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Conference Paper

The Position Dependence of the SCF Screened Potential in Several Nonbenzenoid Hydrocarbons Containing a Four-Membered Ring*

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The bond lengths and SCF screened potentials of bicyclo[4.2.0]octa-1,3,5,7-tetraene (*1*), bicyclo[6.2.0]deca-1,3,5,7,9-pentane (*2*), cyclobuta[1,2:3,4]dicyclopentene (*3*), cyclopenta[3,4]cyclobuta[1,2]cycloheptene (*4*), benzo[3,4]cyclobuta[1,2]cyclooctene (*5*), cyclobuta[1,2,:3,4]dicycloheptene (*6*), and cyclobuta[1,2:3,4]dicyclooctene (*7*) were calculated by using the SCF screened potential MO CI method. From the bond lengths and the characteristics of the screened potentials, it is concluded that molecules *1, 2, 3, 4, 6,* and *7* are polyolefinic and molecule *5* has both aromatic and polyolefinic characters.

INTRODUCTION

Cyclobutadiene has recently become the center of reawakened interest[1-5] since Lin and Krantz[6] provided the first physical evidence for the structure (the object of an intensive search since Kekulé's abortive attempt 108 years ago[7]). Very recently, Masamune et al.[8] have concluded from the infrared spectra of cyclobutadiene and its derivatives that the cyclobutadiene ring in the ground state is not square but very likely rectangular.

The aromatic characteristics of nonbenzenoid aromatic hydrocarbons containing a four-membered ring such as bicyclo[4.2.0]octa-1,3,5,7-tetraene (*1*), bicyclo[6.2.0]deca-1,3,5,7,9-pentaene (*2*), cyclobuta[1,2:3,4]dicyclopentene (*3*), cyclopenta[3,4]cyclobuta[1,2]cycloheptene (*4*), benzo[3,4]cyclobuta[1,2]cyclooctene (*5*), cyclobuta[1,2:3,4]dicycloheptene (*6*), and cyclobuta[1,2:3,4]dicyclooctene (*7*) have long been of interest from both theoretical and synthetical points of view. Many attempts to synthesize these hydrocarbons (*1*—*7*) have been made hitherto.[9-12] Molecule *1* has detected as a reactive intermediate.[11] Molecules *2, 3, 4, 5, 6,* and *7* have not yet been synthesized. Based on Dewar's definition of aromaticity,[13] many theoretical investigations about the aromatic characteristics of *1, 3, 4,* and *6* have been carried out.[14-18]

Recently, Koyanagi and Yamaguchi[19] have pointed out that the position dependence of the SCF screened potential reflects sensitively the local behaviors of π-electrons and becomes a theoretical aromaticity criterion.

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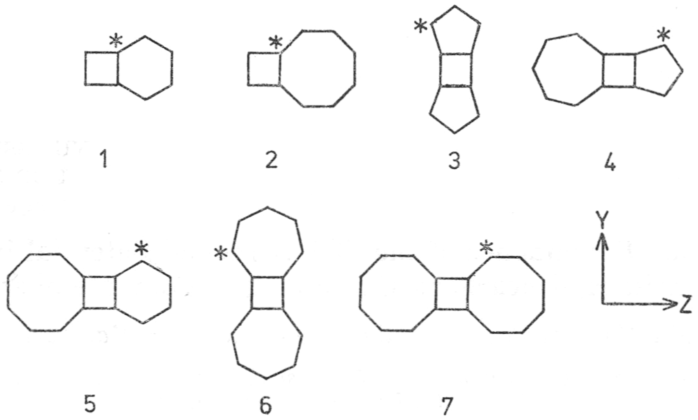

Figure 1. Numbering of atoms and choice of axes. Carbon atoms are numbered consecutively, starting with the starred atom and proceeding clockwise along the periphery.

The aim of this paper is to add, in view of these circumstances, to the understanding of the aromatic characteristics of these molecuels (*1*—*7*) through an attempt to calculate bond lengths and screened potentials using a SCF screened potential MO CI method.[20-23]

METHOD OF CALCULATION

A procedure that combines the SCF screened potential with the variable bond-length techniques is used in the Pariser-Parr-Pople SCF MO CI method.[24,25] At each step of the SCF calculation, the new bond lengths are obtained from the corresponding bond orders.[26] The screened potential is evaluated by using the bare potential obtained from the new bond lengths. The bare potential is calculated using the Mataga-Nishimoto formula.[27] This screened potential is 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. 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.[19]All the singly-excited states are considered in the calculation of the RPA polarization part.

RESULTS AND DISCUSSION

Molecular-symmetry Groups and Bond Distances. The symmetry groups and bond lengths corresponding to the most stable nuclear configurations for *1*, *2*, *3*, *4*, *5*, *6*, and *7* are shown in Table I.

In molecules *3*, *4*, *6*, and *7*, two different self-consistent nuclear arrangements, one belonging to the full symmetry group of a molecule and the other belonging to a reduced symmetry group, were obtained. In molecule *3*, for example, the starting bond distortions, belonging to A_g, B_{2g}, and B_{1u} represen-

TABLE I

Predicted Symmetry Groups and Bond Lengths

molecule (symmetry)	bond	bond length Å	molecule (symmetry)	bond	bond length Å
1 (C_{v2})	1—2	1.370		10—11	1.443
	1—6	1.433		11—12	1.393
	1—8	1.491			
	2—3	1.429	*5* (C_{2v})	1—2	1.393
	3—4	1.370		1—14	1.402
	7—8	1.342		2—3	1.400
				5—6	1.467
2 (C_{2v})	1—2	1.354		5—14	1.408
	1—8	1.487		6—7	1.353
	1—10	1.460		6—13	1.484
	2—3	1.464		7—8	1.468
	3—4	1.351		8—9	1.349
	4—5	1.465		9—10	1.469
	9—10	1.358			
			6 (C_{2v})	1—2	1.456
3 (C_{2v})	1—2	1.454		1—14	1.358
	1—10	1.358		2—3	1.355
	2—3	1.357		3—4	1.456
	3—4	1.454		4—5	1.356
	4—5	1.370		5—6	1.455
	4—10	1.476		6—7	1.374
	9—10	1.465		6—14	1.468
				13—14	1.471
4 (C_s)	1—2	1.363			
	1—12	1.444	*7* (C_{2v})	1—2	1.461
	2—3	1.445		1—16	1.357
	3—4	1.367		2—3	1.352
	4—5	1.471		3—4	1.463
	4—12	1.452		7—8	1.455
	5—6	1.368		7—16	1.486
	5—11	1.451		8—9	1.471
	6—7	1.442		8—15	1.374
	7—8	1.365		9—10	1.348
	8—9	1.442		10—11	1.472
	9—10	1.365		11—12	1.347

tations, all converge into the unique self-consistent set of bond lengths belonging to point group D_{2h}, and those belonging to B_{3u} converge into the set of bond lengths belonging to point group C_{2v}. The stabilization energies which favor the lower-symmetry nuclear arrangements for *3, 4, 6,* and *7* are predicted to be 0.62, 2.38, 5.27, and 1.83 kcal mol^{-1}, respectively. In these molecules, there are marked double-bond fixations in the periphery. It can be concluded that molecules *3, 4,* and *6* are derived from 5-(2,4-cyclopentadien-1-ylidene)-1,3-cyclopentadiene, 7-(2,4-cyclopentadiene-1-ylidene)-1,3,5-cycloheptatriene, and 7-(2,4,6-cycloheptatrien-1-ylidene)-1,35-cycloheptatriene respectively, by intramolecular union[28] between positions separated by three bonds.[16] The calculated bond lengths indicate that molecule *7* is made up of two 1,3,5,7-cyclooctatetraene molecules. The above results for *3, 4,* and *6* are almost the same as the results obtained by using the bare potential SCF MO CI method.[16,29,30]

On the other hand, in molecules *1, 2,* and *5,* self-consistency was achieved only for the fully-symmetrical nuclear arrangement belonging to point group C_{2v}. Molecules *1* and *2* show in a greater or lesser degree a double-bond fixation in the peripheral carbon skeleton. The calculated bond lengths indicate that molecules *1* and *2* are composed of a vinyl molecule and 1,3,5-cyclohexatriene and 1,3,5,7-cyclooctatetraene, respectively. In molecule *5,* it is predicted that the bond lengths of the six-membered ring are almost the same as those in the free benzene molecule and there are marked double-bond fixations in the other region of the periphery. It is considered that molecule *5* is made up of benzene and 1,3,5,7-cyclooctatetraene.

Position Dependence of SCF Screened Potential. The carbon atoms in 1,3,5-hexatriene are numbered as in Figure 2. Terasaka et al.[21] divided the SCF screened potentials V into the following groups: V_{11}, V_{12}, V_{13}, . . .; V_{22}, V_{23}, V_{24}, . . .; . . .. In Figure 2, the SCF screened potentials in each group are plotted against a number that indicates the kinds 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. Figure 2 shows that there are two kinds of numbers: that is, at an even number, one kind of screened potential exists, while at an odd number there exist two kinds of screened potentials.[21] The screened potentials of *1, 2, 3, 4, 5, 6,* and *7* are shown in Figure 3, 4, 5, 6, 7, 8, and 9, respectively. The position dependence of the SCF screened potential in the six-membered ring of *1* shows trends similar to those of the polyene.

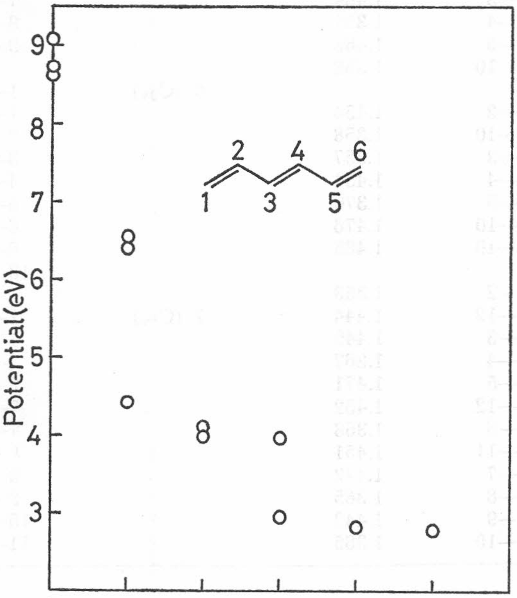

Figure 2. The SCF screened potentials in 1,3,5-hexatriene plotted against the number (for the meaning of the number, see the text).

Figures 4(a), 7(b), and 9(a) indicate that the characteristics of the screened potentials of the eigth-membered ring of *2, 5,* and *7* are almost the same as

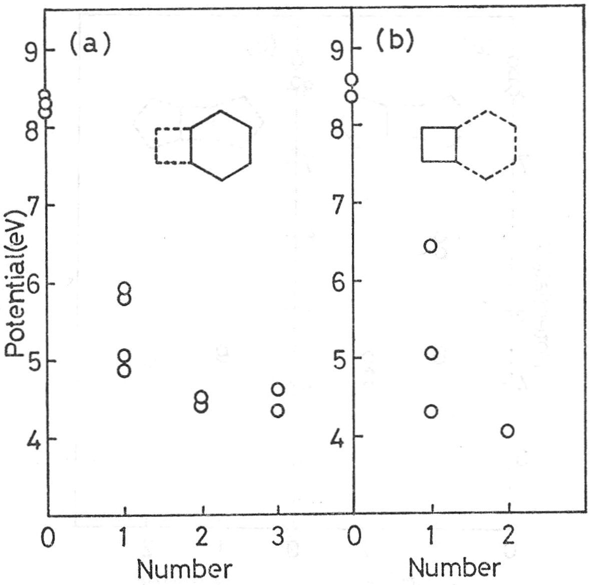

Figure 3. The SCF screened potentials in bicyclo[4.2.0]octa-1,3,5,7-tetraene plotted against the number (for the meaning of the number, see the text); (a) the 6-membered ring, (b) the 4-membered ring.

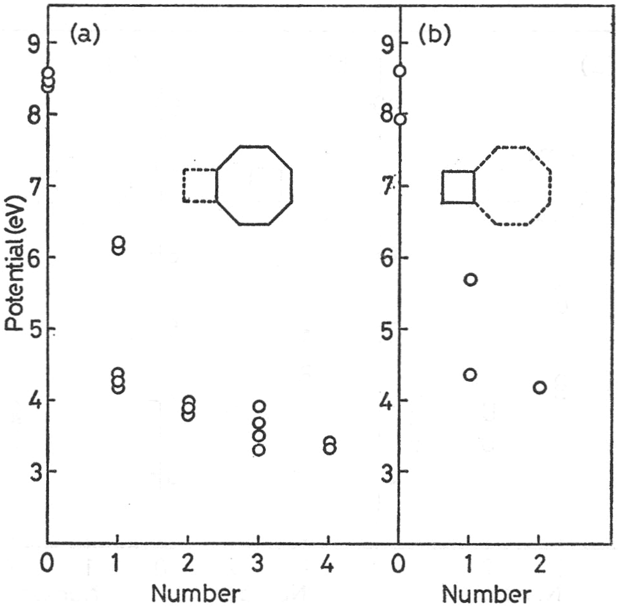

Figure 4. The SCF screened potentials in bicyclo[6.2.0]deca-1,3,5,7,9-pentaene plotted against the number (for the meaning of the number, see the text); (a) the 8-membered ring, (b) the 4-membered ring.

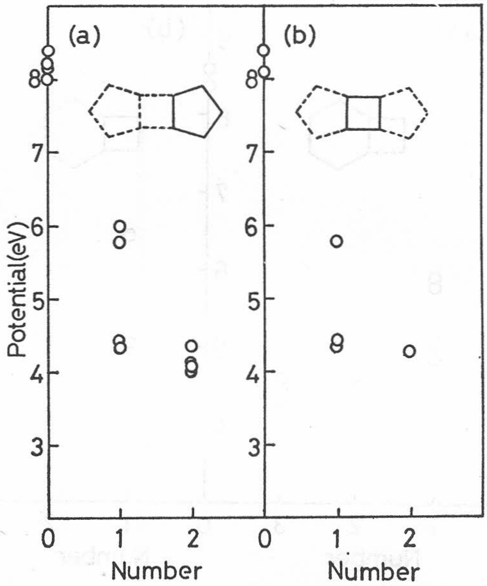

Figure 5. The SCF screened potentials in cyclobuta[1,2:3,4]-dicyclopentene plotted against the number (for the meaning of the number, see the text); (a) the 5-membered ring, (b) the 4-membered ring.

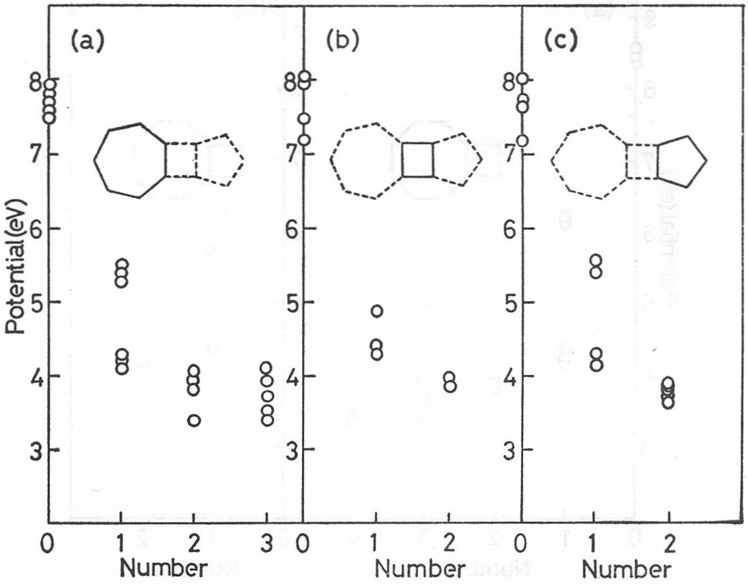

Figure 6. The SCF screened potentials in cyclopenta[3,4]-cyclobuta[1,2]cycloheptene plotted against the number (for the meaning of the number, see the text); (a) the 7-membered ring, (b) the 4-membered ring, (c) the 5-membered ring.

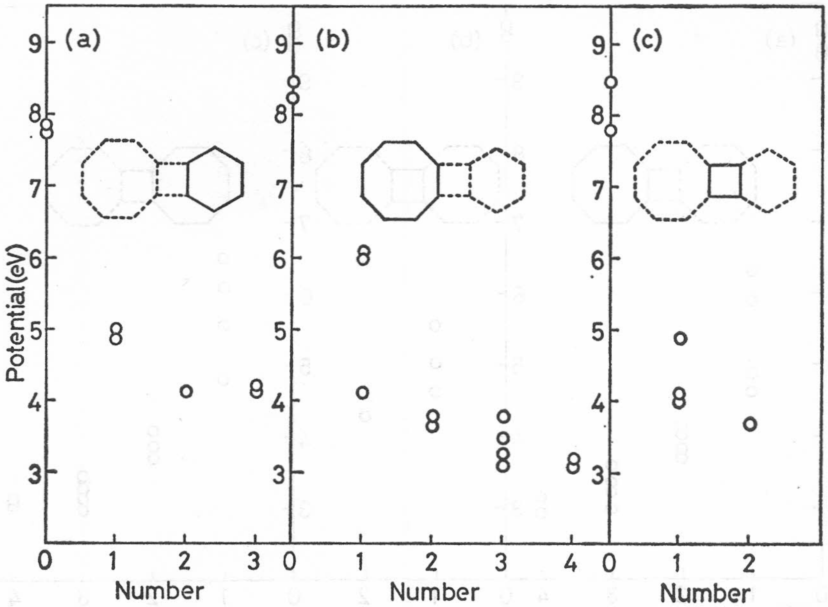

Figure 7. The SCF screened potentials in benzo[3,4]cyclobuta[1,2]cyclooctene plotted against the number (for the meaning of the number, see the text); (a) the 6-membered ring, (b) the 8-membered ring, (c) the 4-membered ring.

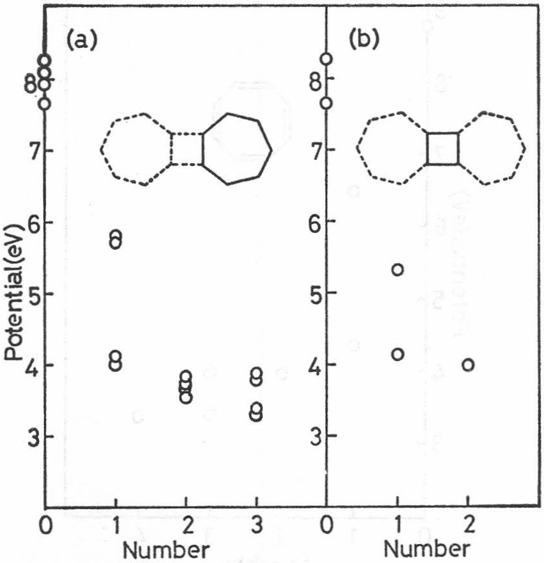

Figure 8. The SCF screened potentials in cyclobuta[1,2:3,4]-dicycloheptene plotted against the number (for the meaning of the number, see the text); (a) the 7-membered ring, (b) the 4-membered ring.

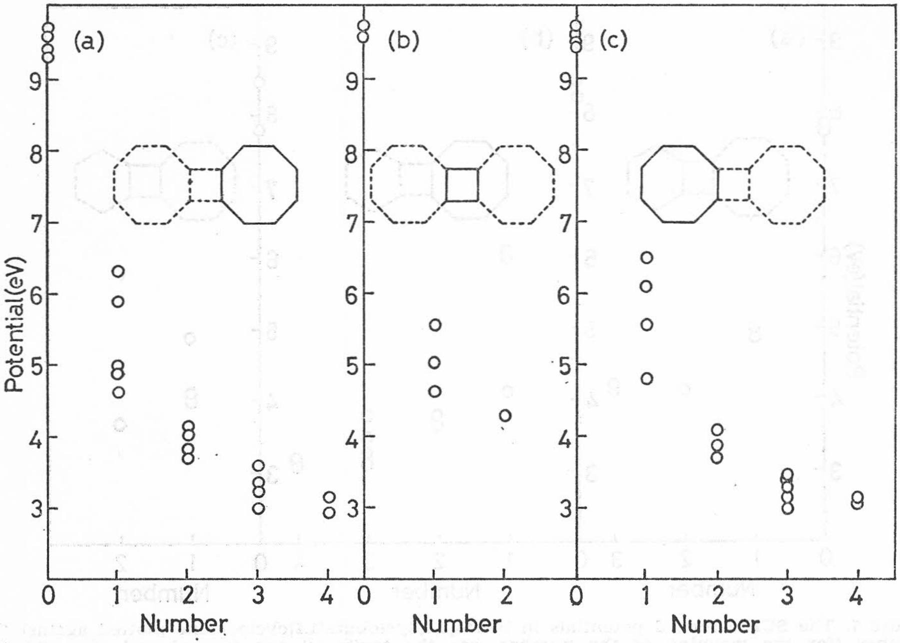

Figure 9. The SCF screened potentials in cyclobuta[1,2:3,4]-dicyclooctene plotted against the number (for the meaning of the number, see the text); (a) the 8-membered ring, (b) the 4-membered ring, (c) the 8-membered ring.

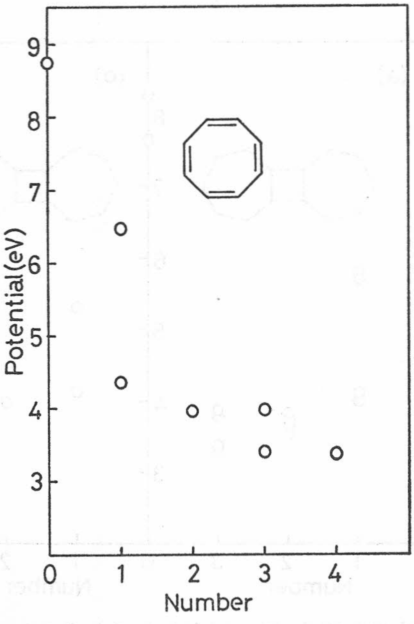

Figure 10. The SCF screened potentials in 1,3,5,7-cyclooctatetraene plotted against the number (for the meaning of the number, see the text).

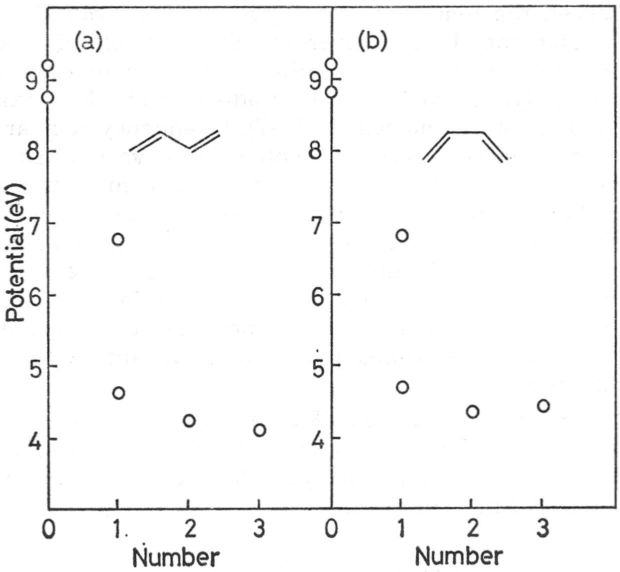

Figure 11. The SCF screened potentials in 1,3-butadiene plotted against the number (for the meaning of the number, see the text); (a) *trans*-1,3-butadiene, (b) *cis*-1,3-butadiene.

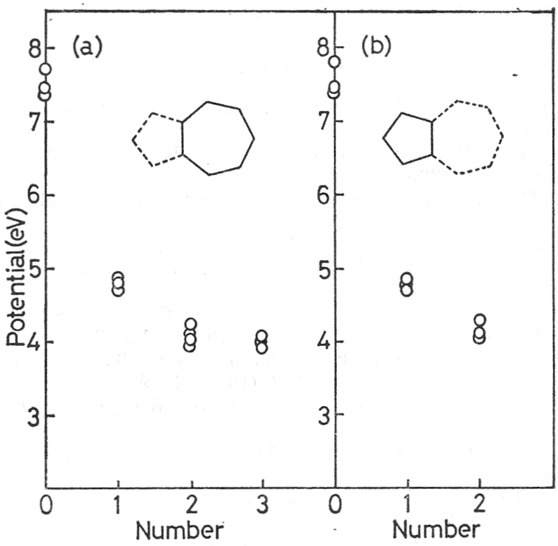

Figure 12. The SCF screened potentials in azulene plotted against the number (for the meaning of the number, see the text); (a) the 7-membered ring, (b) the 5-membered ring.

those of 1,3,5,7-cyclooctatetraene (see Figure 10). It is well known that the 1,3,5,7-cyclooctatetraene molecule exhibits a strong bond alternation, as revealed by its tub form.[31]

Figures 5(a) and 6(c) show that the position dependence of the screened potential in the five-membered rings of *3* and *4* has a tendency similar to that of 1,3-butadiene (see Figure 11). Figure 11 shows that there are no significant differences between the tendency of the potentials of *trans*-1,3-butadiene and that of *cis*-1,3-butadiene. In the seven-membered rings of *4* and *6*, at each of the numbers the characteristics of the screened potentials are almost the same as those of polyenes such as 1,3-butadiene and 1,3,5-hexatriene. In the four-membered rings of all molecules (*1*—*7*), a tendency similar to that in the polyenes appears. The SCF screened potential is very sensitive to a bond alternation. There are two kinds of screening (screening and anti-screening) at the odd numbers in molecules such as polyenes and cyclooctatetraene, in which there exists a strong double-bond fixation.[21] The screened potential in the six-membered ring of *5* shows a tendency similar to that of aromatic molecules such as azulene, in which there exist no double-bond fixations (see Figure 12).[21] In azulene, there is only one kind of screening at the odd numbers and the various screened potentials have almost the same value at each of the numbers.

From the characteristics of the SCF screened potentials, it can be concluded that the six-membered ring in *5* is aromatic and the remaining rings in *5* and molecules *1, 2, 3, 4, 6,* and *7* are polyolefinic. Molecule *5* may have both aromatic and polyolefinic characters.

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SAŽETAK

Ovisnost SCF zasjenjenog potencijala o položaju u nekoliko nebenzenoidnih ugljikovodika s četveročlanim prstenom

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Interes za elektronsku strukturu nebenzenoidnih ugljikovodika s četveročlanim prastenom pobuđen je pošto su Lin i Kranz dali fizikalne dokaze o strukturi ciklobutadiena.

Uporabom MO CI metode sa SCF zasjenjenim potencijalom istražena je ovisnost SCF zasjenjenog potencijala kod nekoliko nebenzenoidnih aromatskih ugljikovodika s četveročlanim prstenom.

Sve početne distorzije veza koje pripadaju A_g, B_{1g} i B_{3u} reprezentacijama konvergiraju u jedinstven samousklađeni skup duljina veza koje pripadaju molekulskoj grupi simetrije D_{2h} dok distorzije koje pripadaju B_{2u} reprezentaciji konvergiraju u drugi skup koji pripada grupi C_{2v}.

Za D_{2h}-strukture postoji samo jedna vrsta zasjenjenog potencijala dok za C_{2v}-strukture postoje dvije vrste potencijala, zasjenjeni i anti-zasjenjeni, tendencija slična onoj koju nalazimo u poliena.

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