On the Stable Molecular-shapes of C_mH_{m-4} Cata-condensed Nonalternant Hydrocarbons

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The energetically most favorable molecular-symmetry groups and geometrical structures of C_mH_{m-4} cata-condensed nonalternant hydrocarbons were examined systematically on the basis of the symmetry rule and the semiempirical SCF MO method. The first excitation energies in the fully-symmetrical nuclear arrangements were found to decrease with increasing the number of carbon atoms, showing a tendency to converge to a certain limiting value, *ca.* 0.8 eV. Molecules larger than a certain critical size ($m\sim10$) were predicted to suffer the second-order Jahn-Teller distortion, exhibiting a double-bond fixation in the peripheral carbon skeleton. Using the most stable geometrical structures obtained, the electronic spectra of these molecules were calculated. Furthermore, the predictions of the stable molecular-shapes in the lowest excited singlet states were briefly mentioned.

Recently, we have developed the symmetry rule[1-3] for predicting the stable molecular shapes of conjugated hydrocarbons.[4,5] This rule is based on the pseudo, or the second-order Jahn-Teller effect,[6,7] which is due to the stabilization, occuring when a certain bond distortion mixes two electronic states nearly degenerate in the fully-symmetrical nuclear arrangement. On the basis of this rule, we examined systematically, in a previous paper,[8] the problem of the molecular-symmetry reduction in C_mH_{m-2} cata-condensed nonalternant hydrocarbons. As a result, we found that there is a good correlation between the molecular-symmetry reduction and the number of carbon atoms(m): 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 the 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 molecular size($m=14$).

The purpose of this paper is to examine further the possibility of a relationship between the number of carbon atoms and the molecular-symmetry reduction in C_mH_{m-4} cata-condensed nonalternant hydrocarbons considered as formed by the introduction of two cross-links between the carbon atoms of like parity of C_mH_m cyclic polyenes. Moreover, we investigate the second-order Jahn-Teller effects on the bond-length distributions and the excitation energies of these nonalternant hydrocarbons.

Theoretical

The method employed for predicting the energetically most favorable molecular-symmetry groups of conjugated hydrocarbons is the symmetry rule based on the second-order Jahn-Teller theorem.[7] We outline this rule briefly. Let us start by assuming for a conjugated molecule a fully-symmetrical nuclear arrangement as the unperturbed configuration. We assume that in the unperturbed nuclear configuration all the symmetrical bond distortions have taken place until the first-order energy equilibrium is reached. The unperturbed electronic wave functions ψ_0, ψ_1,$\cdots$, ψ_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 associated with the normal vibration Q_i should be regarded as $\{k-2\sum_n{}'|\langle\psi_n|(\partial H_\pi/\partial Q_i)_0|\psi_0\rangle|^2/(E_n-E_0)\}$ 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, *i.e.*, the curvature of $E(Q_i)$ with respect to Q_i, 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.

In order to estimate the value of the force constant, we have to take into account the infinite sum over the excited states in the above equation. However, to derive the symmetry rule we made the following drastic approximation: from the viewpoint of energy gap law, the infinite sum over the excited states is replaced by one term corresponding to the lowest excited state. In spite of the very crude approximation, Pearson and we have shown that this is justified in a variety of small molecules, complex ions and conjugated hydrocarbons.[1-5]

The symmetry rules[1] for predicting the stable molecular shapes in the closed-shell ground states are as follows: the symmetry of the nuclear 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 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 excited state is given by $\sqrt{2}\,\phi_i\phi_j$.[6]

Eigenvalues and wavefunctions for the fully-symmetrical nuclear arrangements are calculated using the self-consistent configuration interaction formalism of the Pariser-Parr-Pople method.[9-11]

Results and Discussion

Ground-state Molecular-symmetry Groups and Geometries. The symmetries and the energies of the lowest excited singlet states of C_mH_{m-4} cata-condensed nonalternant hydrocarbons (Fig. 1) obtained by assuming the fully-symmetrical nuclear arrangements are listed in Table 1. The first excitation energies for the fully-symmetrical nuclear arrangement of C_mH_{m-4} systems are shown in Fig. 2, in which those of C_mH_{m-2} systems are also shown by the open circles. It is seen that the dependence of the energy gap on the number of carbon atoms is remarkably different between C_mH_{m-2} systems. That is, in the former systems there is no such a sharp distinction of the energy gap dependence between $4n$ and $4n+2$ π-electron systems as that observed in the latter systems: the energy gaps are intermediate of those for the $4n$ and $4n+2$ π-electron systems of C_mH_{m-2}, decreasing as the number of car-

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

Molecule[a] (Point group)[b]	First excited state		Second excited state	
	E_1-E_0 (eV)	Symmetry	E_2-E_1 (eV)	Symmetry
I(D_{2h})	2.41	B_{2u}	2.39	B_{3g}
II(D_{2h})	1.32	B_{3g}	2.29	B_{1u}
III(C_{2v})	1.57	B_2	2.11	A_1
IV(D_{2h})	1.22	B_{2u}	2.15	B_{1u}
V(C_{2v})	1.42	B_2	2.19	A_1
VI(D_{2h})	1.75	B_{2u}	1.78	B_{1u}
VII(C_{2v})	1.30	B_2	2.20	A_1
VIII(D_{2h})	1.00	B_{3g}	1.54	B_{1u}
IX(C_{2v})	1.07	B_2	1.51	A_1
X(C_{2v})	1.00	B_2	1.62	A_1
XI(C_{2v})	1.04	B_2	1.71	A_1
XII(C_{2v})	1.15	B_2	1.64	A_1
XIII(D_{2h})	0.81	B_{2u}	1.75	B_{1u}
XIV(D_{2h})	0.98	B_{2u}	1.51	B_{3g}
XV(C_{2v})	0.81	B_2	1.62	A_1
XVI(D_{2h})	0.82	B_2	1.75	A_1
XVII(C_{2v})	1.00	B_2	1.52	A_1
XVIII(C_{2v})	0.98	B_2	1.63	A_1
XIX(D_{2h})	0.83	B_{3g}	1.20	B_{1u}
XX(C_{2v})	0.84	B_2	1.25	A_1
XXI(C_{2v})	0.81	B_2	1.20	A_1
XXII(C_{2v})	0.83	B_2	1.23	A_1
XXIII(C_{2v})	0.85	B_2	1.34	A_1

a) See Fig. 1. b) The apparent fully-symmetrical point group.

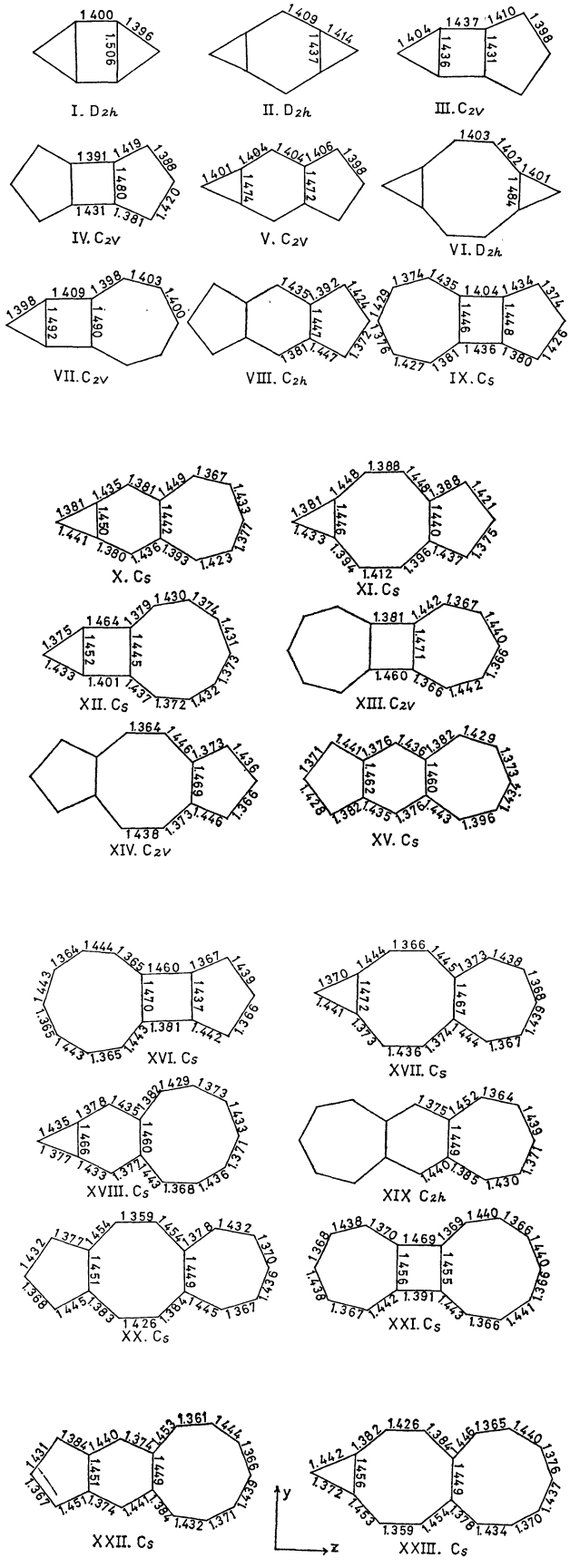

Fig. 1. Predicted stable molecular-symmetry groups and equilibrium bond lengths (in Å unit) and choice of axes.

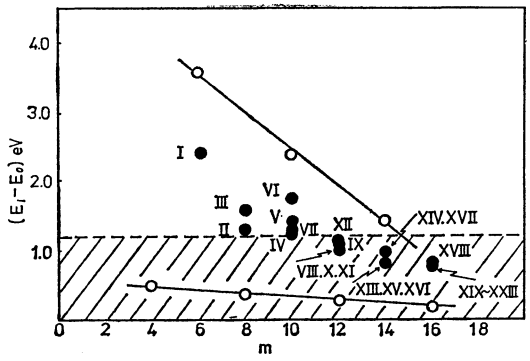

Fig. 2. Dependence of the first excitation energies for the fully-symmetrical nuclear configurations on the number of carbon atoms (m) in C_mH_{m-4} systems. Open circles mean values in C_mH_{m-2} systems.

bon atoms increases, and showing a tendency to converge to a certain limiting value, *ca.* 0.8 eV. This may be explained qualitatively by considering the orbital energy changes due to the introduction of cross-link into the unperturbed cyclic polyene. In the Hückel MO description, the energy change of the ith molecular orbital may be evaluated using the first-order perturbation theory:

$$\delta\varepsilon_i = \sum_{\mu\nu} 2C_{\mu i}C_{\nu i}\beta$$

where C_μ and C_ν are atomic-orbital coefficients for atoms μ and ν between which a cross-link is introduced. As an illustration, we show in Fig. 3 the correlation of the Hückel molecular orbitals of benzene(C_6H_6) with those of C_6H_4 and C_6H_2 (I) and in Fig. 4 that of molecular orbitals of cyclic polyene(C_8H_8) with those of C_8H_6 and C_8H_4(III). That energy gaps E_1–E_0 for C_mH_{m-4} are smaller than those for C_mH_{m-2} systems with $4n+2$ π-electrons is due to the fact that the separation between the highest occupied and the lowest vacant molecular orbitals becomes smaller by increasing the number of the cross-link between the like parity of carbon atoms of cyclic polyene. On the other hand, energy gaps for C_mH_{m-4} larger than those for C_mH_{m-2} systems with $4n$ π-electrons is ascribable to the fact that the separation between the highest occupied and the lowest vacant orbitals becomes larger by increasing the number of the cross-link, in contrast to the case of the above mentioned $4n+2$ π-electron systems.

The problem of the molecular-symmetry reduction can now be discussed on the basis of the symmetry rules and Table 1. The dashed line in Fig. 2 represents the critical value for the molecular-symmetry reduction, and in the hatched area the molecule should distort into a less symmetrical nuclear configuration.

As to the smallest member of C_mH_{m-4} systems, *i.e.*, I(m=6), the lowest excited state is of B_{2u} symmetry and the energy gap is considerably larger than the critical value. We may predict that this molecule undergoes no molecular-symmetry resuction to C_{2v} from D_{2h}. It is, however, of interest to note that the type of the nuclear displacement with the smallest force constant is that of bond-length alternation in the peripheral carbon skeleton. A similar situation

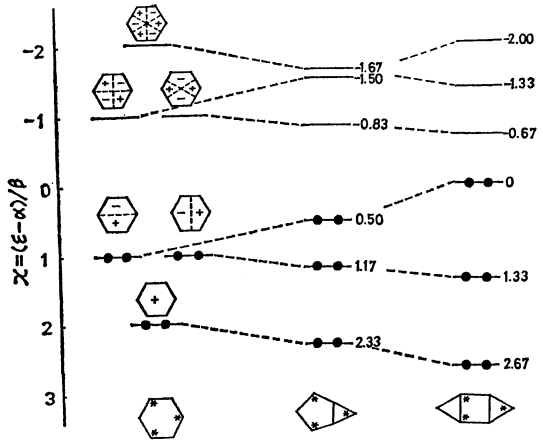

Fig. 3. Correlation of molecular orbitals of benzene (C_6H_6) with those of C_6H_4 and C_6H_2(I).

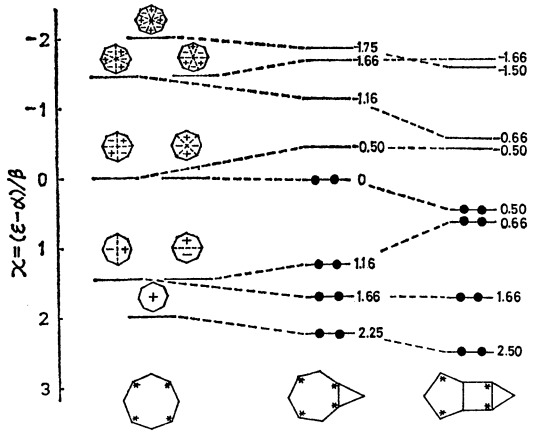

Fig. 4. Correlation of molecular orbitals of cyclic polyene (C_8H_8) with those of C_8H_6 and C_8H_4(III).

is also seen in the unperturbed cyclic polyene, benzene.

As for molecules (m=8), II and III, the energy gaps are relatively larger than the critical value and the symmetries of the lowest excited states are B_{3g} and B_2, respectively. From the view-point of energy gap law, there is no possibility for the molecular-symmetry reduction to occur in both molecules.

In case of m=10 (IV—VII), the energy gaps are predicted to be slightly large as compared with the critical value, and all these molecules, except bowtine (IV), do not suffer the second-order Jahn-Teller distortion.

Of the molecules with 12 carbon atoms, only *s*-indacene (VIII) has been synthesized by Hafner's group.[12] It is of interest to note that in these valence isomers the energy gaps are nearly the same, *i.e.*, about 1.0 eV, which are smaller than the critical value. Thus, these molecules may undergo the second-order bond distortions, reducing their ground-state molecular-symmetry groups to C_{2h}(VIII) and C_s (IX—XII) from D_{2h} and C_{2v}, respectively.

In case of m=14 (XIII—XVIII), the energy gaps are smaller than the critical value, so that these molecules are predicted to lower their ground-state molecular-symmetry groups to C_{2v}(XIII and XIV) and C_s (XV—XVIII) from D_{2h} and C_{2v}, respectively, by

Table 2. Singlet transition energies and intensities

Molecule (Point group)	Transition symmetry[a]	ΔE (eV)	f (c. g. s)	Molecule (Point group)	Transition symmetry[a]	ΔE (eV)	f (c. g. s)
IV(C_{2v})	A_1	1.32	0.01		A′	2.68	0.02
	B_2	3.36	0.01		A′	3.45	0.48
	B_2	3.59	0.18	XVI(C_s)	A′	1.53	0.01
VIII(C_{2h})	A_g	1.39(1.77)[b]	Forb. (log ε=2.59, tailing)[b]		A′	2.83	0.17
					A′	3.15	0.08
	B_u	2.62(2.42)	0.59(4.63)	XVII(C_s)	A′	1.52	0.03
	B_u	3.78(3.61)	0.21(4.81)		A′	2.74	0.01
IX(C_s)	A′	1.48	0.02		A′	3.13	0.02
	A′	2.77	0.01	XVIII(C_s)	A′	1.44	0.09
	A′	3.34	0.16		A′	2.82	0.15
X(C_s)	A′	1.41	0.01		A′	3.56	0.42
	A′	2.70	0.64	XIX(C_{2h})	A_g	1.49	Forb.
	A′	3.98	0.13		B_u	2.20	0.66
XI(C_s)	A′	1.39	0.01		B_u	3.20	0.30
	A′	2.90	0.10	XX(C_s)	A′	1.54	0.03
	A′	3.52	0.28		A′	2.48	0.04
XII(C_s)	A′	1.58	0.03		A′	2.88	0.50
	A′	2.93	0.10	XXI(C_s)	A′	1.68	0.06
	A′	3.82	0.43		A′	2.49	0.00
XIII(C_{2v})	A_1	1.50	0.01		A′	3.02	0.46
	B_2	2.79	0.14	XXII(C_s)	A′	1.53	0.00
	B_2	3.01	0.13		A′	2.24	0.61
XIV(C_{2v})	A_1	1.54	0.02		A′	3.33	0.26
	B_2	2.72	0.00	XXIII(C_s)	A′	1.56	0.03
	B_2	2.91	0.04		A′	2.51	0.23
XV(C_s)	A′	1.34	0.08		A′	3.20	0.50

a) For molecules which belong to the point group C_{2h}, the z axis is taken to be perpendicular to the molecular plane. b) The spectrum of a hexacarbometoxydihydroxy derivative; E. LeGoff and R. B. LaCount: *Tetrahedron Lett.*, **1964**, 1161.

the interaction of the ground-state with the lowest excited state through the unsymmetrical C–C stretching vibration.

Finally, in case of m=16 (XIX—XXIII) all the valence isomers have almost the same energy gaps, *i.e.*, about 0.8 eV, and it is predicted that these molecules undergo the second-order Jahn-Teller distortion, and their molecular-symmetry groups are reduced to C_{2v} (XIX) and C_s (XX—XXIII) from D_{2h} and C_{2v}, respectively.

The ground-state molecular-shapes for the energetically most favorable nuclear arrangements are predicted from the distribution of the two-center components of transition densities between the ground and the lowest excited singlet states, some of which are shown in Fig. 5.

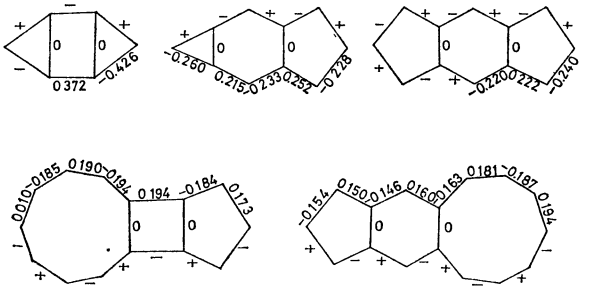

Fig. 5. Distribution of two-center components of transition densities (ρ_{01}).

In order to obtain the information on the actual magnitude of distortions or the equilibrium nuclear configurations with respect to C–C bond lengths at which the real molecule will settle, we performed the calculation using the variable bond-length SCF MO method, taking into account the distorted structures as a starting geometry.[11,13]

Results of SCF MO calculations show that almost all molecules undergo the second-order Jahn-Teller distortion, as predicted from the symmetry rule.

As to the distribution of C–C bond length, it should be noted that the second-order double-bond fixation, *i.e.*, the bond-length alternation in the peripheral carbon skeleton, is the common phenomenon in these cata-condensed nonalternant hydrocarbons (Fig. 1).

Stabilization Energies. Figure 6 shows the correlation of stabilization energies with the energy gaps calculated assuming the fully-symmetrical nuclear arrangements. We define the stabilization energy ΔE_s 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

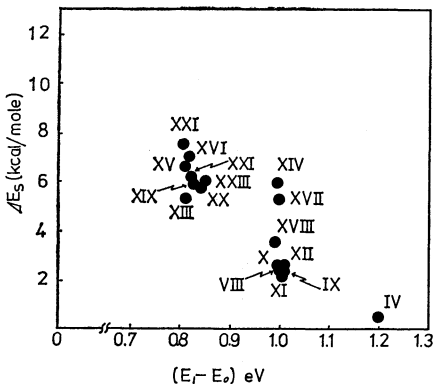

Fig. 6. Correlation of stabilization energies ΔE_s with energy gaps(E_1-E_0).

and σ-bond energies, the latter being calculated using harmonic oscillator model with the force constant equal 714 kcal mol^{-1} Å^{-2}.[14] As is seen in this figure, there is a fairly good correlation between ΔE_s and the energy gaps E_1–E_0. Particularly, it is noticed that in the valence isomers with 12 carbon atoms, the ΔE_s are almost the same.

Electronic Spectra. We calculated the excitation energies using the bond-lengths for the energetically favorable equilibrium configuration. The employed method is based on the semiempirical Pariser-Parr-Pople SCF MO CI method, and the configuration mixing of 28 singly excited states is included.

It is shown that the lowest excitation energies for the reduced molecular geometries are larger than those for the fully-symmetrical ones, and are almost constant (1.4—1.6 eV) from molecule to molecule. On the other hand, the next lowest excited states would not be remarkably changed by the molecular-symmetry reduction, lying in the region about 2.2 eV (compare Table 1 with Table 2).

Excited-state Molecular-symmetry Groups. In connection with the ground-state molecular-symmetry groups, we briefly mention the stable molecular shapes in the first excited singlet states. The criterion for the molecular-symmetry reduction in an 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 excited singlet states. That is, the stable molecular shapes in the excited states belong to their fully-symmetrical nuclear arrangements.

Conclusion

On the basis of the symmetry rule and the semiempirical SCF MO method, the problem of the molecular-symmetry reduction in C_mH_{m-4} cata-condensed non-alternant hydrocarbons was systematically examined. It was revealed that there is a fairly good correlation between the molecular-symmetry reduction and the number of carbon atoms: that is, the molecular-symmetry reduction should set in about $m\sim10$. In these systems, there is no such a sharp distinction of molecular-symmetry reduction between $4n$ and $4n+2$ π-electron systems as that seen in C_mH_{m-2} systems. The predicted types of the energetically most favorable bond distortion, 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 obtained stable molecular shapes are found to correspond to one of the Kekulé-like structures. It is concluded that such phenomena in these non-alternant hydrocarbons arise from the fact that the type of the symmetry of the lowest excited state in the fully-symmetrical nuclear arrangement is that of bond-length alternation in the peripheral carbon skeleton, and that the lowest excited state is very close to the ground state.

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The numerical calculation was carried out at Tohoku university with a NEAC 2200—700 computer.

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