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APPLICATION OF MOLECULAR ORBITAL CALCULATIONS TO THE BICYCLO[3.2.2]NONATRIENYL ANION AND SOME RELATED IONS

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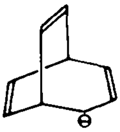
Abstract—The stabilities and the electronic structures of (CH)$_9$ and (CH)$_9^-$ systems were investigated using INDO MO calculation. The total overlap populations of the C–C bonds of bicyclo[3.2.2]nonatrienyl anion indicated its high degree of conjugation, in contrast to less conjugated bicyclo[3.2.2]nonatrienyl cation. On the other hand, the (CH)$_9$ intermediate of the D$_{3h}$ symmetrical structure was shown to be much less conjugated than the D$_{3h}$ symmetrical (CH)$_9^-$ ion. It was suggested from the calculated results that the sum of the total overlap populations of all C–C bonds involved in a (CH)$_n$ molecule could be a quantitative measure of aromaticity for the (CH)$_n$ systems in the three-dimensional structures.

Although many theoretical and experimental studies on (CH)$_n^+$ systems of the three-dimensional structures such as (CH)$_5^+$[1], (CH)$_7^+$[2] and (CH)$_9^+$[3] have been reported, there are only a few studies on (CH)$_n$ systems. This paper deals with our investigation on the stabilities and electronic structures of (CH)$_9$ systems by INDO MO method. Our interest was directed especially toward bicyclo[3.2.2]nonatrienyl anion **1**, because Goldstein, Murahashi *et al.*[4] have very recently found the facile rearrangement of 9-barbararyl anion **3** to **1**, firstly synthesized by Grutzner and Winstein,[5] whereas bicyclo[3.2.2]nonatrienyl cation **4** is well-known to be extremely unstable and easily degenerate to barbararyl cation **6** at low temperature (*ca.* −135°) in superacid media.[3b] Differences in the electronic structure of the bicyclo[3.2.2]nonatrienyl anion from that of the cation were explained in terms of the total overlap populations.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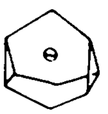
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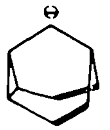
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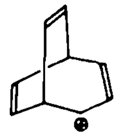
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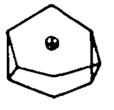
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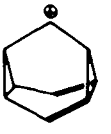
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Based on the results it is proposed that the sum of the total overlap populations of all C–C bonds involved in a (CH)$_n$ molecule could be a quantitative measure of aromaticity for (CH)$_n$ systems of the three-dimensional structures. Though the rules of "bicycloaromaticity" was proposed by Goldstein[1b] and successfully predicted the aromaticity of unsaturated (CH)$_n$ bicyclic hydrocarbons, our new concept of "three-dimensional aromaticity" could be more generally applied to a wide range of (CH)$_n$ systems (i.e. the systems including many half-bondings such as (CH)$_5^+$ ion of the C$_{4v}$ symmetrical structure).

Systematic treatment of (CH)$_9$ *systems.* All of the molecular orbital calculations employed in this study are based on INDO (intermediate neglect of differential overlap) approximation by Pople, Beveridge and Dobosh.[6] Our treatment for (CH)$_9$ systems is systematically composed of the following two steps; (1) the determination of the geometrical structure giving the energy minimum on the potential energy surface with respect to the geometrical parameters, (2) the electronic population analysis[7] of the molecule at energy minimum structure.

In order to determine the molecular geometry of the bicyclo[3.2.2]nonatrienyl anion, all the geometrical parameters (the bond lengths and the bond angles) must be optimized. However, since this procedure consumes too much computing time, θ_1 and θ_2 in Fig. 1 were chosen as significant geometrical parameters, and the other bond angles and bond lengths were appropriately chosen according to the literature.[8] Thus bond angles, θ_1 and θ_2, were independently changed until an absolute minimum in energy was obtained. In the treatment of the D$_{3h}$ symmetrical (CH)$_9$ system **2**, all the C–C bond lengths and the C–C–C bond angles were optimized,

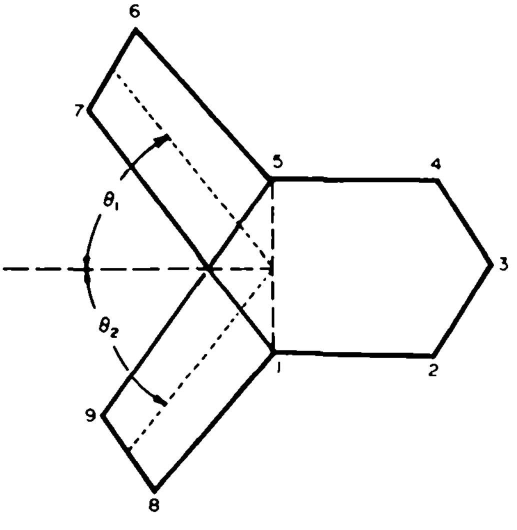
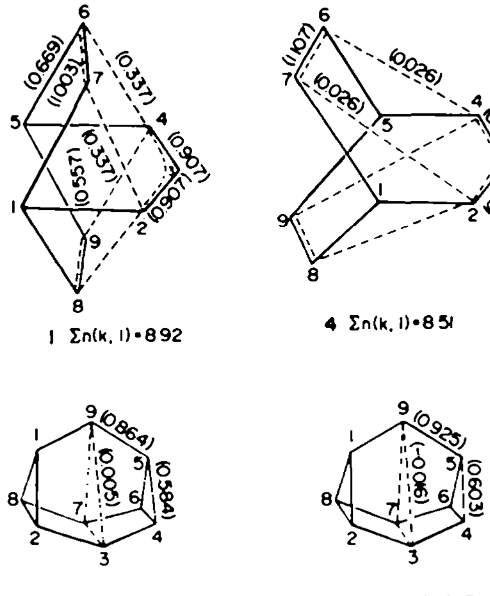


Fig. 1. Geometrical parameters of 1.

because there are not as many geometrical parameters due to its high symmetry.

RESULTS AND DISCUSSION

As the result of the systematic treatment described above for 1, the energy minimum was obtained when both θ_1 and θ_2 were 112°. This unexpectedly large bond angle suggests that the C_6–C_7 and C_8–C_9 π-moieties bent toward the C_2–C_3–C_4 π-moiety and the resulting conjugative interaction of the C_2–C_7 (C_2–C_8) and C_4–C_6 (C_4–C_9) stabilizes the molecule. For comparison, the geometrical parameters of 2 were similarly obtained. At the energy minimum structure, considerable electron delocalization over the molecule was demonstrated (Fig. 2). Because important geometrical parameters were chosen in the determination of the geometry giving energy minimum of 2 and especially of 1, it is difficult to compare directly the stability of 1 to that of 2, but the electronic energy of −8101.3 eV for 1 was much lower than −7896.8 eV for 2. The stability of the latter is considered to be close to that of 3.[9] Thus the calculated result is in good agreement with the experimental result that the rearrangement of 9-barbararyl anion 3 into 1 easily proceeds presumably via the intermediate 2 as shown in the following scheme.



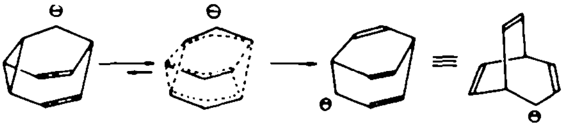
1 Σn(k, l) = 8.92

4 Σn(k, l) = 8.51

2 Σn(k, l) = 8.79

5 Σn(k, l) = 9.17

Fig. 2. The total overlap populations of the C–C bonds of 1, 2, 4 and 5.



3 2 1

Contrary to the case of the $(CH)_9$ anions, the molecular energy of the positively charged $(CH)_9^+$ system in the D_{3h} symmetrical structure 5 was established to be one of the energy minima and to enjoy a high degree of electron delocalization, while bicyclo[3.2.2]nonatrienyl cation 4 was found to be very unstable.

The C–C bonding states of the $(CH)_9$ anions and cations can be clearly visualized by the total overlap populations[10] as given in Fig. 2, because total overlap population is known to be proportional to overlap energies.[11] The total overlap population value of 0.337 for the C_2–C_7, C_4–C_6, C_2–C_8 and C_4–C_9 is significantly large in comparison with a standard value of 0.693 for a C–C single bond calculated in neopentane. This conjugative bond formation between C_2 and C_7 (C_4–C_6, C_2–C_8 and C_4–C_9) is inconsistent with the observation of a considerably larger coupling constant of $J_{2,7}$ (1.5 Hz) in the ¹H NMR spectrum of 1.[4,12] The value of 1.003 for the C_6–C_7 and C_8–C_9 bonds is much smaller than a standard value of 1.127 for a C–C double bond of ethylene and a little larger than a standard value of 0.961 for an aromatic bond of benzene. The value of 0.873 for the C_2–C_3 and C_3–C_4 bonds corresponds to the intermediate value between that of aromatic and that of single bonds. Thus, the $C_7C_2C_3C_4C_6C_7$ and $C_2C_3C_4C_9C_8$ moieties are regarded as highly conjugative ones, which are clearly understood as bishomocyclopentadienyl systems. As a result of the bond formation of the C_2–C_7, C_4–C_6, C_2–C_8 and C_4–C_9, the total overlap populations of the C_1–C_2 (C_4–C_5) and C_1–C_7 (C_1–C_8, C_5–C_6 and C_5–C_9) decrease to 0.557 and 0.669, respectively, which are somewhat smaller than 0.693 for a standard C–C single bond. These suggest that a carbon atom inherently possesses a maximum bonding ability (maximum valence), which is sufficiently used to make bonds in aromatic molecules, whereas insufficiently in antiaromatic molecules. In this sense, the system 1 can be regarded as a three-dimensional aromatic system. Since the $(CH)_n$ systems are all unsaturated, they tend to be in better bonding states by electron delocalization in the three-dimensional structures.

The comparison of the geometrical and electronic structures of bicyclo[3.2.2]nonatrienyl cation 4 with those of the anion 1. By a similar treatment of 4, the corresponding θ_1 and θ_2 in the cation at energy minimum structure were found to be 69° and the total overlap populations of the C–C bonds were represented in Fig. 2. The overlap population of 0.026 for the C_2–C_7, C_4–C_6, C_2–C_8 and C_4–C_9 bonds of 4 is very small, indicating the absence of electron delocalization in the $C_2C_3C_4C_6C_7$ and the $C_2C_3C_4C_9C_8$ moieties. Thus 4 is unstable due to bishomoantiaromatic instability of the positively charged 5-membered ring systems. In other words, 4 is regarded as a three-dimensional antiaromatic system.

The electronic states of the anion 2 and the cation 5 of the D_{3h} symmetrical structure were next investigated and compared with each other. In the case of the positively charged $(CH)_9^+$ system, the D_{3h} symmetrical structure was established to be one of the energy minima and to enjoy a high degree of conjugation.[4,8] As is seen in Fig. 2, the total overlap populations of both the C_1–C_2 and the C_2–C_3 bonds of 2 are considerably smaller than those of 5, which reveals that 2 is not so much conjugated and stabilized as 5.

It is obvious from the results described above that the total overlap population is closely connected with the electron delocalization energy. Since the total overlap population, n(k, l) is proportional to the electronic bond energy (ϵ_{kl}) between carbon atoms k and l, ϵ_{kl} is given by

$$\epsilon_{kl} = n(k, l)\beta_{kl} \tag{1}$$

where β_{kl} is the bond energy parameter. The total electronic bond energy (E) of all C–C bonds involved in a

$(CH)_n$ molecule is given by

$$E = \sum_{k,l} \epsilon_{kl} = \sum_{k,l} n(k, l)\beta_{kl}. \qquad (2)$$

Accordingly, the sum of the total overlap populations, $\Sigma_{k,l}\, n(k, l)$, could be a quantitative measure of aromaticity for unsaturated $(CH)_n$ systems of the three-dimensional structures. In accord with this criterion, the values for **1**, **2**, **4** and **5** are 8.92, 8.79, 8.51 and 9.17. Thus barbararyl anion **1** is regarded as a "three dimensional aromatics", whereas the cation **4** is "three-dimensional antiaromatic" system. The average total overlap populations per one (CH) units for the system **1** and **4** are 0.99 and 0.94, respectively, indicating the better electronic bonding state in **1** than that in **4**. The values of 8.79 for **2** and of 9.17 for **5** are also similarly understood and in accord with the results experimentally obtained.

This definition of aromaticity is now to be applied to a variety of $(CH)_n$ systems ($C_4 \sim C_9$) by using several semiempirical MO calculations. The results will be reported in the near future.[13]

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[10] INDO coefficients are normalized consistent with the neglect of differential overlap. Hence the sum of bond and atom populations calculated from these coefficients will not equal the total number of valence electrons in the molecule. However, the effect of renormalizing the MO's does not alter the sense of bond strength in this instance.

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