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HOMOCONJUGATION IN 7-NORBORNADIENYL CATIONS

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Abstract—The electronic structure of 7-norbornadienyl and its 2-methyl substituted cations have been investigated using CNDO/2 method. The structure of the carbonium ions are discussed with their molecular energy curves and electronic population analyses. These carbonium ions are shown to be homoconjugated and stable by their overlap populations.

ALTHOUGH molecular orbital calculations have been recently applied to a study of nonclassical carbonium ions,[1-5] there is no direct evaluation of the bonding concerned. An estimation of the bonding by overlap populations is one of the subjects of this work. The species chosen here are the most typical homoconjugated ions, the 7-norbornadienyl (I) and its 2-methyl substituted (II) cations. The 7-norbornadienyl cation species was first studied solvolytically by Winstein and Ordronneau.[6] The reported 10^{14} factor by which the rate of 7-norbornadienyl chloride exceeded that of the saturated 7-norbornyl analog set a world's record for anchimeric acceleration. Theoretical treatment for I was carried out by Piccolini and Winstein,[7] and the delocalization energy was qualitatively calculated by assuming resonance integrals for homoconjugated bonds. The simple LCAO MO or the omega-method used by them is based on π-electron approximation. However, orbital overlaps of I, which involve nonclassical electron delocalization, are obviously not π, but intermediate between σ and π. In such a case, all valence electrons must be included in the MO calculation. All calculations in our study were carried out using the CNDO/2 method by Pople *et al.*,[8] which takes account of all the valence electrons. The geometrical structures, electronic charge distributions and overlap populations of I and II have been calculated and are discussed in this study. The high stability of the 7-norbornadienyl system is also discussed by comparing the stabilization energy of I, obtained by replacement of hydrogen by a methyl group, with those of several organic compounds.

Calculations

Our treatment is composed of two steps: (1) the determination of the molecular geometry by minimizing the molecular energy with respect to geometrical parameters, (2) the evaluation of the electronic populations in the structure at energy minimum. In order to determine the molecular geometry of 7-norbornadienyl carbonium ion (I), all

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the geometrical parameters (the bond lengths and the bond angles) should be tested to change. However, since this procedure consumes too much computing time, the bond angles of θ and ψ in Fig. 1 were chosen as the significant geometrical parameters and the other bond lengths and bond angles were taken as follows. The bond lengths of 1·522 Å, 1·333 Å, and 1·558 Å for C_1C_2, C_2C_3 and C_1C_7 and the bond angles of 109·1°, 96·4°, 102·2° and 38·9° for $\angle C_1C_2C_3$, $\angle C_2C_1C_7$, $\angle C_2C_1C_6$ and $\angle C_1C_6C_2$ respectively, were taken from the literature by Wilcox *et al.*[9] H_1 and H_4 are at equal angles from the other bonds at C_1 and C_4, H_2, H_3, H_5 and H_6 are in planes defined by C_1, C_4 and their carbon atoms. The structure of I could in principle be calculated by minimizing its molecular energy with respect to the angles, θ and ϕ.

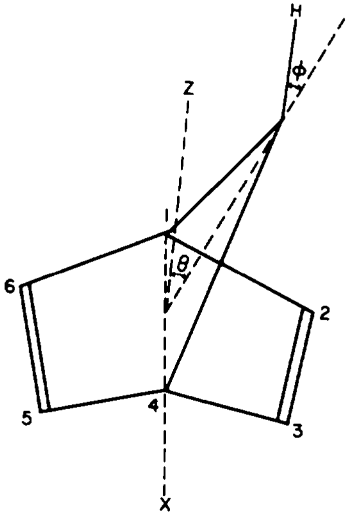

Fig. 1. Molecular axes and bond angles, θ and ϕ.

All calculations employed are based on the CNDO/2 (complete neglect of differential overlap) approximation to the full SCF equations of Roothaan.[10] The criterion of self-consistency is that density changes in all the orbitals are less than 0·0002. The calculation of the geometry was organized as follows. The angle θ was first calculated by minimizing the molecular energy, assuming that H_7 is in the $C_1C_4C_7$ plane ($\phi = 0$). Using the computed value θ, ϕ was calculated. With new value for ϕ, θ was recalculated. This procedure was repeated until an absolute minimum in energy with respect to θ and ϕ was obtained. Here the angles were calculated to within 1°.

The electronic charge distributions and overlap populations in the geometrical structure of I at energy minimum were calculated from the literature by Mulliken,[11] and represented in Fig. 2. It was shown by Chesnut and Wormer[12] that the overlap populations summed over the orbitals of the atoms generally reflect the symmetry of the molecules. 2-Methyl substituted 7-norbornadienyl cation (II) was treated similarly, and the results given in Fig. 3. In this calculation also, the geometry of the skeleton $C_1C_2C_3C_4C_5C_6$ was fixed and the bond angles (θ, ψ) were taken as the important geometrical parameters. Energies of several methyl substituted organic species were calculated by the CNDO/2 method and summarized in Table 1., which indicates that the 7-norbornadienyl system is highly stabilized.

RESULTS AND DISCUSSION

The bond angles in structure I at energy minimum, θ and ϕ, were determined to be 55° and 18°, respectively, from the potential energy surface obtained by the method described above. The total energy of I at its energy minimum was $-54\cdot894$ a.u. The unsymmetrical structure ($\theta = 55°$), which was theoretically concluded to be most stable, is supported on the basis of the NMR spectrum of I observed by Story and Saunders.[13] A symmetrical structure, which was once envisioned,[6] was obviously much less stable than the unsymmetrical one. The difference in molecular energy between the symmetrical ($-54\cdot601$ a.u.) and the unsymmetrical structures in our calculation was 0·293 a.u. (184 Kcal). This value is obviously too large and the barrier to bridge flipping is certainly an order of magnitude smaller. This descrepancy from experimental fact may arise from both the tendency that CNDO/2 generally gives the larger value of the energy of stabilization[12] and the assumption that the bond lengths are held constant. However, it should be also noticed that the calculation of molecular energy is carried out by assuming the existence of the full positive charge on the carbonium ions, nevertheless a considerable amount of the positive charge actually must be moved from the carbonium ion to its environment, e.g., counter anion and solvent. Therefore, it seems less strange that any calculation method would not give quantitatively good results. Too large a calculated bond angle ($\theta = 55°$) is also explained by the same reason above. Since under experimental conditions the carbonium ion exists in a solvent containing a counter anion, the anion and the solvent interact with the carbonium ion and the part of charge is expected to be dispersed from the carboniom ion to its environment. The MO treatment, on the other hand, is always performed by assuming that the carbonium ion exists in a vacuum, and the positive charge must delocalize only over the carbonium ion itself. Therefore, the bridgehead C_7 is forced to bend down much more toward the C_2—C_3 bond in order to disperse the positive charge over the homoconjugated system $C_2C_3C_7$. Thus MO calculations in general tend to give somewhat exaggerated values, but the results are considered to be significant enough to discuss the geometries and the stabilities of most molecules.

The calculated value of 55° for the bond angle θ clearly indicates that the C_7 atom bends toward the double bond C_2—C_3 and the resulting high degree of three center bonding between C_2, C_3 and C_7 lowers its own energy. The situation can be more distinctly visualized by estimating the overlap populations for the bonds, C_2—C_7, C_3—C_7 and C_2—C_3. The overlap populations of the bonding in I were presented in Fig. 2. As seen the value of 0·445 for the bond C_2—C_7 or C_3—C_7 is significantly large in comparison with 0·949 for C_2—C_3, which corresponds to the sum of a whole σ-bond and a weak π-bond. This result is in good agreement with the observation of the considerably large coupling constant of $J_{2\text{-}7}$ (2·7 cps) in the NMR spectrum of I.[13] The value of 0·949 for the C_2—C_3 bond nearly equals the overlap population of 0·960 calculated for a typical aromatic bond in benzene. As a result of the bond formation of C_2—C_7 and C_3—C_7, the overlap population for the C_1—C_7 or the C_4—C_7 bond diminishes to the value of 0·616, which is somewhat smaller than the overlap population of 0·704 for a typical single C—C bond calculated in neopentane. Thus, the system $C_2C_3C_7$ can be understood as a three center homoconjugated system. Since overlap populations should be in general good measures for bond energies, the large values of

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2 † Extended Hückel calculation has been also applied to the 7-norbornadienyl cation by Hoffmann[2] to give a value of 27° for θ.

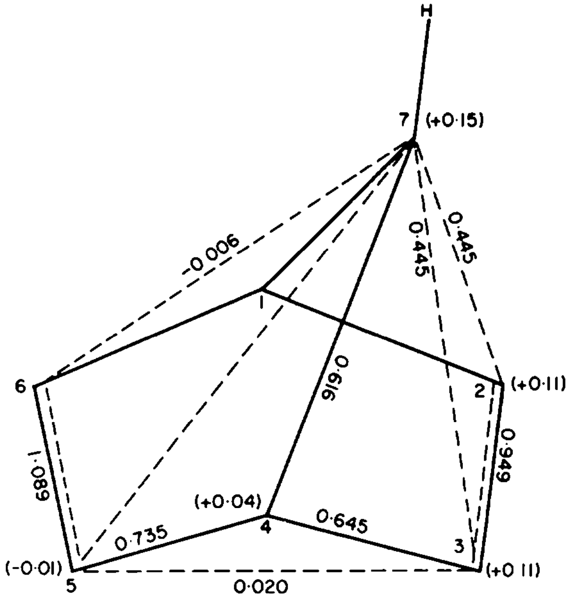
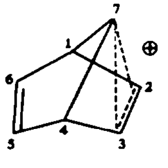


Fig. 2. The electronic charges and the overlap populations of I.

0·445 for the C_2—C_7 and the C_3—C_7 demonstrate much stabilization of the system. (I) by homoconjugation.

On the other hand, the overlap population of 1·089 for the C_5—C_6 bond is comparable to the value of 1·127 for a typical double bond calculated in ethylene. No or weak interaction between $C_5(C_6)$ and C_7, or between C_5 and C_3 was suggested from the calculation. From all the calculated overlap populations, the geometrical structure of I is represented as shown in Scheme 1.

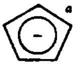
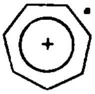
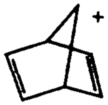
SCHEME 1



I

From the calculated value of 18° for the bond angle ϕ, it was suggested that the bridging carbon atom (C_7) in I has a tendency to rehybridize from sp^2 toward sp^3. In the basis of such rehybridization, the C_7 atom can be reasonably understood in term of pentacovalent carbon. The electronic charge of each carbon atom in I was given in Fig. 2. The positive charge almost equally delocalized to C_7, C_2 and C_3, but not to C_5 and C_6. The lower chemical shift of τ 2·4 at the 2 or 3 position than that of τ 3·7 at the 5 or 6 position in the NMR spectrum of I[13] is well coincident with the positive charge distribution. This charge distribution and overlap populations give an image of a bishomocyclopropenium cation toward the $C_2C_3C_7$ system.

Table 1. The energy difference between the system (R—H) and the system replaced with methyl group (R—CH_3)

R	Energy of R—H	Energy of R—CH_3	ΔE
$^{+}CH_3$	−8·666 a.u.	−17·464 a.u.	8·798 a.u.
 [a]	−23·000	−31·731	8·731
 [a]	−39·165	−47·867	8·702
 [a]	−47·097	−55·789	8·692
 [a]	−54·600	−63·299	8·699
	−54·894	−63·592	8·698

[a] Bond lengths were determined by minimizing the molecular energy.

The same calculation procedure was applied to the 2-methyl 7-norbornadienyl cation (II) and the results given in Fig. 3. Whether II is a classical or nonclassical carbonium ion is also of interest.[14] The resulting geometrical parameters ($\theta = 55°$, $\phi = 20°$), the electronic charge distributions and the overlap populations in Fig. 3 are very similar to those of the unsubstituted cation (I). That is, replacement with a methyl group has little effect on the geometrical structure and the electronic state of I. This indicates system II to be nonclassical and highly stabilized by its homoconjugated bonds. In order to confirm this, the energy gain of several systems by the replacement of a hydrogen atom with a methyl group were calculated and listed in Table 1. Since an unstable system is considered to be more stabilized by a methyl group, it seems reasonable that the energy gain by methyl replacement of the unstable methyl carbonium ion (8·798 a.u.) is the largest, whereas that of the stable benzene (8·692 a.u.) is the smallest. The energy gain of I, 8·698 a.u., is just comparable to that of benzene and smaller than those of any systems such as cyclopropenium cation, cyclopentadienide anion and tropylium cation.

In summary from the above theoretical consideration, the 7-norbornadienyl carbonium ion is shown to be an extraordinary stabilized system, which include the strongly homoconjugated bonds, C_2—C_7 and C_3—C_7. It would be generally concluded that dotted lines conveniently given to represent homoconjugated bonds in many nonclas-

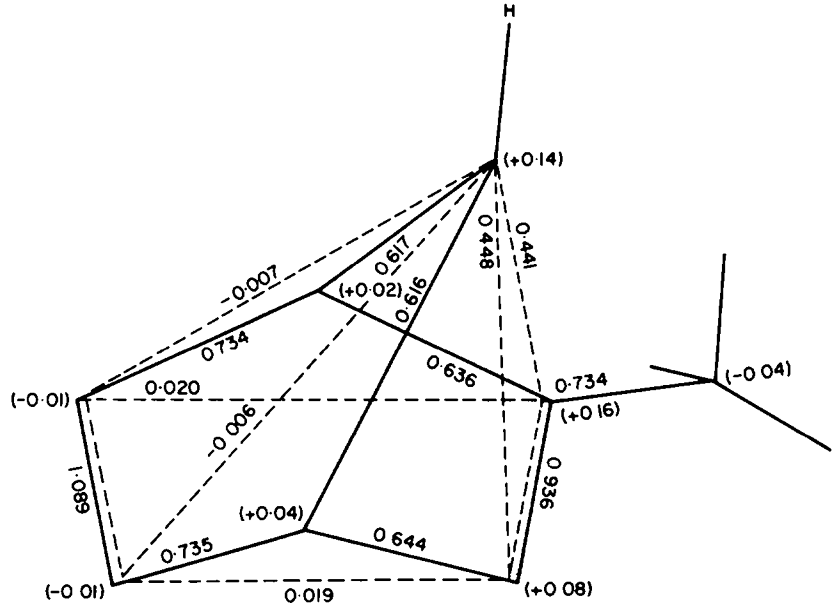


Fig. 3. The electronic charges and the overlap populations of II.

sical carbonium ions, can be semiquantitatively evaluated by the overlap populations in their equilibrium structure. When this work was performed, the CNDO/2 treatment seemed the best compromise between relevant quantum-mechanical completeness and computational manageability, but it has been recently pointed out by Schleyey *et al.*[4] and Snyder[5] that the application of CNDO/2 to carbonium ion problems not necessarily gives good results. However, more refined MO treatment would be possible to afford quantitatively better overlap populations to the homoconjugated bonds.

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