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Energy Component Analysis of the Pseudo Jahn-Teller Effect in Pentalene and Heptalene

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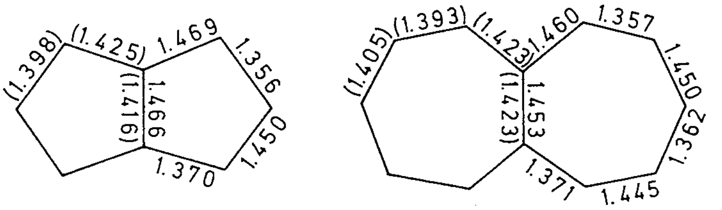
An energy component analysis of the pseudo Jahn-Teller effect from D_{2h} to C_{2h} within the PPP-type HF approximation reveals that the energetic stability for heptalene arises essentially from a lowering of the electron-nuclear attraction energy, while that for pentalene arises entirely from a decrease in the interelectronic repulsion energy.

The pseudo, or second-order, Jahn-Teller effect in a molecule is the stabilization which occurs when a distortion of proper symmetry mixes two electronic states which are nearly degenerate in the symmetrical nuclear arrangement.1) As a typical example of the non-alternant hydrocarbons that undergo symmetry reductions, we take heptalene. Assuming the fully symmetrical D_{2h} nuclear arrangement for the molecule, the lowest excited singlet state of the B_{3g} symmetry is predicted to be only 0.26 eV higher than the ground state by the PPP-type SCF MO CI method.2,3) As a result, it is shown that the distorted C_{2h} structure, in which a marked bond-length alternation exists in the peripheral carbon skeleton, is indeed energetically favoured as compared with the symmetrical D_{2h} structure with the delocalized π-bonds (Fig. 1).

Our interest is where the energetic stability actually originates from, when such non-alternant molecules suffer symmetry reductions, i.e., lattice instabilities.4) In order to examine the dominant factors,5) we attempt an energy component analysis of the pseudo Jahn-Teller effect within the PPP-type HF MO approximation.2) In this paper we deal with pentalene and heptalene, since they are well known to be the pseudo Jahn-Teller molecules from both theoretical and experimental viewpoints.3)

The stabilization energy due to the pseudo Jahn-Teller effect is the difference in total energy between the fully symmetrical and the distorted geometrical structure. Here, the total energy is assumed to be the sum of the π-bond and σ-bond energies, the latter being calculated using the harmonic oscillator model.[6)] In this treatment, a symmetry reduction generally brings about a raising of the σ-bond energy,[7)] and we thus consider here only the change in π-bond energy between the D_{2h} and C_{2h} structures in Fig. 1.[3)]



Pentalene Heptalene

Fig. 1. Bond lengths (A) of the D_{2h} and C_{2h} structures of pentalene and heptalene. The figures in parentheses are the bond lengths of the D_{2h} structures.

Heptalene. When this molecule suffers a lattice instability from D_{2h} to C_{2h}, a sizable change in energy takes place mainly in the HOMO and the LUMO, the former being lowered and the latter raised in energy. This is because the lowest excited singlet state is represented virtually by an orbital jump from the HOMO to the LUMO at the D_{2h} structure and, thus, the vibronic interaction takes place substantially between the two orbitals.[8)] Table 1 shows that the energy of one-electron part E(1), which consists of the kinetic and the electron-nuclear attraction energy, is lower for the C_{2h} structure than for the D_{2h} one, irrespective of the methods used. This energy lowering arises entirely from the HOMO. A detailed analysis reveals that the electron-nuclear attraction term in the core-Coulomb integral[1a,2a)] is the factor that leads to the energy lowering of the HOMO and, hence, to the energetic stability of the C_{2h} structure.

Pentalene. A different situation is observed in this molecule. The

Table 1. Energies (eV) of one- and two-electron parts for heptalene and pentalene at the D_{2h} and C_{2h} structures

Molecule	Structure	E(1)	E(2)	E(total)
Heptalene	D_{2h}	-634.52 (-799.69)[a)]	250.48 (326.83)	-384.04 (-472.86)
	C_{2h}	-635.17 (-800.59)	250.35 (326.89)	-384.82 (-473.70)
Pentalene	D_{2h}	-346.50 (-437.41)	129.54 (171.34)	-216.96 (-266.07)
	C_{2h}	-345.88 (-436.34)	128.36 (169.81)	-217.52 (-266.53)

a) The values in parentheses refer to those obtained by the Pariser-Parr formula[2a)] and the others by the Mataga-Nishimoto approximation[2c)] when estimating two-center repulsion integrals.

energy of one-electron part is higher for the C_{2h} structure than for the D_{2h} one. On the contrary, the energy of two-electron part E(2), which is given by the sum of twice the Coulomb repulsion integral J_{ij} and minus the exchange integral K_{ij} over all the occupied orbitals, is lower for the C_{2h} structure than for the D_{2h} one. If examined in detail, the energies due to the sum of the exchange terms are almost the same in the two structures. But the energy due to the sum of the Coulomb repulsion terms is less for the C_{2h} structure than for the D_{2h} one. This reduction in the interelectronic repulsion energy originates mostly from the Coulomb repulsion integral of the HOMO. Since the energy lowering from the two-electron part exceeds in size the energy raising from the one-electron part, it can be said that in pentalene the energetic stability of the C_{2h} structure benefits from a decrease in the interelectronic repulsion energy.

From a perturbational MO method, we give an explanation why the dominant factors should differ between the two molecules. When the molecules suffer symmetry reductions from D_{2h} to C_{2h} through the distortion of bond-length alternation type (b_{3g}),$^{3)}$ the mixing in of the LUMO into the HOMO occurs.$^{8)}$ For heptalene, it follows that the partial electronic charge densities in the perturbed HOMO for the C_{2h} structure increase on atoms 2, 4, 5, 7, 9, 10, 11, and 12, while those decrease on atoms 1, 3, 6, and 8 (Fig. 2). Accordingly, the value of the electron-nuclear attraction energy between a partial electronic charge, say on atom 11 and nuclear charges on the remaining atoms decreases, while that between a partial electronic charge, say on atom 1 and nuclear charges on the remaining atoms increases. On the whole, the perturbed HOMO is lowered in energy by the electrostatic interaction through the increased partial electronic charges on the atoms of cross-bond. An increase or decrease in the electronic charge on the atoms of cross-bond affects largely on the electron-nuclear attraction energy, since they possess the three nearest neighbour atoms. For pentalene, on the other hand, the mixing in of the LUMO into the HOMO results in an increase in

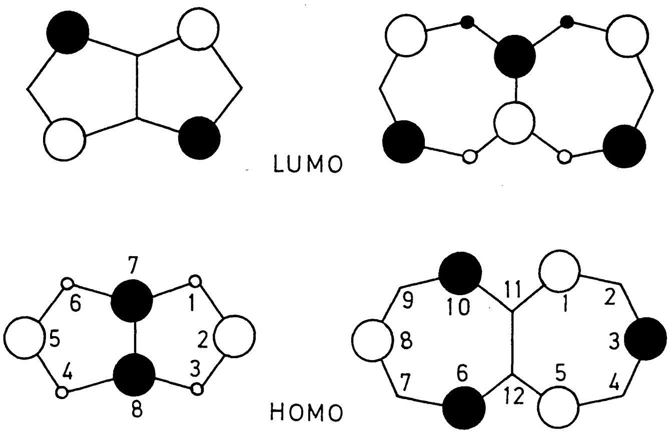


Fig. 2. The HOMO and LUMO in the D_{2h} structure of pentalene and heptalene. White and black circles indicate the plus and minus signs of atomic-orbital coefficients, respectively.

the partial electronic charge densities on atoms 1, 3, 4, and 6 and in a decrease in those on atoms 2, 5, 7, and 8. Hence the electron-nuclear attraction energy is raised in the C_{2h} structure compared with that in the D_{2h} one. On the contrary, the Coulomb repulsion energy of the perturbed HOMO decreases because the electron distribution is spread over the whole carbon skeleton. As a result, the perturbed HOMO of the C_{2h} structure is lower in energy than the HOMO in the D_{2h} one.

From the above results obtained by the PPP-type HF MO method, we can derive a simple rule which determines the dominant factor responsible for the energetic stability of the pseudo Jahn-Teller bond distortion. In the cata-condensed non-alternant molecules with an occupied non-bonding orbital within the simple HMO method, the factor is the electron-nuclear attraction energy. On the other hand, in such molecules with a vacant non-bonding orbital, the factor is the interelectronic repulsion energy. This rule is shown to hold for other non-alternant molecules, and the details will be discussed elsewhere. In this connection, further studies by means of an ab initio MO method are now under consideration.

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