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The Position Dependence of the SCF Screened Potential in Several Pseudo-Jahn-Teller Nonbenzenoid Aromatic Hydrocarbons

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Synopsis. The SCF screened potentials of pentalene, heptalene, and *s*-indacene were calculated by using the SCF screened potential MO CI method. The characteristics of the screened potential in the nuclear arrangement belonging to the lower molecular symmetry group, C_{2h}, are similar to those of the polyene.

Recently, Terasaka *et al.*[1] have shown that there are two kinds of screening (screening and anti-screening) in molecules such as polyene in which there exists a strong bond alternation, while there is only one kind of screening in molecules such as benzene and azulene which do not show a clear bond alternation.

The purpose of this paper is to investigate the position dependence of the SCF screened potential in pseudo-Jahn-Teller nonbenzenoid hydrocarbons, such as pentalene (I), heptalene (II), and *s*-indacene (III), by using the SCF screened potential MO CI method in combination with the variable bond-length technique.[1,2] It may be possible to use the results of such calculations to deepen our understanding of the aromatic characteristics of nonbenzenoid aromatic hydrocarbons.

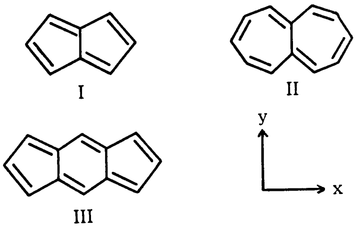

Fig. 1. Numbering of molecules and choice of axes.

Method of Calculation

A procedure that combines the SCF screened potential with the variable bond-length technique[1,2] is used in the Pariser-Parr-Pople SCF MO CI method.[3,4] At each step of the SCF calculation, the new bond lengths are obtained from the corresponding bond orders.[5] The screened potential is evaluated by using the bare potential (Mataga-Nishimoto[6]) obtained from the new bond lengths. This screened potential is thus used in the calculation of the next SCF step. The calculation is repeated until self-consistency is reached. As the starting geometrical structures for iterative calculation, we adopt various distorted structures in which bond lengths are distorted, so that the set of displacement vectors may form a basis for an irreducible representation of the full symmetry group, D_{2h}, of molecules I, II, and III. In the case of I, for example, there are 3, 2, 2, and 2 distinct bond distortions belonging to a_g, b_{1g}, b_{2u}, and b_{3u} respectively. If self-consistency is achieved at two or more different nuclear arrangements, the total energies should be compared with each other in order to determine which one is most favorable. The total energy is assumed to be the sum of the π-electron energy and the σ-electron energy, the latter being calculated by using the harmonic oscillator model, with the force constant equal to 714 kcal/Å.[7] All the singly-excited states are considered in the calculation of the RPA porlarization part.

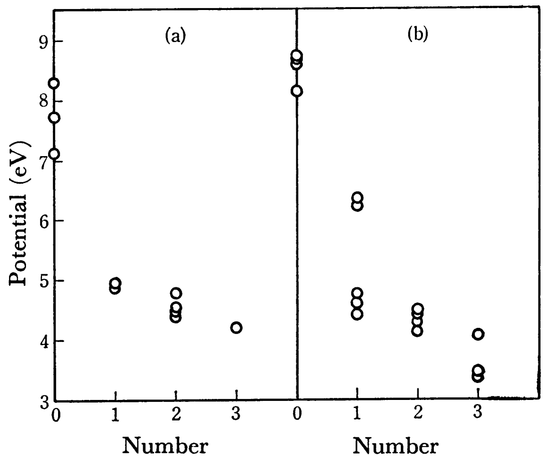

Fig. 2. The SCF screened potentials in pentalene plotted *vs.* the number; (a) the nuclear arrangement D_{2h}, (b) the nuclear arrangement C_{2h}.

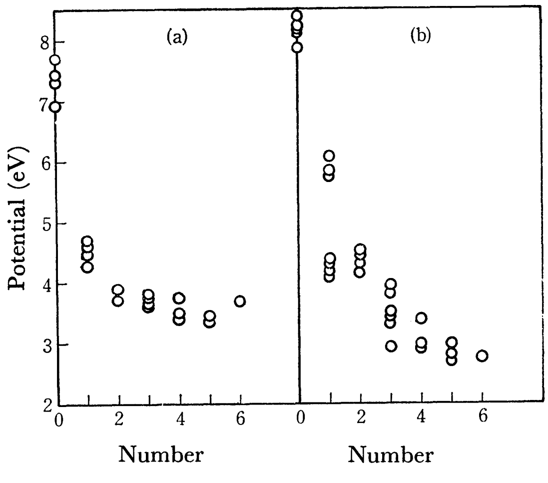

Fig. 3. The SCF screened potentials in heptalene plotted *vs.* the number; (a) the nuclear arrangement D_{2h}, (b) the nuclear arrangement C_{2h}.

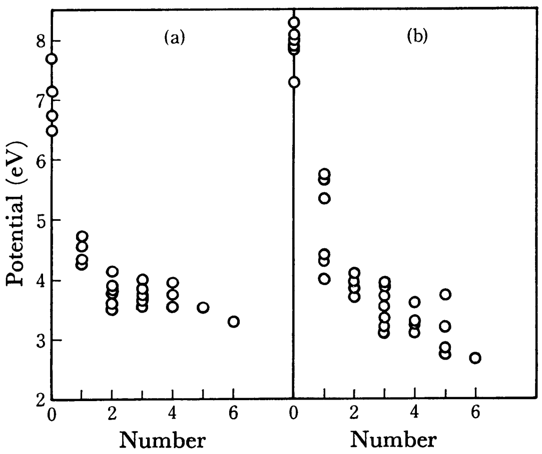

Fig. 4. The SCF screened potentials in *s*-indacene plotted *vs.* the number; (a) the nuclear arrangement D_{2h}, (b) the nuclear arrangement C_{2h}.

Results and Discussion

The starting bond distortions, belonging to the a_g, b_{2u}, and b_{3u} representations, all converge into the unique self-consistent set of bond lengths belonging to the molecular symmetry group D_{2h}, while the distortions belonging to b_{1g} converge into another set of bond lengths belonging to C_{2h}. The nuclear arrangement belonging to C_{2h} is energetically more favored than that belonging to D_{2h}. The stabilization energies for I, II, and III are predicted to be 8.2, 12.0, and 2.2 kcal/mol respectively. There exists a strong bond alternation in the peripheral carbon skeleton of the nuclear arrangement, C_{2h}. There is no bond alternation in the peripheral carbon skeleton of the nuclear arrangement, D_{2h}. The above results are almost the same as the results obtained by using the bare potential SCF CI method.[8]

In Figs, 2, 3, and 4, the SCF screened potentials, V, in the nuclear arrangements, D_{2h} and C_{2h}, of I, II, and III are plotted against a number that indicates the kind of screened potential, that is, 0: one-center potentials V_{11}, V_{22}, V_{33},⋯; 1: the nearest two-center potentials V_{12}, V_{23}, V_{34},⋯, *etc.* There is only one kind of screened potential at each of the numbers in the D_{2h} structures of I, II, and III (*cf.* Fig. 9 of Ref. 1). There is one kind of screened potential at the even numbers in the C_{2h} structures of these molecules. However, under the influence of the bond-length alternation, there are two kinds of screened potentials, screening and anti-screening, at the odd numbers in the C_{2h} structures of I, II, and III. Such characteristics of the screened potentials in the C_{2h} structures of I, II, and III show a tendency similar to those of the polyene shown in Fig. 7 of Ref. 1.

References

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