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ISOMERIC SYSTEM OF $C_5H_5^-$ AND $C_5H_5^+$ IONS

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The geometrical and electronic structures of $C_5H_5^-$ and $C_5H_5^+$ systems have been studied applying CNDO/2 method. The antiaromatic $C_5H_5^+$ system in the planar structure was found to be much stabilized in three dimensional C_{4v} symmetrical structure.

The $(CH)_n$ systems have recently received increased interest by theoretical investigators as well as experimental chemists. Especially, the geometrical and electronic structures of nonplanar $(CH)_n$ systems remains unexplored up to the present. This communication deals with $C_5H_5^-$ and $C_5H_5^+$ ions. Although cyclopentadienyl anion is a nonbenzenoid aromatic system, cyclopentadienyl cation is so called "antiaromatic system" in its planar structure, which could not be detected so far. Our concern in this study is directed for investigating how the $C_5H_5^+$ ion would be stabilized in its nonplanar structure and what electronic structure it does have.

Of the $(CH)_n$ systems, $C_7H_7^+$ and $C_9H_9^+$ systems were already discussed in our previous papers[1,2] using CNDO/2 method. Both the systems were found to be stabilized by homoconjugated bonds. That is, the $C_7H_7^+$ system (I) was shown to contain a bishomocyclopropenium ion moiety in the equilibrium structure and one of the energy minimum structure of the $C_9H_9^+$ system (II: D_{3h} symmetrical structure) have cyclopropylcarbinyl-resonance frameworks.

Our treatment in these studies are fundamentally composed of the following two steps; 1) the determination of the most stable structure by minimizing the molecular energy with respect to the geometrical parameters, 2) the estimation of the electron densities and the overlap populations[4] in the structure of energy minimum. The species chosen in this investigation are $C_5H_5^-$ (III) and $C_5H_5^+$ (IV) systems. The calculated results of III, which is the most general aromatic system consistent with Hückel's rule, is first described in the following. The C-C bond lengths for III in the most stable D_{5h} symmetrical structure were calculated to be 1.401 Å.[*1] No additional stabilization was observed from various kinds of small geometrical deformations toward this D_{5h} symmetrical structure. Thus it was suggested that the aromatic system is the most stable in its planar symmetrical structure.

As a result of similar treatment for the $C_5H_5^+$ system (IV_a: the D_{5h} symmetrical structure), the lowest energy of 38.6425 a.u. was obtained when the bond lengths are 1.410 Å. Small geometrical deformations from IV_a shown in Fig. 1 resulted in

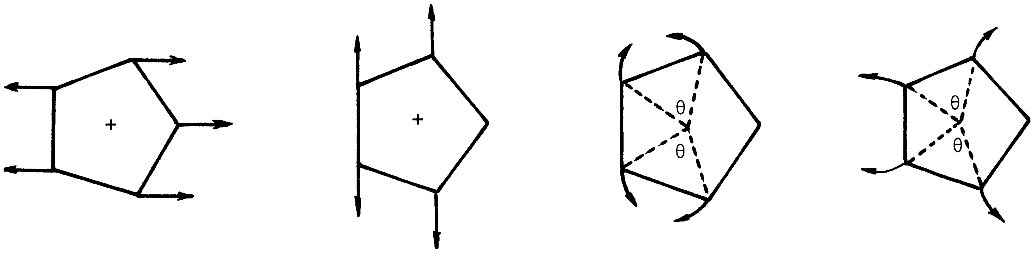

Fig. 1 Geometrical Deformations from IV_a

the lowering molecular energy.

It is especially noteworthy that deformation from the $C_5H_5^+$ plane represented in Fig. 2 makes IV_a stable (e.g., total energy[*2] at $\gamma = 5°$, -38.6435 a.u.; $\gamma = 15°$, -38.6507 a.u.; $\gamma = 90°$, -38.7139 a.u.), suggesting that the three dimensional structure, IV_b (D_{3h}), visualized in Fig. 3, is stable one. Then the calculation of the molecular energy for IV_b with respect to ℓ_1 and h_1 was repeated and the lowest energy for the structure IV_b was obtained to be -38.9014 a.u. with ℓ_1 = 1.58 Å, h_1 = 1.21 Å.

[*1] In this calculation, all the C-H bond lengths were fixed to be 1.08 Å according to the literature.[5]

[*2] The total energy calculated from CNDO/2 method is not quantitatively reliable.[6] But, qualitative conclusion seems sufficiently applicable for discussion, since prominent discrepancy from the fact was not found through our calculations on C_nH_n system (n: 3 - 8).

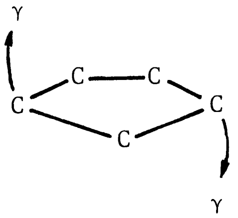

Fig. 2 A Deformation from the Plane

However, it is immediately shown that IV_b is not the most stable structure on the potential energy surface, because such deformation as represented in Fig. 4 yielded additional stabilization energy. Therefore, the C_{4v} symmetrical structure, IV_c, is expected to be that having the lowest molecular energy among various geometrical structures for the $C_5H_5^+$ system. As regards the structure IV_c (Fig. 5), geometrical parameters, ℓ_2 and h_2, were tested to change. As a result, the much lower energy (-39.1335 a.u.) than those for IV_a and IV_b was obtained when ℓ_2 = 1.47 Å, h_2 = 1.14 Å and $C_1C_5 = C_2C_5 = C_3C_5 = C_4C_5$ = 1.356 Å. Any geometrical perturbation to this C_{4v} structure did not afford additional stabilization energy.[*3]

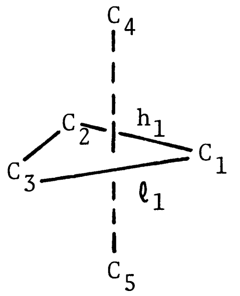

Fig. 3 D_{3h} Symmetrical Structure (IV_b)

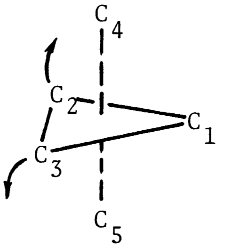

Fig. 4 A Deformation from IV_b

Electronic charges and overlap populations for IV_c are calculated and given in Fig. 6. As seen in Fig. 6, positive charge is delocalized all over the molecule. The overlap populations indicate IV_c to be one of nonclassical type carbonium ions. The overlap populations of 0.718 for C_1-C_2, C_2-C_3, C_3-C_4 and C_4-C_1 bonds just correspond to that of 0.704 for a typical single bond calculated in neopentane, while those (0.530) for C_1-C_5, C_2-C_5, C_3-C_5 and C_4-C_5 bonds are smaller than the overlap population of a single

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[*3] The trivial geometrical parameter ψ, which is the angle between the C-H bond and the $C_1C_2C_3C_4$ plane, was tested to change and a little lower energy (-39.1339 a.u.) was obtained then ψ = 3°.

bond but a considerably large value. The C_5 atom can be reasonably understood in terms of pentacovalent carbon.

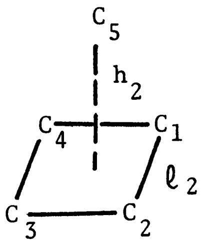

Fig. 5 C_{4v} Symmetrical Structure (IV_c)

In summary, among many possible geometrical $C_5H_5^+$ structures, the system IV_c is the most stable one, which accords with Hoffmann's work by the extended HMO.[7] It could be concluded that antiaromatic systems in the planar structure could gain much stabilization energy in their three dimensional symmetrical structure.

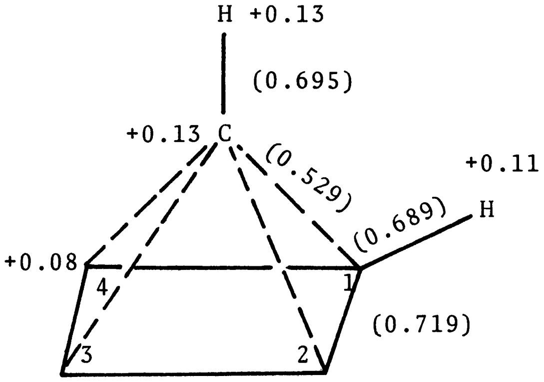

Fig. 6 Electronic Charges and Overlap Populations in IV_c

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