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Abstract

Full Text

Physical Chemistry

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MOLECULAR ORBITALS OF SYSTEMS OF FUSED FIVE-, SIX-, AND SEVEN-MEMBERED RINGS

(Presented by Academician I. I. Chernyaev, 29 VI 1957)

One of the major achievements of quantum chemistry was the prediction that the cycle (C_5H_5), having one vacant place in a favorable molecular orbital (MO), should be stable in the form of a singly charged anion, while the cycle (C_7H_7), having only three favorable MOs, on which only 6 ( )-electrons can be accommodated, should be stable in the form of a singly charged cation. These predictions were confirmed by the preparation of the anion (C_5H_5^-) (for example, in (C_5H_5Na), ((C_5H_5)_2Mn), etc. ((^1))) and of the tropylium cation (C_7H_7^+) ((^2)). Recently a report appeared on the synthesis of a stable carbonium cation from three fused six-membered rings (V in Table 1 ((^3))); moreover, it was indicated that the possibility of the existence of this cation had earlier been predicted in a calculation by Dewar and Pettit ((^4)) by the MO method, which led to the conclusion that such a cation is significantly stable.

In connection with this, we became interested in the question of the MOs of systems of three fused rings including five- and seven-membered cycles, and we calculated the MO energies of such systems by the usual MO method in the LCAO approximation. The results of the calculation, expressed in terms of the Coulomb integrals (C) and resonance integrals ( ), are given in Table 1, where the energies of all favorable MOs and of the two lowest unfavorable ones are listed. Our calculation confirms the conclusion of Dewar and Pettit concerning system V, since this system has 6 favorable MOs for 12 electrons, while the 13th ( )-electron must be on an orbital whose exchange energy is zero, so that easy removal of this electron may be expected, whereas the energy of the occupied MOs is sufficient to ensure the stability of the system (C{13}H{13}^+) ((12C + 17.82)).

For systems III, IV, VI, and VII, as the calculation shows, the number of favorable MOs is equal to the number of available pairs of ( )-electrons, so that such systems should exist as neutral molecules, in accordance with the possibility of writing for them structural formulas with double bonds and with all carbon atoms tetravalent.

Next, we found that system II, with 11 ( )-electrons, has 6 favorable MOs, so that such a fused system should have a tendency to add an extra electron with formation of (C{11}H{11}^{-}). It is interesting to note that pentalene does not have such a tendency (it has 4 favorable MOs and 8 ( )-electrons), and fusion of a third six-membered ring to naphthalene in V likewise does not lead to the appearance of a vacant place in a favorable MO, so that the presence of such a vacant place is a specific feature precisely of system II, consisting of two five-membered and one six-membered rings. The opposite situation obtains in system VIII, which has only 7 favorable MOs and 15 ( )-electrons, so that the cycle (C{16}H{16}) should, like tropylium, be stable in the form of a singly charged cation. System VIII also differs from the system of two fused seven-membered rings (“heptalene”), which has 5 favorable MOs and one MO with zero exchange energy. The most interesting results, in our opinion, are those for systems I and IX. For the first of them we found 6 favorable MOs, whereas the number of ( )-electrons is equal to 10. This means that in the cycle (C{10}H{10}) (I) one may expect a tendency to add 2 extra electro-

···with the formation of a dianion. It should, however, be noted that the addition of 2 extra electrons may be hindered by their repulsion. On the other hand, in the case of IX there are 16 π-electrons and only 7 favorable MOs, so that such a system should tend to give up 2 electrons, with transition to a dication. Since in this case there are no obstacles associated with electron repulsion, we believe that such a condensed system of 3 seven-membered rings should exist in the form of a salt ([{C}{16}{H}{16}]$^{\{2+\}\{X\}}${2-}).

Table 1

Energies of molecular orbitals

I	II	III	IV	V
[[structure I]]	[[structure II]]	[[structure III]]	[[structure IV]]	[[structure V]]
(C + 2.52)(C + 1.53)(C + 1.53)(C + 0.57)(C + 0.35)(C + 0.35)(C - 1.00)(C - 1.88)	(C + 2.49)(C + 1.62)(C + 1.62)(C + 0.81)(C + 0.62)(C + 0.46)(C - 0.62)(C - 1.21)	(C + 2.48)(C + 1.71)(C + 1.68)(C + 1.00)(C + 0.83)(C + 0.48)(C - 0.28)(C - 0.59)	(C + 2.47)(C + 1.68)(C + 1.68)(C + 1.00)(C + 0.83)(C + 0.64)(C - 0.28)(C - 1.00)	(C + 2.45)(C + 1.73)(C + 1.73)(C + 1.00)(C + 1.00)(C + 1.00)(C)(C - 1.00)(C - 1.00)
Number of electrons10	11	12	12	13

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VI	VII	VIII	IX	X
[[structure VI]] (C + 2.43)(C + 1.77)(C + 1.77)(C + 1.21)(C + 1.13)(C + 1.00)(C + 0.24)(C - 0.46)(C - 0.71)	[[structure VII]] (C + 2.45)(C + 1.79)(C + 1.77)(C + 1.30)(C + 1.13)(C + 0.76)(C + 0.24)(C - 0.33)(C - 0.71)	[[structure VIII]] (C + 2.42)(C + 1.80)(C + 1.80)(C + 1.33)(C + 1.24)(C + 1.10)(C + 0.45)(C - 0.31)(C - 0.45)	[[structure IX]] (C + 2.41)(C + 1.83)(C + 1.83)(C + 1.34)(C + 1.34)(C + 1.30)(C + 0.62)(C - 0.21)(C - 0.21)	[[structure X]] (C + 2.54)(C + 1.74)(C + 1.72)(C + 1.18)(C + 1.00)(C + 0.68)(C - 0.51)(C - 1.00)
Number of electrons 14	14	15	16	13

System X has MOs of the same character as V.

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Note: Figure translations are in progress. See original paper for figures.

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