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ELECTRONIC STRUCTURES OF SOME CATA-CONDENSED NONALTERNANT HYDROCARBONS: PENTALENOPENTALENES, AZULENOAZULENES, AND PENTALENOAZULENES

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Abstract—On the basis of the second-order Jahn–Teller theory and the semiempirical SCF MO method, we have examined the energetically most favorable ground-state geometrical structures with respect to C–C bond lengths of some cata-condensed nonalternant hydrocarbons consisting of five- and seven-membered rings. It is predicted that both the geometrical valence isomers of pentalenopentalenes, 1 and 2, should suffer molecular-symmetry reduction, exhibiting a marked double-bond fixation in the peripheral carbon skeleton, while in azulenoazulenes, 3 and 4, no molecular-symmetry reduction occurs. The electronic spectra have been calculated using the energetically favorable geometrical structures obtained by the SCF MO calculations. The theoretical values for azuleno[1,2-b]azulene (3) are in good agreement with experimental data.

For predicting the energetically most favorable molecular-symmetry groups and geometrical structures with respect to C–C bond lengths of conjugated hydrocarbons, particularly of nonalternant hydrocarbons, we have developed a symmetry rule based on the second-order Jahn–Teller theory.[1-5] It is predicted that the stable ground-state nuclear arrangements of pentalene and heptalene 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 is found that in azulene no molecular-symmetry reduction occurs.

Recently, the derivatives of azuleno[1,2-*b*]azulene have been synthesized by Toda and others,[6] and their physical properties have been reported. Azuleno[1,2-*b*]azulene (3) and its valence isomer (4) are the cata-condensed nonalternant hydrocarbons formed by fusing two azulene molecules (Fig. 1). Other interesting cata-condensed nonalternant hydrocarbons are pentalenopentalenes, 1 and 2, formed by fusing two pentalene molecules and pentalenoazulenes, 5 and 6, formed by fusing the pentalene and azulene molecules.

The purpose of this paper is to examine the energetically most favorable ground-state geometrical structures with respect to C–C bond lengths of these nonalternant hydrocarbons using the semiempirical SCF MO method. On the basis of the obtained results, we discuss the problem of whether these nonalternant hydrocarbons would show the chemical properties of their component molecular systems or not. Moreover, the excitation energies of these molecules will be calculated using the energetically most favorable geometrical structures.

THEORETICAL

Since the symmetry rule for predicting the energetically most favorable molecular shapes of conjugated hydrocarbons is well discussed in our previous papers,[1,2] we give here only a brief outline of the theory. Let us start by assuming for a conjugated molecule a fully-symmetrical nuclear arrangement as the unperturbed configuration. We further 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, $\psi_1, \ldots, \psi_n, \ldots$ and the corresponding eigenvalues E_0, $E_1, \ldots, E_n, \ldots$ are assumed to be known. If we distort the nuclei from the symmetrical nuclear arrangement by means of the *i*th normal coordinate of the nuclear displacement Q_i, 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 the 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.[7,8]

The symmetry rule for predicting the stable molecular shape in the ground state is stated 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

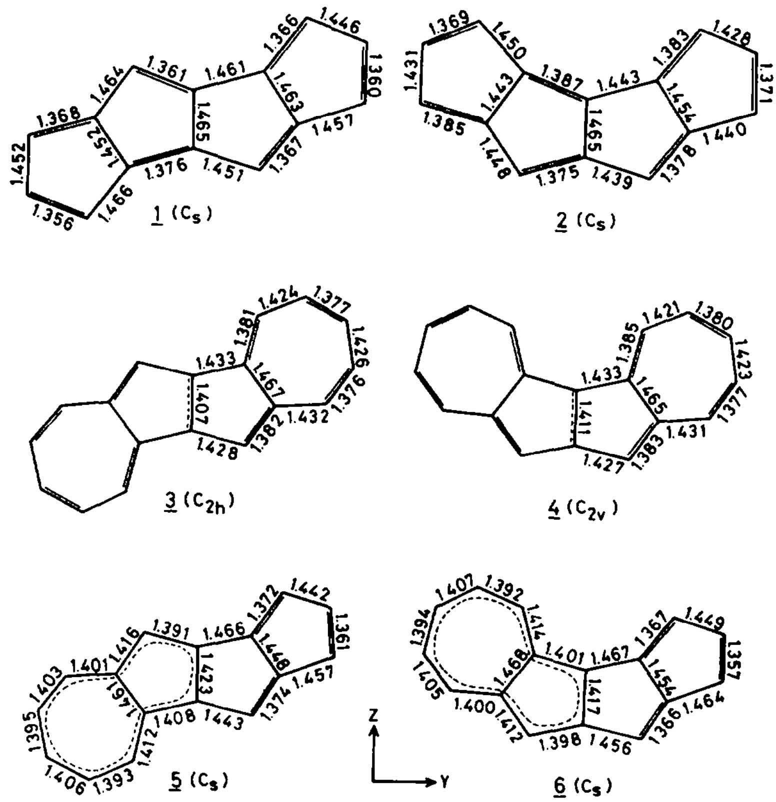


Fig. 1. Predicted molecular-symmetry groups, equilibrium C–C bond lengths (in Å unit), and the choice of molecular axes. For molecules which belong to the point group C_{2h}, the z axis is taken to be perpendicular to the molecular plane. 1: Pentaleno[1,2-*b*]pentalene, 2: Pentaleno[1,2-*a*]pentalene, 3: Azuleno[1,2-*b*]azulene, 4: Azuleno[1,2-*a*]azulene, 5: Pentaleno[1,2-*b*]azulene, 6: Pentaleno[1,2-*a*]azulene.

represented by a one-electron transition between molecular orbitals ϕ_i and ϕ_f, the transition density between the ground and the lowest excited state is given by $\sqrt{2}\phi_i\phi_f$.

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-symmetrical nuclear arrangements of the cata-condensed nonalternant hydrocarbons were calculated by using the semiempirical SCF MO CI method in conjunction with the variable bond-length technique.[9–11] The results are listed in Table 1. The two-center components of the transition densities for some selected molecules are shown in Fig. 2.

The problem of the molecular-symmetry reduction can be discussed on the basis of the symmetry rule and Table 1. The molecular symmetry group of pentaleno[1,2-*b*]pentalene (1) should be reduced from C_{2h} to C_s by the interaction with the lowest-excited state through the b_u nuclear displacement, since the energy gap is considerably smaller than the critical value, *ca.* 1.2 eV. The type of bond distortion is predicted from the distribution of the two-center components of the transition density ρ_{01} shown in Fig. 2. In pentalenol[1,2-*a*]pentalene (2), the lowest-excited state is of A_1 symmetry. In order to examine the possibility of the molecular-symmetry reduction, we take into account the second-excited state of B_2 symmetry. Since the energy gap in question is comparable to the critical value, there is a possibility of

Table 1. Energies and symmetries of the lowest-excited singlet states of cata-condensed nonalternant hydrocarbons with the highest molecular symmetries

Molecule (point group)	Lowest-excited state E_1-E_0 (eV)	Symmetry
1 (C_{2h})	0.26	B_u
2 (C_{2v})	1.16	A_1
	1.32*	B_2^*
3 (C_{2h})	1.64	B_u
4 (C_{2v})	1.97	A_1
	2.36*	B_2^*
5 (C_s)	1.82	A'
6 (C_s)	1.50	A'

* The energy and the symmetry of the second-lowest singlet state.

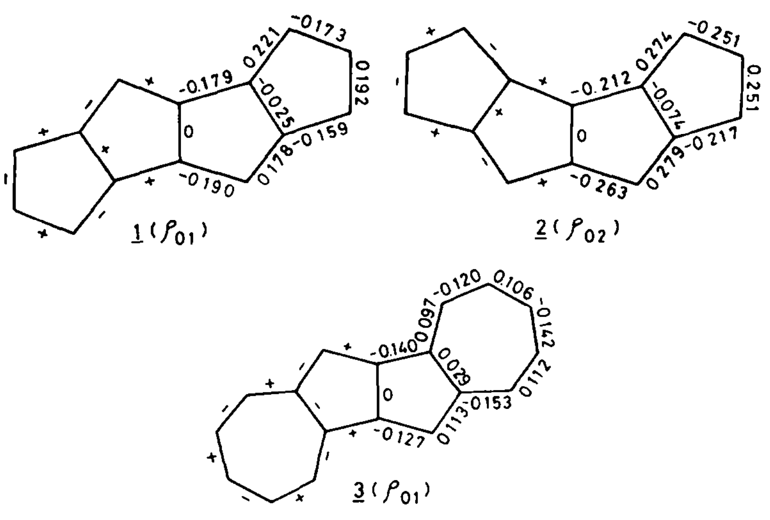


Fig. 2. Distributions of two-center components of transition densities for molecules 1, 2, and 3. The absolute values of the left moiety are obtained from those of the right one by the C_2 rotation in 1 and 3 and by the reflection in 2.

the molecular-symmetry reduction from C_{2v} to C_s by the interaction with the second-excited state through the b_2 nuclear displacement. In this case, the type of bond distortion is predicted from the distribution of two-center components of the transition density ρ_{02}. On the other hand, in azuleno[1,2-*b*]azulene (3) and azuleno[1,2-*a*]azulene (4), the energy gaps are definitely large as compared with the critical value. Thus, there may be no possibility of the molecular-symmetry reduction in both the molecules. Since in pentaleno[1,2-*b*]azulene (5) and pentaleno[1,2-*a*]azulene (6), the fully symmetrical nuclear arrangements belong to the lowest point group of C_s symmetry, molecular-symmetry reduction does not occur in these molecules.

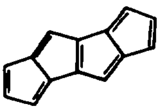
Since the symmetry rule is based on the second-order perturbation theory, it gives only the type of the most favorable bond distortions. In order to obtain the information on the actual magnitude of distortion or the equilibrium bond lengths at which the nuclei of the molecule will settle, we perform the variable bond-length SCF MO calculation, taking into account the distorted structures as the starting geometries.[12]

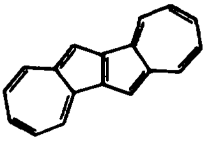
In Fig. 1 we show the molecular-symmetry groups and bond lengths corresponding to the most favorable nuclear arrangements with respect to C–C bond lengths of the cata-condensed nonalternant hydrocarbons.

From SCF MO calculations, it turns out that molecules 1 and 2 having $4n+2$ π-electrons suffer the pseudo Jahn–Teller distortions, resulting in the molecular-symmetry reduction to C_s. In the reduced nuclear arrangements, they show a strong double-bond fixation, *i.e.* the bond-length alternation, in the peripheral carbon skeleton. In view of the distribution of C–C bond lengths, their geometrical structures are said to possess two molecular regions, the pentalene-like and pentafulvene-like regions.

On the other hand, in molecules 3 and 4 belonging also to the $4n+2$ π-electron systems, no molecular-symmetry reduction occurs. However, the double-bond fixation is found in both the seven-membered rings. In other words, these molecules are said to possess the two heptafulvene-like regions. The PMR spectrum of the aryl derivative of 3 reveals that the seven-membered moieties of this molecule show a bond-length alternation.[6]

It is of interest to remark that the central cross bond of 1 or 2 is distinctly long as compared with that of 3 or 4 and the degree of double-bond fixation is larger in the former than in the latter. This is explained in terms of the resonance theory as follows. In 1 Kekulé-type structure **1a** of C_{2h} symmetry in which the two pentalene-like structures are overlapping should be less stable than the other two Kekulé-type structures of C_s symmetry which are considered to be composed of the pentalene-like and pentafulvene-like regions. On the other hand, in 3 Kekulé-type structure **3a** of C_{2h} symmetry in which the two azulene-like structures are overlapping should be more important energetically than the other ones considered to be composed of the azulene-like and heptafulvene-like regions and, consequently, could participate effectively in the resonance.


1a


3a

Molecules 5 and 6, both having $4n$ π-electrons, undergo only a first-order double-bond fixation. It is noted that in both the molecules the carbon skeleton is composed of two distinguishable parts, one in which bond lengths are nearly equalized, *i.e.* the azulene-like region, and the other in which a strong double-bond fixation exists, *i.e.* the pentafulvene-like region. Thus, it is said that in these molecules there are two regions, one aromatic and the other polyolefinic.

We then calculate the stabilization energy due to the molecular-symmetry reduction, which is the difference in total energy between the fully-symmetrical and the distorted structure. The total energy is assumed to be the sum of the π-bond and σ-bond energies, the latter being calculated using the harmonic oscillator model[13] with the force constant equal to 714 kcal $mole^{-1}$ A^{-2}. The stabilization energies for molecules 1 and 2 are calculated to be 6.8 kcal $mole^{-1}$ and 1.2 kcal $mole^{-1}$, respectively. This indicates that the pseudo Jahn–Teller effect is stronger in molecule 1 than in molecule 2. This trend is closely associated with the magnitude of the energy gap at the fully-symmetrical nuclear arrangement: the smaller the energy gap, the larger the stabilization energy.

Electronic spectra

In calculating electronic spectra, we use the bond lengths shown in Fig. 1. The method of calculation employed is the PAriser–Parr–Pople-type SCF MO CI method, and the configuration mixing of 28 singly excited configurations is included.[1,2]

From Table 2 we see that the excitation energy of the lowest-excited state, calculated assuming the reduced molecular-symmetry group for molecule 1, is predicted to be considerably larger than that calculated using the

Table 2. Singlet transition energies and intensities of nonalternant hydrocarbons with the most stable geometrical structures

Molecule (point group)	Transition symmetry	E (eV)	f (cgs)	Obs. (eV)
1 (C_s)	A'	1.24	0.002	
	A'	2.32	0.003	
	A'	3.01	0.145	
	A'	3.75	1.263	
	A'	3.76	0.472	
2 (C_s)	A'	1.41	0.003	
	A'	2.05	0.027	
	A'	2.56	0.011	
	A'	3.37	0.960	
	A'	3.74	0.896	
3 (C_{2h})	B_u	1.64	0.106	1.36, 1.18, 0.99 (logε=2.41, 2.49, 2.34; progression)*
	A_g	2.42	Forb.	2.18 (logε = 2.34; shoulder)
	B_u	2.88	0.129	3.03, 2.88, 2.71, 2.55 (logε = 3.75, 3.87, 4.02, 4.05; progression)
	A_g	3.62	Forb.	
	A_g	3.69	Forb.	
	B_u	3.82	2.715	3.60, 3.47 (logε = 4.76, 5.11)
	B_u	4.17	0.435	
4 (C_{2v})	A_1	1.97	0.177	
	B_2	2.36	0.032	
	B_2	2.64	0.002	
	A_1	3.40	0.704	
	A_1	3.65	0.749	
5 (C_s)	A'	1.82	0.011	
	A'	2.03	0.020	
	A'	2.85	0.146	
	A'	3.33	1.340	
	A'	3.78	0.400	
6 (C_s)	A'	1.50	0.023	
	A'	2.25	0.026	
	A'	3.09	0.222	
	A'	3.55	0.204	
	A'	3.57	0.451	
	A'	4.00	0.853	

* The spectrum of diphenyl derivative; Ref. 6.

fully-symmetrical nuclear arrangement (compare Table 1 with Table 2). A quite similar situation occurs for the excitation energy of the second lowest-singlet state of molecule 2. This is due to the effect brought about by the pseudo Jahn–Teller distortion. The predicted excitation energies and intensities for molecule 3 are in good agreement with the observed values for the diphenyl derivative.

CONCLUSION

In spite of the $4n+2$ π-electron systems, the valence isomers of pentalenopentalene (1 and 2) and those of azulenoazulene (3 and 4) are predicted to exhibit more or less a marked double-bond fixation, the degree of double-bond fixation being larger in the former than in the latter. On the other hand, in molecules 5 and 6 having $4n$ π-electrons, it is found that the peripheral carbon skeleton is composed of two distinguishable parts, one the azulene-like region and the other the pentafulvene-like region. In this sense, they are expected to show both aromatic and polyolefinic characters.

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