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MOLECULAR ORBITALS OF ANTIAROMATIC MOLECULES: CYCLIC POLYMETHINES $(CH)_3$ and $(CH)_4$

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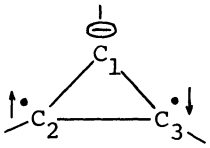
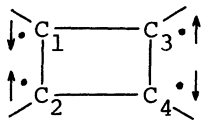
The contour maps of the highest occupied (HO) corresponding orbitals (CMO) of cyclic polymethines $(CH)_n$ (n=3,4) are presented in order to clarify the electron localizations which are closely related with the electron destabilizations in antiaromatic molecules. The symmetry and stability of the HO CMO's are also discussed in relation to the correlation effect between diradical electrons.

The basic problems of the antiaromatic molecules with 4n electrons seem classifiable into three categories[1]: (i) geometry, (ii) spin multiplicity and (iii) instability, i.e., antiaromaticity. The first, i.e., geometry of local minimum, may be elucidated by constructing the quantitative potential surfaces by the configuration interaction (CI)[2,3] and generalized valence-bond (GVB)[4] methods. The second problem concerning the relative stability between singlet and triplet diradicals is qualitatively understandable on the basis of the magnetic (spin) symmetries of the unrestricted Hartree-Fock (UHF) wavefunctions.[5] The last, i.e., antiaromaticity, is regarded as the destabilization of cyclic π-electron systems compared with suitable reference π-electron compounds. The total energy[1,6] and induced paramagnetic ring current[7] have already been discussed in relation to antiaromaticity. The molecular-orbital (MO) theoretical elucidation of antiaromaticity has been performed in line with the singlet instability of the restricted HF (RHF) solutions.[8] However, the triplet instability giving the more stable UHF solution precedes the singlet one relating with the bond alternations[8] in the case of antiaromatic molecules.[4,9] The aim of the present communication is two-fold. One is to present the contour maps of the UHF MO's in order to show clearly the π-electron localization which is closely related with the electronic destabilization (instability) of antiaromatic molecules. The other is to clarify the spatial symmetry and phase relation of the localized π-MO's which are occupied by the diradical electrons.

The cyclic polymethines $(CH)_3$ and $(CH)_4$ with 4 electrons are employed as typical isoelectronic systems of antiaromatic molecules:



(1)



(2)

The isosceles (C_{2v}) and D_{mh}(m=2-4) conformations are assumed for the cyclopropenyl anion (I) and cyclobutadiene (II). The corresponding orbitals of the UHF solutions were determined by the method previously described.[5]

The corresponding orbitals of I are tightly paired except for the highest occupied π-orbital pair, $\chi_{HO}(I)$ and $\eta_{HO}(I)$, in accord with the diradical property of I. The contour maps of the singlet-coupled HOMO pair are depicted in Fig. 1. As is apparent from Fig. 1, the up- and down-spin orbitals (vice versa) are considerably localized on the C_2- and C_3-atoms, respectively. The populations on the C_1-atom, on the other hand, are equivalent between the up- and down-spins, leading to the canonical structure **1** which is responsible for the diradical structure of I. The ethylenic π-orbital on the C_2-C_3 group is destroyed by the strong antibonding interaction with the p-orbital on the C_1 atom. Therefore, the π-orbital localization is caused in contrast to the π-electron delocalization in aromatic molecules. This is in accord with the cyclic destabilization of the anion I. However, the corresponding HOMO's remain to be weakly π-bonding in the C_2-C_3 bond region in an obtuse conformation (ΔR = 0.2 Å in ref. 5) as shown in Fig. 1A. The LCAO coefficients of the $\chi_{HO}(I)$ and $\eta_{HO}(I)$, on the other hand, have faded away on the C_2- and C_3-atoms, respectively, at the less deformed conformation (ΔR = 0.1 Å) as shown in Fig. 1B. This corresponds to an orbital-phase transition point defined previously.[9] The LCAO coefficients with opposite signs grow gradually, passing through the transition point. In fact the corresponding orbitals are weakly antibonding on the C_2-C_3 group in the D_{3h} conformation as shown in Fig. 1C. Thus the orbital phase relations change in the course of the deformation process of I. This

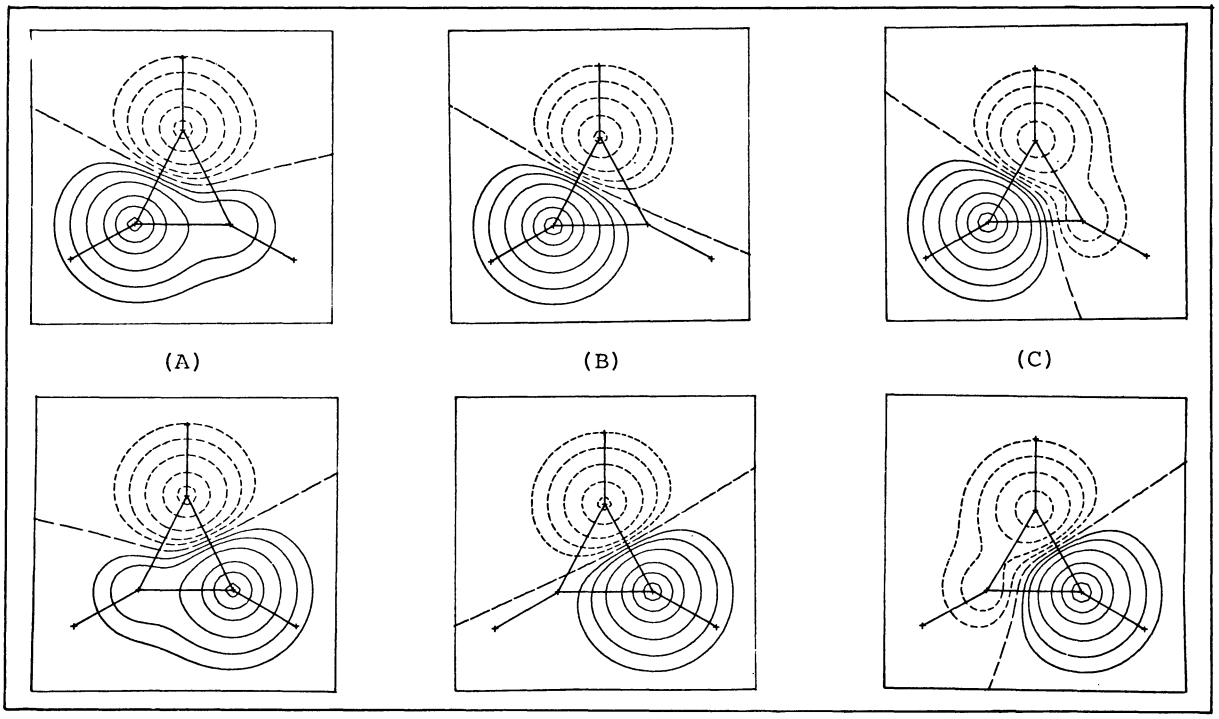
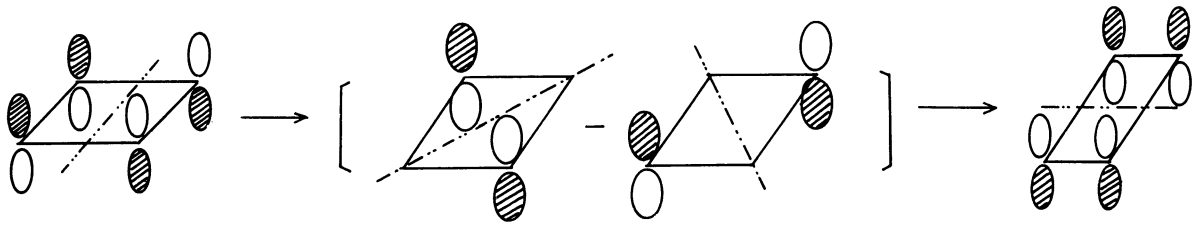


Fig. 1 Contour maps of the corresponding HOMO's, $\chi_{HO}(I)$ and $\eta_{HO}(I)$ of the cyclopropenyl anion I: (A) obtuse conformation (ΔR = 0.2 Å), (B) obtuse conformation (ΔR = 0.1 Å) and (C) D_{3h} conformation.

is quite similar to the phase-inversion process of forbidden diradical (FR) reactions belonging to the Hückel three-center four-electron systems.[10]

The highest occupied corresponding orbitals, $\chi_{HO}(II)$ and $\eta_{HO}(II)$ of cyclobutadiene (II) are illustrated in Fig. 2. The up- and down-spin orbitals (vice versa) are exclusively localized in the (C_2,C_4)- and (C_1,C_3)-regions, respectively, leading to the canonical structure **2**. The ethylenic π-bonds in the C_1-C_2 and C_3-C_4 subunits are broken because of their strong antibonding interactions even in the case of rectangular conformation (ΔR = 0.1 Å) as shown in Fig. 2A. The π-electron localization is clearly demonstrated in accord with the instability of quasi-square planar cyclobutadiene. The LCAO coefficients of the $\chi_{HO}(II)$ and $\eta_{HO}(II)$ have vanished on the (C_1,C_3)- and (C_2,C_4)-atom pairs, respectively, in the D_{4h} conformation as shown in Fig. 2B. This causes a smooth shift of the node line in the course of the deformation process of cyclobutadiene as shown in Fig. 2.

Let us consider the exchange reaction between two ethylenic π-bonds in order to clarify the symmetry properties of the corresponding HOMO's. The orbital-phase relations change in the course of reaction as follows:



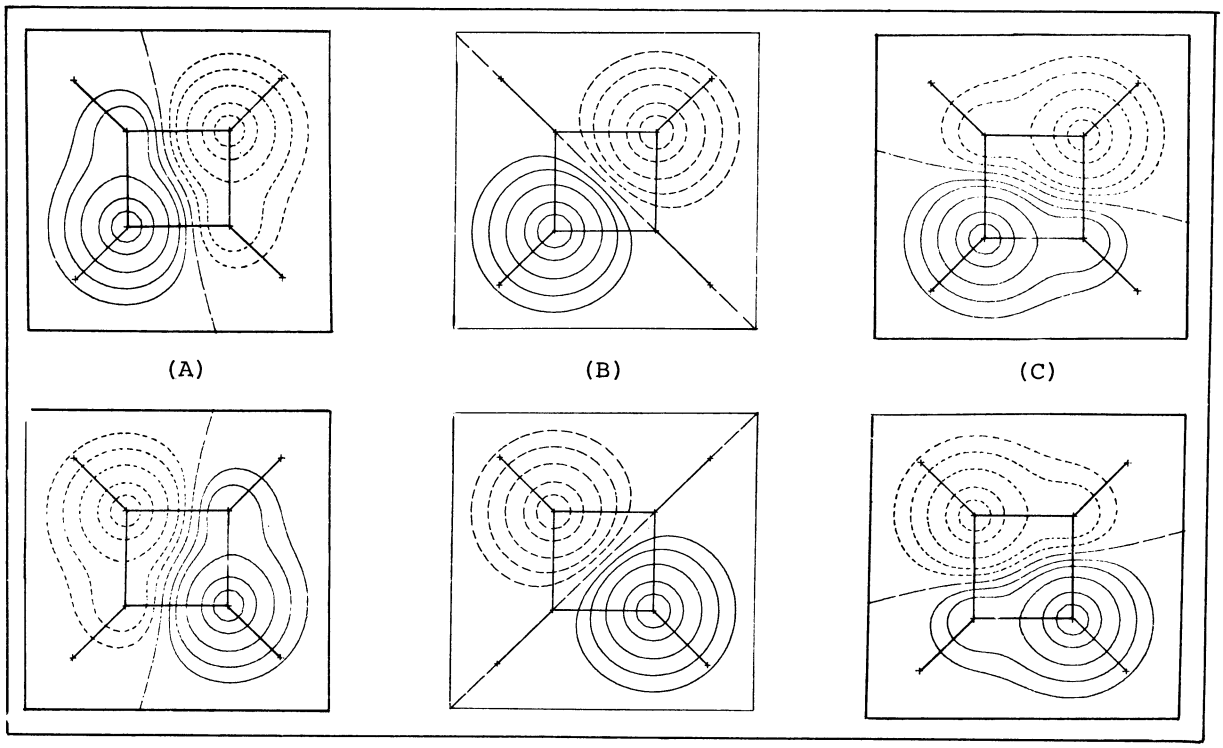


Fig.2 Contour maps of the corresponding HOMO's, $\chi_{HO}(II)$ and $\eta_{HO}(II)$ of the cyclobutadiene: (A) and (C) rectangular conformations, and (B) square planar conformation.

The electronic configurations also change as

$$[\pi_S(II)]^2 \longrightarrow \{\chi_{HO}(1)\eta_{HO}(2) + \eta_{HO}(1)\chi_{HO}(2)\} \longrightarrow [\pi_A(II)]^2$$

The symmetric $\pi_S(II)$ and antisymmetric $\pi_A(II)$ orbitals have the b_{2g} and b_{3g} spatial symmetries of the D_{2h} group, respectively. The corresponding orbitals, on the other hand, belong to the reducible representations of the same group as can be recognized from the equation[4,9]:

$$\chi_{HO} = (\cos \lambda/2)\pi_S + (\sin \lambda/2)\pi_A, \quad \eta_{HO} = (\cos \lambda/2)\pi_S - (\sin \lambda/2)\pi_A \qquad (1)$$

where λ is the orbital mixing parameter. In fact the orbitals themselves have the b_g symmetry of the C_{2h} group, breaking the rotational symmetries concerning the x- and y-axes. Although the orbital symmetries are broken, the singlet geminal has the correct A_1 spatial symmetry because of the following relationship:

$$\{\chi_{HO}(1)\eta_{HO}(2) + \eta_{HO}(1)\chi_{HO}(2)\} = (1+\cos \lambda)[\pi_S(II)]^2 - (1-\cos \lambda)[\pi_A(II)]^2 \qquad (2)$$

The singlet geminal is nothing but the 2-dimensional natural orbital (NO) CI term[2] constructed of the bonding and antibonding NO's. The localization and symmetry breaking of the corresponding HOMO's are therefore closely related with the orbital corrections by the nondynamical correlations[3,5,11] which play an important role in the near-degeneracy systems such as cyclobutadiene II.

The present results indicate that the π-electron localization takes place in the case of antiaromatic molecules because of the mixing between near-degenerate bonding and antibonding NO's to remove the Coulomb repulsion between diradical electrons. Since both NO's are symmetry-adapted, the resulting corresponding orbitals are symmetry-broken in accord with the diradical property of the molecules. Thus, the concepts of orbital instability, orbital symmetry-breaking, and nondynamical correlation are of great use for an understanding of the antiaromaticity, i.e., electron destabilization, in planar 4n-electron systems.

The search of the local minimum of a potential surface is a very interesting problem relating with the singlet instability of antiaromatic molecules.[8] The present results suggest that it could be solved by the geometry optimization procedure[12] for the ground HF (i.e., singlet DODS) solutions.

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