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Molecular-symmetry Reduction in C_mH_{m-2} Cata-condensed Nonalternant Hydrocarbons

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On the basis of the second-order Jahn-Teller effect and the semiempirical SCF MO method, we examined the energetically most favorable molecular-symmetry groups and geometrical structures with respect to C–C bond lengths of the C_mH_{m-2} cata-condensed nonalternant hydrocarbons. In the $4n$ π-electron systems the first excitation energies in the fully-symmetrical nuclear arrangements were predicted to be significantly smaller than a certain critical value, and a molecular-symmetry reduction accompanied by a marked double-bond fixation in the peripheral carbon skeleton to occur. On the other hand, in the $4n+2$ π-electron systems, such energies were found to be considerably large for small members and to decrease rapidly with the number of carbon atoms, resulting in the molecular-symmetry reduction for members larger than a certain critical size. The electronic spectra were calculated using the most stable geometrical structures obtained by the SCF MO method.

For predicting the energetically most favorable molecular shapes with respect to C–C bond lengths of conjugated hydrocarbons, we developed a symmetry rule based on the second-order Jahn-Teller theorem.[1-5] The pseudo, or the second-order Jahn-Teller effect is the stabilization which occurs when a certain bond distortion mixes two electronic states nearly degenerate in the fully-symmetrical nuclear arrangement.[6] On the basis of this theory, we examined the second-order Jahn-Teller effects on bond lengths and stability of

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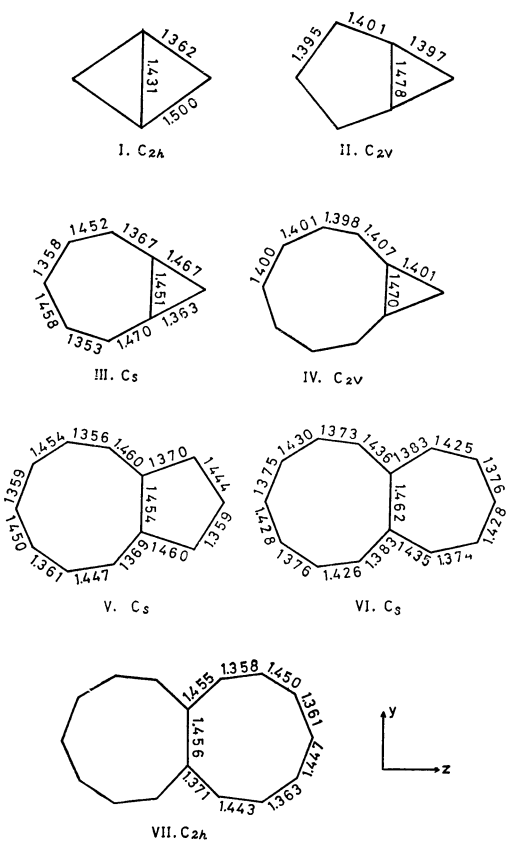

Fig. 1. Molecular-symmetry groups, bond lengths (Å) and choice of axes.

a number of nonalternant hydrocarbons.[1,7-9]

In this paper we apply the symmetry rule to the prediction of the stable geometrical structures of the cata-condensed nonalternant hydrocarbons, whose general formula is C_mH_{m-2} (Fig. 1). Of these systems, pentalene ($m=8$), azulene ($m=10$), and heptalene ($m=12$) have been investigated by several authors.[10-14] They found that the stable ground-state equilibrium configurations of pentalene and heptalene, both having $4n$ π-electrons, should belong to the reduced molecular-symmetry group C_{2h}, exhibiting a marked double-bond fixation in the peripheral carbon skeleton. On the other hand, it was predicted that in azulene belonging to the $4n+2$ π-electron system, no molecular-symmetry reduction occurs. The prediction is in good agreement with available experimental results. We were interested in why azulene does not reduce its molecular-symmetry group from C_{2v} to C_s. The purpose of this paper is to examine systematically the possibility of a relationship between the number of carbon atoms(m) and the molecular-symmetry reduction in the C_mH_{m-2} cata-condensed nonalternant hydrocarbons considered as formed by the introduction of a cross-link between the two carbon atoms of a like parity of the C_mH_m cyclic polyenes.

Theoretical

First we assume a fully-symmetrical nuclear arrangement as the unperturbed nuclear configuration for a conjugated molecule. We further assume that in the unperturbed nuclear configuration all the symmetrical bond distortions take place until the first-order energy equilibrium is reached. The unperturbed electronic wavefunctions $\psi_0, \psi_1, \cdots, \psi_n, \cdots$ and the corresponding eigenvalues $E_0, E_1, \cdots, E_n, \cdots$ are assumed to be known. We now distort the nuclei from the symmetrical first-order nuclear arrangement by means of the ith normal coordinate of nuclear motion Q_i. On the basis of the same approximation as used previously,[1] the energy of the ground state after deformation may be written as

$$E(Q_i) = E_0 + \frac{1}{2}\left\{k - 2\sum_n{}' \frac{|\langle\psi_n|(\partial H_\pi/\partial Q_i)_0|\psi_0\rangle|^2}{(E_n - E_0)}\right\}Q_i^2$$

where k and H_π represent the force constant for an sp^2 hybridized C–C σ-bond and the Hamiltonian for π-electrons, respectively.

According to the above equation, the force constant for the normal vibration Q_i can be identified with the term in the braces and can be negative if a given matrix element $\langle\psi_n|(\partial H_\pi/\partial Q_i)_0|\psi_0\rangle$ is nonvanishing and the associated energy gap $E_n - E_0$ is sufficiently small. If the force constant is negative, the energy should be lowered by the nuclear deformation Q_i, and a pseudo-Jahn-Teller distortion from the symmetrical nuclear arrangement would occur spontaneously.

The symmetry rules[1] for predicting the stable molecular shapes in the ground state are as follows: the symmetry of the normal displacement with the smallest force constant is identical with that of the lowest excited state, ψ_1. If the energy gap $E_1 - E_0$ is smaller than the critical value, *ca.* 1.2 eV, the molecule would be distorted into a less symmetrical nuclear configuration. The most favorable type of bond distortion is predicted by examining the distribution of the transition density ρ_{01} over the molecular skeleton. When the lowest excited state is represented by a one-electron transition between molecular orbitals ϕ_i and ϕ_j, the transition density ρ_{01} between the ground and the lowest exicted states is given by $\sqrt{2}\,\phi_i\phi_j$.[6]

Since it is based on the second-order perturbation theory, the symmetry rule gives only the type of the most favorable bond distortion. In order to obtain information on the actual magnitude of distortion or the equilibrium bond lengths at which the nuclei of the real molecule will settle, we use the variable bond-length SCF MO method.[15]

Results and Discussion

The Ground-state Symmetries and Geometries. The symmetries and energies (measured from the ground state) of the lowest excited states for the fully-symmetri-

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Table 1. Symmetries and energies of first and second excited singlet states of cata-condensed nonalternant hydrocarbons

Molecule (Point group)	First excited state E_1-E_0 (eV)	First excited state Sym-metry	Second excited state E_2-E_1 (eV)	Second excited state Sym-metry
I (D_{2h})	0.48	B_{3g}	4.97	B_{1u}
II (C_{2v})	3.57	B_2	2.32	A_1
III (C_{2v})	0.32	B_2	3.45	A_1
IV (C_{2v})	2.36	B_2	1.41	A_1
V (C_{2v})	0.26	B_2	2.47	A_1
VI (C_{2v})	1.44	B_2	1.08	A_1
VII (D_{2h})	0.20	B_{3g}	1.95	B_{1u}
Pentalene (D_{2h})	0.35	B_{2g}	3.25	B_{1u}
Azulene (C_{2v})	2.05	B_2	1.48	A_1
Heptalene (D_{2h})	0.26	B_{3g}	2.41	B_{1u}

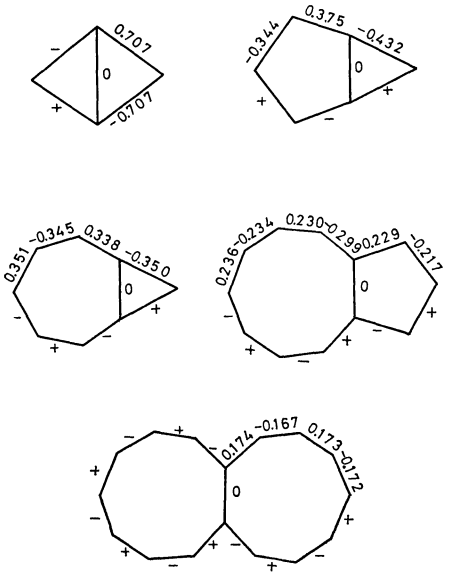

Fig. 2. Distributions of two-center components of transition densities (ρ_{01}).

cal nuclear arrangements of the cata-condensed nonalternant hydrocarbons are listed in Table 1. The two-center components of the transition densities for the some selected molecules are shown in Fig. 2. The correlation of the first excitation energies for the fully-symmetrical nuclear arrangement with the number of carbon atoms of the C_mH_{m-2} systems is shown in Fig. 3, in which the excitation energies for pentalene, azulene, and heptalene, which are the isomers of the molecules III, IV, and V, respectively, are also included. The dashed line represents the critical value for the molecular-symmetry reduction. In the hatched area the molecule should distort into a less symmetrical nuclear configuration.

From Table 1 and Fig. 3, it is seen that in molecules with $4n$ π-electrons the energy gaps E_1-E_0 are all considerably smaller than the critical value, *ca.* 1.2 eV. In the $4n+2$ π-electron systems, the energy gaps decrease with the number of carbon atoms rapidly as compared with the case of the $4n$ π-electron

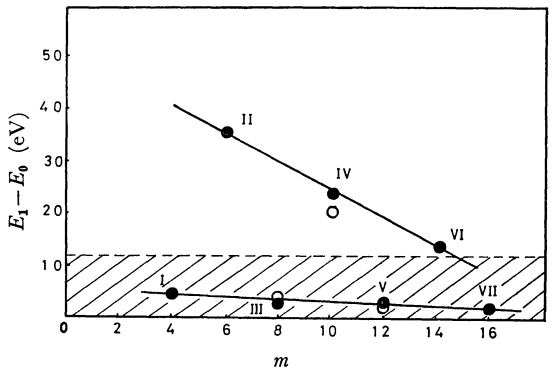

Fig. 3. Correlation of E_1-E_0 with the number of carbon atoms of C_mH_{m-2}. Open circles mean values for pentalene ($m=8$), azulene ($m=10$) and heptalene ($m=12$).

systems. The origin of the smallness of the energy gaps E_1-E_0 in these $4n$ π-electron systems (that is, the near degeneracy of the ground state with the lowest excited state) may be explained as follows. In the C_mH_m cyclic polyenes with $4n$ π-electrons, the ground-state is degenerate with the lowest excited states in the Hückel MO approximation, since the highest occupied molecular orbitals are doubly degenerate and there are four ways of assigning two electrons to the degenerate orbitals. The cata-condensed nonalternant hydrocarbons are considered to be formed by the introduction of a cross-link between the two carbon atoms of a like parity of the C_mH_m cyclic polyenes. The highest occupied molecular orbitals which are doubly degenerate in the unperturbed cyclic polyenes are split only a slight degree by the introduction of such a cross-link. The energy separation between these split orbitals is small and the lowest excited state for the perturbed system is represented by a one-electron transition between these molecular orbitals, so that the energy gap between the lowest excited and the ground states, E_1-E_0, is very small.

On the basis of the symmetry rule, we can predict that molecules I and VII should reduce their ground-state molecular-symmetry groups to C_{2h} from D_{2h} by the interaction with the lowest excited state through the b_{3g} nuclear displacement. Molecules III and V may also lower their ground-state molecular-symmetry groups from C_{2v} to C_s by the interaction with the lowest excited state through the b_2 nuclear displacement. The shapes of the stable molecular structures are predicted from the distribution of transition densities ρ_{01}.

On the other hand, in II and IV, molecules with $4n+2$ π-electrons, the energy gaps are definitely large as compared with the critical value for the molecular-symmetry reduction in the ground state. In molecule VI, the energy gap is comparable with the critical value for the molecular-symmetry reduction.

In order to obtain the equilibrium C–C bond lengths we performed the variable bond-length SCF MO calculation, taking into account all the possible distorted structures as the starting geometry.[16] The molecular-symmetry groups and bond lengths corresponding to the most stable nuclear arrangements for the cata-

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condensed nonalternant hydrocarbons are shown in Fig. 1.

From the result of SCF MO calculation it turns out that, as predicted from the symmetry rule, molecules I, III, V, and VII reduce their ground-state molecular-symmetry groups to C_{2h}, C_s, C_s, and C_{2h}, respectively.

In II and IV, the molecular-symmetry reduction does not occur. However, VI reduces its molecular-symmetry group to C_s from C_{2v}. It should be noted that the molecular-symmetry reduction in the $4n+2$ π-electron systems will be realized if the molecule becomes larger than a certain critical size ($n\sim3$).

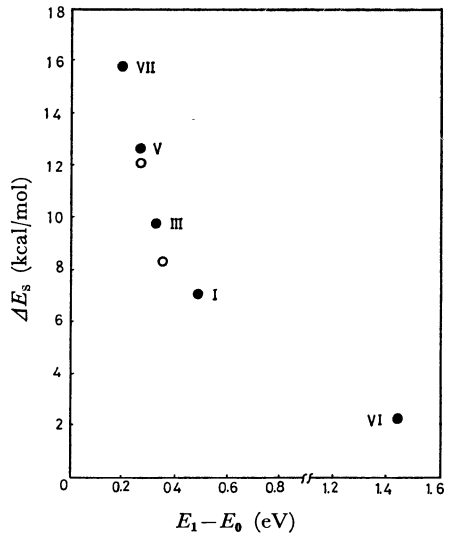

Fig. 4. Correlation of ΔE_s with E_1-E_0. Open circles mean values for pentalene (0.35 eV) and heptalene (0.26 eV).

In Fig. 4 is shown the correlation of the stabilization energies for the molecular-symmetry reduction with the excitation energies E_1-E_0, as calculated by assuming the fully-symmetrical nuclear arrangements. We define the stabilization energy as the difference in total energy between the fully-symmetrical and the reduced molecular geometries. The total energy is assumed to be the sum of π-bond and σ-bond energies, the latter being calculated using the harmonic oscillator model with the force constant equal to 714 kcal mol^{-1} Å^{-2}.[17] We see that there is a good correlation between the stabilization energy ΔE_s and E_1-E_0; the smaller the latter, the larger the former. The stabilization energies for pentalene and heptalene are also included (open circles).

From the viewpoint of the largeness of stabilization energy, we may say that the second-order Jahn-Teller effect becomes strong with the number of carbon atoms in the $4n$ π-electron systems.

As for the C–C bond-length distribution in the stable nuclear arrangements (Fig. 1), it may be said that the double-bond fixation, *i.e.*, bond-length alternation, is the common phenomenon in the reduced molecular geometries, as is expected from the distribution of transition densities ρ_{01}.

Excited-state Molecular-symmetry Groups. It is of interest to note the molecular shape of the lowest excited state. The criterion for the molecular-symmetry reduction in the excited state is that the energy gap E_2-E_1 is less than the critical value, *ca.* 0.6 eV.[1] From this criterion and Table 1 we may predict that all the molecules examined do not reduce their molecular-symmetry groups in the first singlet excited states. That is, the stable molecular shapes in the excited states belong to their fully-symmetrical nuclear arrangements.

Electronic Spectra. In calculating electronic spectra, we used the bond lengths for the energetically stable nuclear arrangements. The method of calculation employed is the Pariser-Parr-Pople MO method, and the configuration mixing of all the singly excited states is included (Table 2).

Table 2. Transition energies and intensities

Molecule (Point group)	Transition symmetry	ΔE (eV)	f (c.g.s)
I (C_{2h})	^1A_g	2.26	Forb.
	^1B_u	5.57	0.632
	^1B_u	10.14	0.912
II (C_{2v})	$^1B_2$	3.57	0.046
	$^1A_1$	5.89	0.137
	$^1B_2$	6.82	0.008
	$^1A_1$	6.85	1.160
III (C_s)	$^1A'$	1.65	0.004
	$^1A'$	4.06	0.327
	$^1A'$	5.07	0.054
	$^1A'$	5.75	0.272
IV (C_{2v})	$^1B_2$	2.36	0.072
	$^1A_1$	3.77	0.032
	$^1B_2$	4.44	0.068
	$^1A_1$	4.96	2.014
V (C_s)	$^1A'$	1.61	0.001
	$^1A'$	3.12	0.273
	$^1A'$	4.01	0.117
	$^1A'$	4.76	0.690
VI (C_s)	$^1A'$	1.81	0.046
	$^1A'$	2.69	0.000
	$^1A'$	3.46	0.313
	$^1A'$	3.93	1.930
VII (C_{2h})	^1A_g	1.67	Forb.
	^1B_u	2.67	0.361
	^1B_u	3.41	0.234
	^1A_g	4.37	Forb.

It should be noted that the excitation energies, particularly the lowest ones, calculated assuming the reduced molecular-symmetry groups for molecules I, III, V, VI, and VII, are predicted to be considerably higher than those calculated using the fully-symmetrical nuclear configurations (compare Table 1 with Table 2).

However, so far there is no experimental data for a comparision with theoretical values, except for pentalene (1-methyl-pentalene), azulene, and heptalene.[18–20]

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Conclusion

The problem of molecular-symmetry reductions in the cata-condensed nonalternant hydrocarbons C_mH_{m-2} has been systematically examined on the basis of the second-order Jahn-Teller theorem. It was assumed that only the lowest excited state plays a dominant role in determining the most favorable nuclear displacement which reduces the molecular-symmetry group to a less symmetrical nuclear configuration. In spite of this very crude approximation, the predicted types of the energetically most favorable bond distortions, determined by examining the two-center components of transition densities, are in good agreement with the results of variable bond-length SCF MO calculations. The success of this approximation for predicting the stable molecular shapes might be ascribed to the fact that in the fully-symmetrical nuclear arrangements of the $4n$ π-electron systems the ground state is nearly degenerate with the lowest excited state, and that the second excited state is well separated from the lowest excited state.

Finally we may say that the pseudo, or the second-order Jahn-Teller effect becomes strong with increasing the number of carbon atoms in the C_mH_{m-2} cata-condensed nonalternant hydrocarbons.

The numerical calculation was carried out at Tohoku University with a NEAC 2000—500 electronic computer.