9H_9^+$ system, bicyclo[3.2.2]nonatrienyl cation (I), yielded the bond angles, 69°, 69°, 126° and 119° for θ_1, θ_2, θ_3 and θ_4, respectively, and the bond lengths, 1.52 Å, 1.40 Å and 1.34 Å for $C_1C_2=C_1C_7=C_1C_8=C_4C_5=C_5C_6=C_5C_9$, $C_2C_3=C_3C_4$ and $C_6C_7=C_8C_9$, respectively, at its energy minimum geometry. The calculated molecular energy of −70.0361 a.u. was much higher than that for IV, in accordance with the antibicycloaromaticity of I. In the five membered systems such as $C_2C_3C_4C_9C_8$ and $C_2C_3C_4C_6C_7$ in Fig. 4, the small overlap populations (0.029) clearly indicate that the systems are antihomoaromatic.

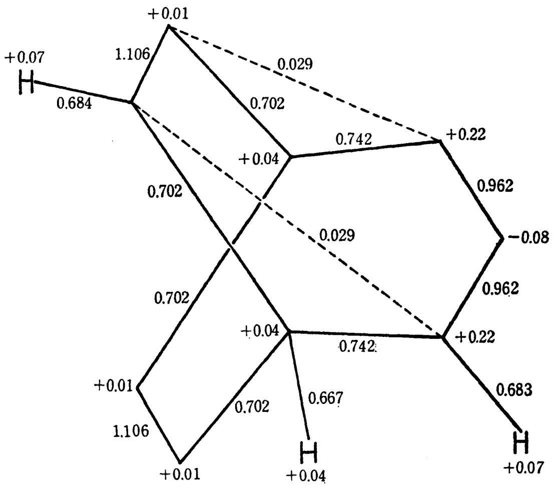


Fig. 4. The electronic charges and the overlap populations for I.

A similar MO calculation for bishomotropylium ion (III), which should be the most stable $C_9H_9^+$ system, is now under investigation.9)

We should like to thank Dr. P. Ahlberg and Dr. D. Blagdon for assistance in many illuminating discussions.

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9) From a calculation for III choosing an appropriate set of geometrical parameters, an molecular energy (−70.0691 a.u.), much more stable than I and comparable to IV, has already been obtained.