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Bond Distortions and Related Phenomena in *Peri*-Condensed Tetracyclic Nonbenzenoid Aromatic Hydrocarbons

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On the basis of the second-order Jahn-Teller effect and SCF MO method, we have examined the geometrical structures with respect to bond length and the ground-state multiplicity and stability of *peri*-condensed tetracyclic nonbenzenoid aromatic hydrocarbons. It was found that of the molecules examined, dibenzo[cd, gh]pentalene (III) and its seven-membered analogue (IV) should have a triplet ground-state, exhibiting no appreciable double-bond fixation in the peripheral carbon skeleton. The other molecules were predicted to suffer the first-order or second-order bond distortions, showing a more or less marked double-bond fixation. The electronic spectra were calculated using the bond distances obtained on the basis of SCF MO method.

In a previous paper[1)] we developed a symmetry rule for predicting the stable molecular shapes with respect to C–C bond length in the ground and electronically-excited states of conjugated molecules. The symmetry rule[2–7)] is based on the second-order Jahn-Teller effect, occurring when a certain bond distortion mixes two electronic states which are nearly degenerate in the symmetrical nuclear arrangement. On the basis of this theory, we examined the bond-length distributions and stabilities of a large number of nonalternant hydrocarbons.

In this paper we examine the bond distortions and related phenomena in *peri*-condensed tetracyclic nonbenzenoid aromatic hydrocarbons containing a pentalene or a heptalene nucleus (Fig. 1). Of these systems, the dianion of dibenzo[cd, gh]pentalene(III) has recently been synthesized by Trost and Kinson.[8)]

There are two equilibrium nuclear arrangements in the ground state for pentalene, the closest derivative of which, 1-methylpentalene, has recently been synthesized by Bloch *et al.*[9)] and for heptalene, which has already been synthesized by Dauben and Bertelli.[10)] One belongs to molecular symmetry group D_{2h} which exhibits only a slight degree of double-bond fixation in the peripheral carbon skeleton, and the other to molecular symmetry group C_{2h} exhibiting a marked double-bond fixation.[1,11–15)] It was revealed that the latter is energetically more stable than the former. These predictions are in good agreement with experimental results.[9,10)] This aroused our interest in an examination of the stable nuclear arrangements and molecular symmetries of condensed hydrocarbons containing a pentalene or a heptalene nucleus.

One interesting prediction of molecular orbital theory is the possibility that certain symmetrical molecules may have a triplet ground state. For example, in the case of 1.2-5.6-dibenzopentalene, the triplet state is predicted to be more stable than the closed-shell singlet state in the symmetrical C_{2v} conformation (Fig. 2). However, in this molecule the closed-shell singlet interacts strongly with the first excited singlet state through the b_2 nuclear displacement because of the small energy gap between them.[1)] As a result, the ground state turns out to be a singlet with C_s conformation.

Breslow *et al.*[16)] observed a thermally accessible triplet state of pentaphenylpentadienyl cation in equilibrium with a singlet state, and also the stable triplet ground state of pentachlorocyclopentadienyl cation. Van Willigen *et al.*[17)] observed the triplet ground states of triphenylbenzene dianion, triphenylene dianion *etc.*, and suggested that in triphenylene dianion the trigonal symmetry is lost. The origin of the molecular sym-

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[1)] T. Nakajima, A. Toyota, and S. Fujii, This Bulletin, **45**, 1022 (1972).

[2)] R. F. Bader, *Mol. Phys.*, **3**, 137 (1960).

[3)] R. F. Bader, *Can. J. Chem.*, **40**, 1164 (1962).

[4)] R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 4947 (1969).

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[16)] R. Breslow, H. W. Chang, R. Hill, and E. Wasserman, *J. Amer. Chem. Soc.*, **89**, 1112 (1967).

[17)] H. van Willigen, J. A. M. van Broekhoven, and E. de Boer, *Mol. Phys.*, **12**, 533 (1967).

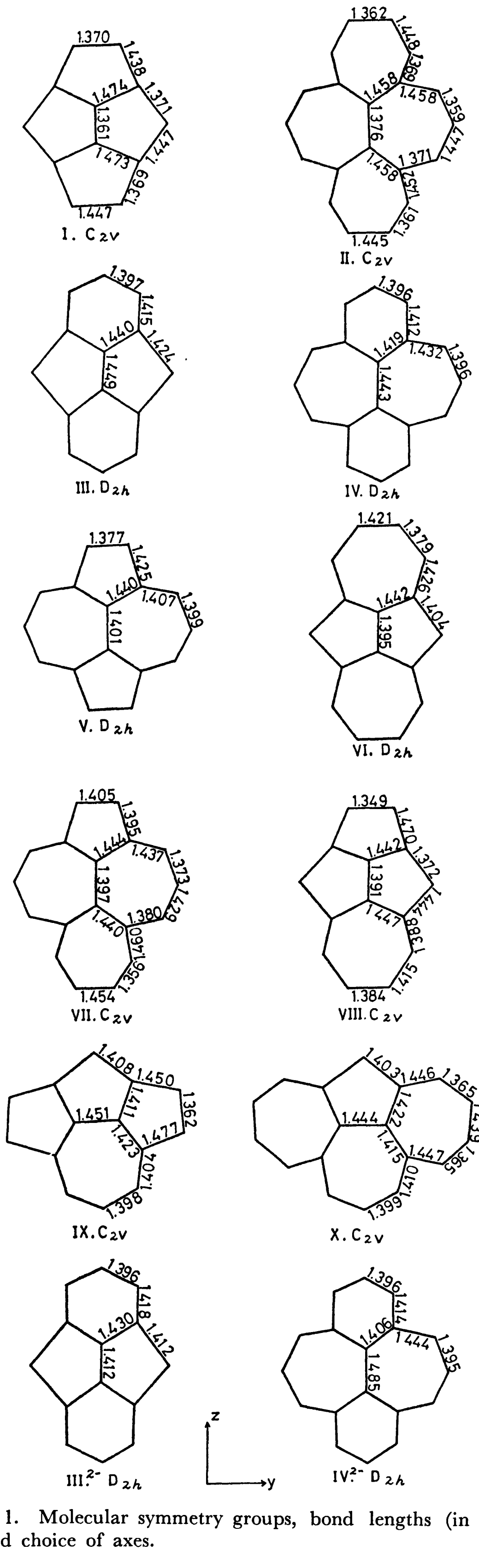

Fig. 1. Molecular symmetry groups, bond lengths (in Å), and choice of axes.

metry reduction has been ascribed to the perturbing effect of alkali counterions, since in this molecule the energy gap between the lowest triplet ground and the first excited triplet states is relatively large, and

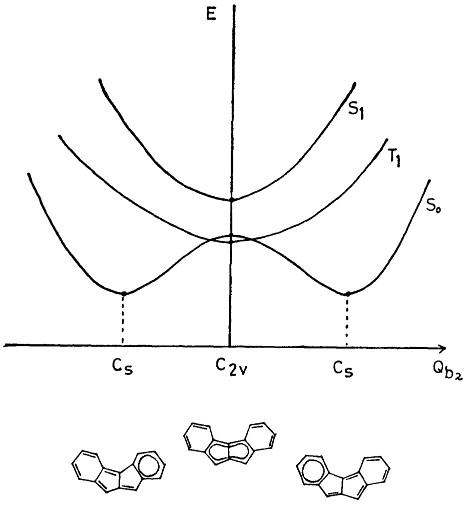

Fig. 2. The potential energy curves for the lowest singlet (S_0), the first singlet excited (S_1) and the lowest triplet states (T_1) of 1.2-5.6-dibenzopentalene.

there is no possibility for the second-order Jahn-Teller distortion to occur.[18,19]

The purpose of this paper is to predict the ground-state multiplicities, energetically most favorable symmetry groups and the equilibrium bond length of the *peri*-condensed nonalternant hydrocarbons, using the symmetry rule which is based on the second-order perturbation theory and the variable bond length SCF MO method.[20] The ground-state π-electronic properties and the electronic spectra were also examined.

Theoretical

We start by assuming a particular symmetrical nuclear configuration for a molecule. This will place the molecule in a certain fully-symmetrical point group. We treat the nuclear displacements as perturbations and use the second-order perturbation theory. On the basis of the same approximation as used previously, we find that the force constant for the *i*th normal nuclear-displacement in the ground state may be written as

$$f_0^i = k - 2\sum_n{}' \frac{\left|\langle\psi_n\left|\frac{\partial H_\pi}{\partial Q_i}\right|\psi_0\rangle\right|^2}{(E_n - E_0)}$$

where k and H_π are the force constant for an sp^2 hybridized C–C σ-bond and the Hamiltonian for π-electrons, respectively. ψ_0 and ψ_n represent the ground and the nth excited wavefunctions with respective energies E_0 and E_n.

The symmetry rules for predicting the stable molecular shapes in the ground state are as follows: the symmetry of the normal nuclear displacement with

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[18] J. A. M. van Broekhoven, H. van Willigen, and E. de Boer, *Mol. Phys.*, **15**, 101 (1968).

[19] J. L. Sommerdijk and E. de Boer, *J. Chem. Phys.*, **50**, 4771 (1969).

[20] H. Yamaguchi, T. Nakajima, and T. L. Kunii, *Theoret. Chim. Acta*, **12**, 349 (1968).

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, about 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 densities ρ_{01} over the molecular skeleton.

The symmetry rule gives only the type of most favorable bond distortion since it is based on the second-order perturbation theory. In order to obtain information on the actual magnitudes of distortions or the equilibrium bond lengths at which the nuclei of the real molecule will settle, we use the variable bond-length SCF MO method.[20]

Results and Discussion

Ground-State Molecular Symmetries and Multiplicities. The symmetries and energies (measured from the lowest singlet state) of the first excited singlet states for the fully-symmetrical nuclear arrangements of the *peri*-condensed hydrocarbons and some of their dianions are given in Table 1, and the two-center components of the transition densities for some selected molecules in Fig. 3.

TABLE 1. SYMMETRIES AND ENERGIES OF FIRST EXCITED SINGLET STATES OF *peri*-CONDENSED NONALTERNANT HYDROCARBONS

Molecule (Point group)	First excited state	
	E_1-E_0 (eV)	Symmetry
I (D_{2h})	0.91	B_{2u}
II (D_{2h})	0.39	B_{2u}
III (D_{2h})	1.13	B_{3g}
III^{2-} (D_{2h})	3.28	B_{3g}
IV (D_{2h})	1.09	B_{3g}
IV^{2-} (D_{2h})	1.10	B_{2u}
V (D_{2h})	1.81	B_{3g}
VI (D_{2h})	1.86	B_{3g}
VII (C_{2v})	1.45	B_2
VIII (C_{2v})	1.34	B_2
IX (C_{2v})	1.34	B_2
X (C_{2v})	1.19	B_2

Molecule II was predicted to have a triplet ground state in the fully-symmetrical D_{2h} conformation. However, in molecules I and II, the energy gap between the lowest singlet and first excited singlet states E_1-E_0 is small, as compared with the critical value 1.2 eV for the molecular symmetry reduction in the ground state. Thus, these molecules might undergo the second-order bond distortions making their ground-state molecular symmetry groups reduced to C_{2v} from D_{2h} by the interaction of the lowest state with the first excited state through the b_{2u} normal displacement.

We may predict that molecules V, VI, VII and VIII undergo no second-order Jahn-Teller distortion, since the energy gap is relatively large as compared with the critical value.

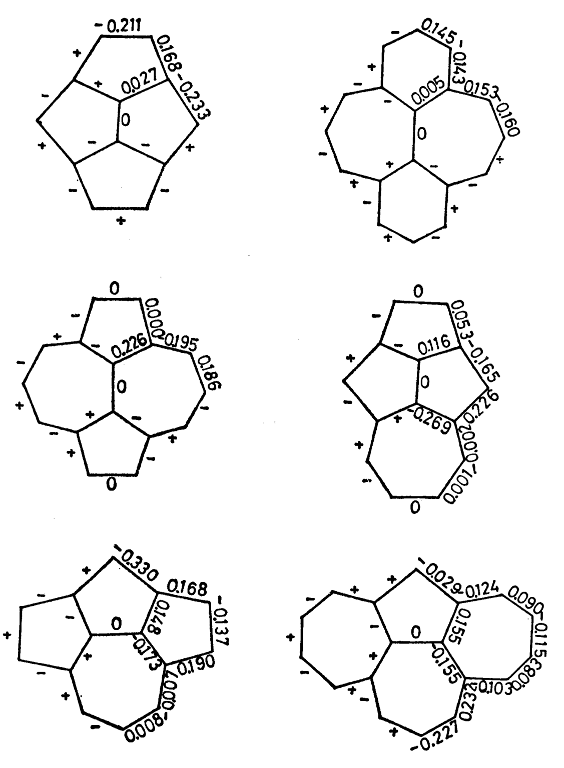

Fig. 3. Two-center components of transition densites (ρ_{01}).

The energy gap in III and IV is comparable with the critical value, and in the symmetrical D_{2h} conformation the ground state is not singlet but triplet. The energy gap in molecules IX and X is also comparable with the critical value, but the ground state is singlet in the symmetrical C_{2v} conformation.

In order to investigate the ground-state molecular-symmetry groups, geometries and multiplicities, we have performed the SCF calculation, taking into account a distorted structure as the starting geometry.[21] The form of the displacement vector has been estimated from the distributions of two-center components of transition density ρ_{01} (Fig. 3).

SCF MO calculations revealed that molecules I and II undergo the second-order bond distortion, as predicted from the symmetry rule, their ground-state molecular symmetry groups being lowered from D_{2h} to C_{2v}. The prediction is in good agreement with the theoretical investigation of Binsch.[22] The stabilization energies which favor the lower-symmetry nuclear arrangements are estimated to be 3.1 and 17.5 kcal mol^{-1}, respectively. It is of interest to note that the second-order effect in molecules containing the seven-membered rings is greater than that in its five-membered analogues, as in the case of heptalene and pentalene.[23]

On the other hand, it turns out that III and IV undergo no second-order bond distortions. Thus, we may conclude that both their stable ground states are triplet states ($^3B_{1u}$), which are energetically more stable than the singlet states by 3.9 and 8.5 kcal, respectively.

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[21] T. Nakajima and A. Toyota, *Chem. Phys. Lett.*, **3**, 272 (1969).

[22] G. Binsch, "Aromaticity, Pseudoaromaticity and Antiaromaticity." The 3rd Jerusalem Symposium, The Israel Academy of Sciences and Humanities, Jerusalem (1971), p. 25.

[23] T. Nakajima, A. Toyota and H. Yamaguchi, *ibid.*, p. 227.

V, VI, VII, VIII, IX, and X were predicted not to undergo second-order bond distortions and all the ground-state molecular symmetries to belong to the fully-symmetrical group.

Dianions of III and IV undergo no second-order bond distortions, both their ground-state multiplicities being singlet.

Ground-State π-Electronic Properties. The calculated equilibrium bond length at the energetically favorable geometrical structures of the molecules examined are shown in Fig. 1. Since all the stable conformations of I, II, VII, VIII, IX and X belong to the molecular symmetry group C_{2v}, they have dipole moments in the ground state. The dipole moments calculated using the theoretical charge densities are 1.16, 1.23, 2.30, 2.70, 2.05, and 1.12 D, respectively

Concerning the distribution of bond length, it is of interest to note that in molecules I and II there is a marked double-bond fixation in the periphery and vinyl segment located at the center of molecule, but no appreciable one in III and IV. The bond lengths of the two benzene rings are very much smoothed out as those of the free benzene molecule.

In V and VI, the C–C skeleton is composed of two distinguishable parts: one in which bond lengths are highly equalized (in a pentalene or a heptalene core), and the other in which there is a marked double-bond fixation (in the remainder of the periphery).

In VII and VIII, a strong first-order double-bond fixation exists in the peripheral C–C skeleton, the bond length of vinyl segment located at the center of molecule being 1.4 Å.

In IX and X, there is a moderate first-order double-bond fixation in the peripheral C–C skeleton.

In dianions of III and IV, the bond lengths of a pentalene or a heptalene core are almost same as those of the free pentalene or heptalene dianion in which bond lengths are nearly equal throughout the whole molecular skeleton.

Electronic Spectra. In calculating electronic spectra, configuration mixing of the singly excited states is partially included: the number of configuration interactions considered is 28 for each molecule. The lower singlet transition energies and intensities calculated using the geometrical structures corresponding to the energetically most stable nuclear configuration are summarized in Table 2. The transition symmetries are also included. Unfortunately, there are at present no experimental spectral data available for a direct comparison of theory and experiment.

TABLE 2. TRANSITION ENERGIES AND INTENSITIES

Molecule (Point group)	Transition symmetry	ΔE (eV)	f (c. g. s.)	Molecule (Point group)	Transition symmetry	ΔE (eV)	f (c. g. s.)
I (C_{2v})	$^1A_1$	1.20	0.008	V (D_{2h})	$^1B_{3g}$	1.81	Forb.
	$^1B_2$	1.68	0.005		$^1B_{2u}$	2.62	0.163
	$^1A_1$	3.05	0.030		^1A_g	3.19	Forb.
	$^1B_2$	3.90	0.482		$^1B_{1u}$	3.46	0.015
	$^1B_2$	4.60	0.101		$^1B_{2u}$	4.19	0.051
II (C_{2v})	$^1B_2$	1.38	0.004	VI (D_{2h})	$^1B_{3g}$	1.86	Forb.
	$^1A_1$	1.41	0.000_1		$^1B_{2u}$	2.68	0.254
	$^1A_1$	2.79	0.004		^1A_g	3.21	Forb.
	$^1B_2$	2.90	0.274		$^1B_{1u}$	3.47	0.058
	$^1B_2$	3.46	0.164		$^1B_{2u}$	3.93	0.007
III (D_{2h})	$^3B_{3g}$	1.21	0.005	VII (C_{2v})	$^1B_2$	1.45	0.017
	$^3B_{2u}$	1.78	Forb.		$^1B_2$	2.24	0.006
	$^3B_{1u}$	2.96	Forb.		$^1A_1$	2.90	0.001
	^3A_g	3.17	0.628		$^1A_1$	3.22	0.000_1
	$^3B_{3g}$	3.53	0.635		$^1B_2$	4.55	0.019
III^{2-} (D_{2h})	$^1B_{3g}$	3.28	Forb.	VIII (C_{2v})	$^1B_2$	1.34	0.024
	$^1B_{2u}$	3.44	0.577		$^1B_2$	2.14	0.028
	$^1B_{1u}$	3.67	0.218		$^1A_1$	2.89	0.069
	$^1B_{3g}$	4.30	Forb.		$^1A_1$	3.45	0.033
	^1A_g	4.51	Forb.		$^1B_2$	3.74	0.046
IV (D_{2h})	$^3B_{3g}$	1.38	0.004	IX (C_{2v})	$^1B_2$	1.34	0.003
	$^3B_{2u}$	1.79	Forb.		$^1A_1$	2.16	0.000_3
	$^3B_{3g}$	2.89	0.501		$^1B_2$	3.40	0.012
	^3A_g	3.09	0.547		$^1A_1$	3.77	0.004
	$^3B_{1u}$	3.31	Forb.		$^1A_1$	4.12	0.029
VI^{2-} (D_{2h})	$^1B_{2u}$	1.10	0.004	X (C_{2v})	$^1B_2$	1.19	0.017
	$^1B_{3g}$	1.14	Forb.		$^1A_1$	2.29	0.005
	$^1B_{3g}$	2.08	Forb.		$^1B_2$	3.18	0.191
	$^1B_{2u}$	3.06	0.828		$^1A_1$	3.36	0.117
	^1A_g	3.26	Forb.		$^1A_1$	3.54	0.208