differences in signal intensities among the various dipeptides and amino acids investigated here. Hydrogen bonding within the carnosine crystal is expected to restrict the freedom of molecular motion and thus to produce longer $T_1$ values than those observed with more mobile solids.[21]

Since small amounts of paramagnetic centers can increase the relaxation rates of the protons without affecting the line widths of the $^{13}$C resonances,[1] the sensitivity of CP/MAS NMR spectra of solids that exhibit slow relaxation can be improved by paramagnetic doping. This observation was confirmed independently after submission of this manuscript.[22] Because there is a high level of dipolar coupling between protons in such solids and each $^{13}$C nucleus can cross polarize to more than one proton, one might expect all the $^{13}$C resonances to increase in intensity to about the same extent. This is indeed found. Although less than 40% of the carnosine molecules in Figure 2A are bonded directly to cobalt(II),[14,17] the peak intensities of the carnosine $^{13}$C resonances are all affected equally. Thus addition of low concentrations of paramagnetic centers should be useful for increasing the sensitivity of CP/MAS $^{13}$C NMR spectroscopy for solids with long proton $T_1$ values.

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**Registry No.** Carnosine, 305-84-0; homocarnosine sulfate, 19841-48-6; glycyl-L-histidine hydrochloride, 3486-76-8; anserine nitrate, 5937-77-9; L-histidine, 71-00-1; β-alanine, 107-95-9; cobalt chloride, 7646-79-9.

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# Geometrical Structures of Electronically Excited States of Conjugated Hydrocarbons

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**Abstract:** On the basis of the pseudo Jahn–Teller theory, the geometrical structures with respect to C–C bond lengths of electronically excited states of conjugated hydrocarbons are examined. The Walsh–Pearson rule that the first excited state of a molecule should belong to the same point group as the ground state of its mono- or dinegative ion is insufficient for alternant hydrocarbons and does not hold for nonalternant hydrocarbons of a certain type. It is shown that in alternant hydrocarbons, the first excited singlet state does not undergo a molecular-symmetry reduction due to bond distortion, and in highly symmetrical alternant hydrocarbons such as benzene, the second excited singlet state suffers the same type of molecular-symmetry reduction due to bond distortion and, consequently, belongs to the same point group as the ground states not only of the mono- and dinegative ions but also of the mono- and dipositive ions. The first excited singlet states of pentafulvalene and nonafulvalene are predicted to belong to the same point group as the ground states of the respective positive ions.

On the basis of the pseudo, or second-order, Jahn–Teller effect and of molecular orbital (MO) theory, Pearson[2] has proposed a symmetry rule for predicting the geometrical structures of electronically excited molecules. The rule can be simply stated: the first excited state of a molecule containing $n$ electrons should belong to the same point group as the ground state of a similar molecule having $n + 1$ or $n + 2$ electrons. The extra one or two electrons are assumed to be in that molecular orbital which becomes occupied in the excited state.

Exactly the same rule was given by Walsh[3] as early as 1953. His reasoning was based on the so-called Walsh diagram, in which the energies of the vacating MO and the filling MO are plotted against the change of nuclear positions.

The underlying assumption on which the Walsh–Pearson rule is based is that the promoted electron, being in a very unstable MO, is the one that is active in causing a structural change. The vacancy in the stable MO is presumed to be less active.

Pearson[2] has demonstrated how well the rule works for a variety of inorganic molecules, including transition-metal complexes and simple organic molecules. In this paper, we examine the applicability of the Walsh–Pearson rule to the prediction of the geometrical structures with respect to C–C bond lengths of the electronically excited states of conjugated hydrocarbons. It will be shown that the rule is insufficient for alternant hydrocarbons and does not hold for nonalternant hydrocarbons of a certain type.[4] It is revealed that the vacancy in the stable MO, which was ignored in deriving the Walsh–Pearson rule, is of primary importance in predicting the geometrical structures of excited states of pentafulvalene and nonafulvalene and is as important as the occupancy in an unstable MO in predicting those of alternant hydrocarbons.

## Preliminary Theory

Assuming for a planar conjugated hydrocarbon the most symmetrical arrangement of C nuclei as the unperturbed system and using the second-order perturbation theory, we find that the ground-state energy after nuclear deformation by means of the C–C stretching normal mode $Q_\nu$ is given by[5]

$$E(Q_\nu) = E_0 + \left\langle \psi_0 \left| \frac{\partial H}{\partial Q_\nu} \right| \psi_0 \right\rangle Q_\nu + \frac{1}{2}\left\{ \left\langle \psi_0 \left| \frac{\partial^2 H}{\partial Q_\nu^2} \right| \psi_0 \right\rangle - 2 \sum_{n \neq 0} \frac{\left| \left\langle \psi_n \left| \frac{\partial H}{\partial Q_\nu} \right| \psi_0 \right\rangle \right|^2}{E_n - E_0} \right\} Q_\nu^2 \quad (1)$$

If the initial ground state, $\psi_0$, is nondegenerate, as is the case with

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(1) (a) Tohoku University. (b) Yamagata University.

(2) (a) Pearson, R. G. *Chem. Phys. Lett.* **1971**, *10*, 31-34. (b) Pearson, R. G. "Symmetry Rules for Chemical Reactions"; Wiley: New York, 1976; pp 474-489.

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most of the molecules dealt with in this paper, the second term in eq 1 is nonzero only for the totally symmetric nuclear displacements. Assuming the equilibrium nuclear arrangement with respect to the totally symmetric bond distortions, which can be obtained by using the variable bond-length SCF MO method (vide infra), as the initial structure, the second term in eq 1 can be taken to be zero. The force constant for $Q_\nu$ can then be identified with the term in braces. Invoking the $\sigma$–$\pi$ separability and neglecting the second derivative of the resonance integral $\beta(r)$ with respect to bond legnth $r$, we express the force constant as[6]

$$f_0{}^\nu = f_\sigma - 2\sum_{n\neq 0}\frac{\left|\left\langle\psi_n\left|\frac{\partial H_\pi}{\partial Q_\nu}\right|\psi_0\right\rangle\right|^2}{E_n - E_0} \tag{2}$$

where $f_\sigma$ is the force constant for the approximately sp$^2$ hybridized C $\sigma$ bond. The force constant for $Q_\nu$ can be negative if the second term, i.e., the sum over the excited states, is larger than $f_\sigma$. In such a case, the energy should be lowered by the bond distortion $Q_\nu$ and if the symmetry of $Q_\nu$ is nontotally symmetric, a molecular-symmetry reduction would occur. This is the pseudo, or second-order, Jahn–Teller effect.[2b,5]

In estimating the probable value of the force constant, we use the approximation that the infinite sum over excited states is replaced by one or two dominant terms corresponding to the lowest one or two excited states.[2b,5] Our approach is then simply to examine whether a given molecule in the most symmetrical nuclear arrangement has significantly low excited state(s) and, if it does, whether any of the matrix elements, $\langle\psi_n|\partial H_\pi/\partial Q_\nu|\psi_0\rangle$, are vanishing. Since $Q_\nu$ and $(\partial H_\pi/\partial Q_\nu)$ have the same symmetry and the ground state is totally symmetric in general, the integral is nonzero only when $\psi_n$ and $Q_\nu$ have the same symmetry. The symmetry of the lowest excited state(s) now determines the symmetry of the bond distortion that occurs energetically most easily.

Although the symmetry of the softest bond distortion can be determined, its actual type cannot be uniquely determined because there are, in general, several types of bond distortion belonging to the same symmetry. In order to predict which type of bond distortion is actually energetically most favorable, it is useful to express the matrix element in terms of the transition density $\rho_{0n}$ between the ground and excited states, both states assumed to be singlet:[7]

$$\left\langle\psi_n\left|\frac{\partial H_\pi}{\partial Q_\nu}\right|\psi_0\right\rangle = \int \rho_{0n}\frac{\partial V_\pi}{\partial Q_\nu}\mathrm{d}v \tag{3}$$

where $V_\pi$ is the one-electron nuclear–electron potential energy operator. If $\psi_n$ corresponds to the orbital transition $\phi_i \rightarrow \phi_k$, $\rho_{0n}$ is given by $2^{1/2}\phi_i\phi_k$. For a given excited state, the matrix element is largest for $Q_\nu$ whose distribution of bond distortions matches best with the distribution of the two-center components of $\rho_{0n}$ in bond regions.

In the lowest excited state, assuming that first-order totally symmetric bond distortions have taken place, we can express the force constant for $Q_\nu$ in a similar way as[8]

$$f_1{}^\nu = f_\sigma - 2\sum_{n\neq 1}\frac{\left|\left\langle\psi_n\left|\frac{\partial H_\pi}{\partial Q_\nu}\right|\psi_1\right\rangle\right|^2}{E_n - E_1} \tag{4}$$

If the same approximation as used in the ground state for the infinite sum is used, the symmetry of the softest bond distortion in the lowest excited state is determined by the direct product of the symmetries of the lowest excited and the second excited state.

The infinite sum in eq 4 includes the term corresponding to $\psi_0$. Since, unlike all other terms, the term with $n = 0$ is a negative number, it is concluded that the bond distortion that is active or favored in the ground state is inactive or disfavored in the excited state.

We now express the matrix element $\langle\psi_n|\partial H_\pi/\partial Q_\nu|\psi_1\rangle$ in eq 4 in terms of relevant MO's. Let $\psi_1$ correspond to the orbital jump $\phi_i \rightarrow \phi_k$ and $\psi_n$ to $\phi_j \rightarrow \phi_l$. The matrix element is then expressed as

$$\left\langle\psi_{j\rightarrow l}\left|\frac{\partial H_\pi}{\partial Q_\nu}\right|\psi_{i\rightarrow k}\right\rangle = \int \rho_{j-l,i-k}\frac{\partial V_\pi}{\partial Q_\nu}\mathrm{d}v = \begin{cases} \left\langle\phi_l\left|\frac{\partial V_\pi}{\partial Q_\nu}\right|\phi_k\right\rangle & \text{if } i=j \text{ and } k\neq l \\ -\left\langle\phi_j\left|\frac{\partial V_\pi}{\partial Q_\nu}\right|\phi_i\right\rangle & \text{if } i\neq j \text{ and } k=l \\ 0 & \text{if } i\neq j \text{ and } k\neq l \end{cases} \tag{5}$$

The transition density $\rho_{j-l,i-k}$ is given by $\phi_l\phi_k$ if $i = j$ and $k \neq l$ and by $-\phi_i\phi_j$ if $i \neq j$ and $k = l$. Equation 5 indicates that if $i = j$ and $k \neq l$, the symmetry of $Q_\nu$ is determined by the direct product of symmetries of $\phi_l$ and $\phi_k$, $\Gamma_{\phi_l}\Gamma_{\phi_k}$, and if $i \neq j$ and $k = l$, it is determined by $\Gamma_{\phi_i}\Gamma_{\phi_j}$. If $i \neq n$ and $k \neq l$, the matrix element is vanishing.

The pseudo Jahn–Teller effect, being based on second-order perturbation theory, gives only a probable value of the force constant for the softest nuclear distortion. In order to obtain the actual magnitude of bond distortion or the equilibrium bond lengths at which the C nuclei of a conjugated hydrocarbon will settle, we use the variable bond-length SCF formalism of the Pariser–Parr–Pople semiempirical LCAO MO method.[6,9] The resonance integral is assumed to be of exponential form, $\beta(r) = be^{-ar}$, the value of $a$ being 1.7 Å$^{-1}$ for the ground state and 3.3 Å$^{-1}$ for excited states.[10] Occasionally self-consistency is achieved at two different equilibrium structures, one possessing the full molecular symmetry and the other possessing a lower molecular symmetry. In such a case, the latter should, in principle, be more stable than the former. In order to estimate the difference in total energy between the two equilibrium structures, we assume that the total energy is the sum of the $\pi$- and $\sigma$-bond energies, the latter being calculated by using a harmonic oscillator model with the force constant equal to 714 kcal mol$^{-1}$ Å$^{-2}$.[6,9]

Comparing the lowest (singlet) excitation energies, $(E_1 - E_0)$, calculated by assuming the most symmetrical nuclear arrangement, with the results obtained by using the variable-bond-length SCF MO method for a variety of nonalternant hydrocarbons, we have proposed a criterion for the occurrence of molecular-symmetry reduction in the ground states of conjugated hydrocarbons:[6] if $E_1 - E_0$ of a conjugated hydrocarbon evaluated by assuming the most symmetrical (planar) structure is smaller than ca. 1.2 eV, a molecular-symmetry reduction occurs in the ground state. It should be noted in this connection that strictly speaking, the proposed critical value is valid only when the lowest excited state corresponds to a single MO transition, say, $\phi_i \rightarrow \phi_k$. If it corresponds to a configuration mixture of two MO transitions, as is often the case with (even) alternant hydrocarbons (vide infra), the critical value should be larger than the above value.

For the lowest excited state, as far as the second excited state also corresponds to a single MO transition, the critical value is expected to be approximately one-half of the above value. The reason for this is given as follows: the matrix element $\langle\psi_1|\partial H_\pi/\partial Q_\nu|\psi_0\rangle$ is expressed in terms of relevant MO's as, say, $2^{1/2}\langle\phi_k|\partial V_\pi/\partial Q_\nu|\phi_i\rangle$. On the other hand, according to eq 5, $\langle\psi_2|\partial H_\pi/\partial Q_\nu|\psi_1\rangle$ is written, if $\psi_2$ corresponds to $\phi_i \rightarrow \phi_l$, as $\langle\phi_l|\partial V_\pi/\partial Q_\nu|\phi_k\rangle$, and if $\psi_2$ corresponds to $\phi_j \rightarrow \phi_k$, as $-\langle\phi_j|\partial V_\pi/\partial Q_\nu|\phi_i\rangle$. Therefore, $|\langle\psi_2|\partial H_\pi/\partial Q_\nu|\psi_1\rangle|^2$ is approximately one-half of $|\langle\psi_1|\partial H_\pi/\partial Q_\nu|\psi_0\rangle|^2$ if the values of the integrals in terms of MO's are assumed to be nearly constant irrespective of

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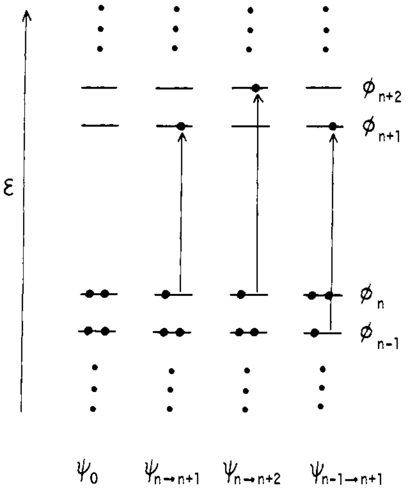

**Figure 1.** $\pi$-Electron configurations for the ground state ($\psi_0$) and the lower excited states of a conjugated hydrocarbon having $2n$ $\pi$ electrons.

MO's employed. It is difficult, however, to verify this assumption, and we can only justify it if it works in the application at hand.

## Theory for Conjugated Hydrocarbons

In Figure 1 are shown the $\pi$-electron configurations for the ground state, $\psi_0$, and the lower excited states, $\psi_{n\to n+1}$, $\psi_{n\to n+2}$, and $\psi_{n-1\to n+1}$, of a conjugated hydrocarbon having $2n$ $\pi$ electrons. If the lowest excited (singlet or triplet) state corresponds to the orbital transition $\phi_n \to \phi_{n+1}$ and the second one to $\phi_n \to \phi_{n+2}$, the symmetry of $Q_\nu$ in the lowest excited state is given by $\Gamma_{\phi_{n+1}}\Gamma_{\phi_{n+2}}$. In this case, the symmetry of the softest bond distortion in the lowest excited state is predicted to be the same as that in the ground state of the mononegative or the dinegative ion produced by placing the extra one or two electrons in $\phi_{n+1}$, the lowest excited state in both the negative ions being assumed to correspond to the orbital transition $\phi_{n+1} \to \phi_{n+2}$. This is the case in which the Walsh–Pearson rule holds. On the other hand, if the second excited state corresponds to $\phi_{n-1} \to \phi_{n+1}$, the symmetry of the softest bond distortion in the lowest excited state, $\psi_{n\to n+1}$, is determined by $\Gamma_{\phi_{n+1}}\Gamma_{\phi_n}$ and should be the same as that in the ground state of the monopositive or the dipositive ion produced by taking off one or two electrons from $\phi_n$.

Now, in (even) alternant hydrocarbons, $\psi_{n\to n+2}$ and $\psi_{n-1\to n+1}$ belong to the same irreducible representation, and it is easily shown that the following equation holds:

$$\Gamma_{\phi_{n-1}}\Gamma_{\phi_n} = \Gamma_{\phi_{n+1}}\Gamma_{\phi_{n+2}} \tag{6}$$

Moreover, in these molecules, $\psi_{n\to n+2}$ and $\psi_{n-1\to n+1}$ are degenerate, and the first-order configuration interaction between the two states lifts the degeneracy, yielding two separated states, $\psi_\alpha = (\psi_{n\to n+2} - \psi_{n-1\to n+1})/2^{1/2}$ and $\psi_\beta = (\psi_{n\to n+2} + \psi_{n-1\to n+1})/2^{1/2}$. The former is lower in energy than the latter. Note that in highly symmetrical alternant hydrocarbons such as benzene, $\phi_{n+1}$ and $\phi_{n+2}$ as well as $\phi_{n-1}$ and $\phi_n$ are degenerate, and the configuration interactions among the four configurations ($\psi_{n\to n+1}$, $\psi_{n\to n+2}$, $\psi_{n-1\to n+1}$, and $\psi_{n-1\to n+2}$) of equal energy lead to three excited (singlet or triplet) states with different energies.

In anthracene and the higher linear polyacenes, the lowest excited singlet state, called p, is assigned to $\psi_{n\to n+1}$ ($^1L_a$ in Platt's notation, $^1B_{1u}$) and the second one, called $\alpha$, to $\psi_\alpha$ ($^1L_b$, $^1B_{2u}$).[11,12] We now examine the transition density $\rho_{p\alpha}$. It is written in terms of relevant MO's as

$$\rho_{p\alpha} = (\phi_{n-1}\phi_n + \phi_{n+1}\phi_{n+2})/2^{1/2} \tag{7}$$

The first term, $\phi_{n-1}\phi_n$, is nothing but the transition density between the ground and the lowest excited state of the mono- or dipositive ion produced by vacating one or two electrons from $\phi_n$, and the second term, $\phi_{n+1}\phi_{n+2}$, is that of the mono- or dinegative ion produced by placing an extra one or two electrons in $\phi_n$ (the transition densities for the dipositive and dinegative ions are $2^{1/2}\phi_{n-1}\phi_n$ and $2^{1/2}\phi_{n+1}\phi_{n+2}$, respectively). Now, using the pairing theorem that holds for alternant hydrocarbons,[13] we can easily show that the two-center components of $\phi_n\phi_{n'}$ and $\phi_n{}^p\phi_{n'}{}^p$ in bond regions, if $\phi_n$ and $\phi_{n'}$ are bonding orbitals and $\phi_n{}^p$ and $\phi_{n'}{}^p$ are the respective paired antibonding orbitals, are equal in absolute value but opposite in sign, so that values of $\phi_n\phi_{n'} + \phi_n{}^p\phi_{n'}{}^p$ in bond regions are all null. Since $\phi_{n+1}$ and $\phi_{n+2}$ are the paired orbitals of $\phi_n$ and $\phi_{n-1}$, respectively, it turns out thus that the values of $\rho_{p\alpha}$ are zero in all the bond regions. It follows from this fact that although the lowest excited singlet state can, from symmetry considerations, mix with the second one through the $B_{1u} \times B_{2u} = B_{3g}(R_x)$ mode,[12] which gives rise to a molecular-symmetry reduction $D_{2h} \to C_{2h}$; actually it undergoes no molecular-symmetry reduction due to bond distortion, even if the energy separation between the two states is smaller than the critical value. Obviously, the second excited singlet state also does not suffer a molecular-symmetry reduction, for the second excited singlet state and the third one ($\beta$, $^1B_b$, $^1B_{2u}$) have the same symmetry.

In naphthalene, phenanthrene, benzophenanthrenes exclusive of triphenylene, pyrene, and picene,[11] and polyenes,[14] the lowest excited singlet state correpsonds to $\psi_\alpha$ ($A_g{}^-$ in *trans*-polyenes) and the second one to $\psi_{n\to n+1}$ ($B_u{}^+$ in *trans*-polyenes). Therefore, the lowest excited singlet states in these molecules are expected, from the reason mentioned above, not to suffer a molecular-symmetry reduction due to bond distortion. In the polycyclic hydrocarbons under consideration, the third excited singlet state corresponds to $\psi_\beta$ ($^1B_b$), and the transition density between the second and the third excited state, $\rho_{p\beta}$, is given as

$$\rho_{p\beta} = (\phi_{n+1}\phi_{n+2} - \phi_{n-1}\phi_n)/2^{1/2} \tag{8}$$

Since the two-center components of $\rho_{p\beta}$ in bond regions are not vanishing and the distribution of $\rho_{p\beta}$ in bond regions is nontotally symmetric in general, a molecular-symmetry reduction due to bond distortions would occur in the second excited singlet state if it is allowed energetically. Equation 8 indicates further that the second excited state, if it suffers a molecular-symmetry reduction, should belong to the same point group as the ground state of the mono- or dipositive ion as well as of the mono- or dinegative ion.

In highly symmetrical alternant hydrocabrons such as benzene, [18]annulene, coronene, and triphenylene (except [30]annulene, which suffers a molecular-symmetry reduction, $D_{6h} \to D_{3h}$, in the ground state),[6b] the lowest excited singlet state corresponds to $\psi_\alpha$ ($^1L_b$, $^1B_{2u}$ ($A_1{}'$ in triphenylene)) and the second one, called p, to $\psi_p$ ($^1L_a$, $^1B_{1u}$ ($A_2{}'$ in triphenylene)), with $\psi_p$ for these molecules expressed as $\psi_p = (\psi_{n\to n+1} + \psi_{n-1\to n+2})/2^{1/2}$; $\phi_{n-1}$ and $\phi_n$ are now a pair of the highest bonding degenerate real MO's, and $\phi_{n+1}$ and $\phi_{n+2}$ are a pair of the lowest antibonding degenerate real MO's. It is easily shown that $\rho_{\alpha p} \equiv 0$ and in these molecules also the lowest excited state does not undergo a molecular-symmetry reduction due to bond distortion. The third excited singlet state in these molecules is doubly degenerate and corresponds to $\psi_\beta$ ($B_b$, $E_{1u}$ ($E_1{}'$ in triphenylene)) and $\psi_{\beta'}$ ($B_a$, $E_{1u}$ ($E_1{}'$ in triphenylene)), with $\psi_{\beta'}$ expressed as $\psi_{\beta'} = (\psi_{n\to n+1} - \psi_{n-1\to n+2})/2^{1/2}$. The transition densities between the second and third excited state are given by

$$\rho_{p\beta} = \phi_{n+1}\phi_{n+2} - \phi_{n-1}\phi_n \tag{9}$$

$$\rho_{p\beta'} = ({\phi_{(n-1)}}^2 - {\phi_n}^2 + {\phi_{(n+1)}}^2 - {\phi_{(n+2)}}^2)/2 \tag{10}$$

Since the two-center components of both $\rho_{p\beta}$ and $\rho_{p\beta'}$ in bond regions are not vanishing in general, a molecular-symmetry reduction due to bond distortions would occur in the second excited state if it is allowed energetically.

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On the other hand, since in the monopositive and mononegative ions of these molecules the ground state is (doubly) degenerate, in order to predict its geometrical structure, we must invoke the first-order Jahn–Teller effect. The value of the matrix element $\langle\psi_0|\partial H/\partial Q_\nu|\psi_0\rangle$ appearing in the second term in eq 1 is now crucial. Like eq 3, the matrix element is rewritten as

$$\left\langle \psi_0 \left| \frac{\partial H}{\partial Q_\nu} \right| \psi_0 \right\rangle = \int \rho_{00} \frac{\partial V}{\partial Q_\nu} dv \qquad (11)$$

where $\rho_{00}$ is the charge density of the ground state. $\rho_{00}$ comprises two components; one is totally symmetric and the other is nontotally symmetric. In the monopositive ions, the symmetric product of the irreducible representation of the ground state ($E_{1g}$ for molecules belonging to $D_{6h}$ or $E''$ for triphenylene ($D_{3h}$)) is $[E_{1g} \times E_{1g}]^+ = A_{1g} + E_{2g}$ or $[E'' \times E'']^+ = A_1' + E'$, and in the mononegative ions, it is $[E_{2u} \times E_{2u}]^+ = A_{1g} + E_{2g}$ or $[E'' \times E'']^+ = A_1' + E'$. Of course, the nontotally symmetric component ($E_{2g}$ or $E'$) is responsible for the first-order Jahn–Teller effect. The nontotally symmetric component of $\rho_{00}$ for the monopositive ions is given by $\phi_{n-1}\phi_n$ and $(\phi_{(n-1)}{}^2 - \phi_n{}^2)/2$ and that for the mononegative ions by $\phi_{n+1}\phi_{n+2}$ and $(\phi_{(n+1)}{}^2 - \phi_{(n+2)}{}^2)/2$. Using the pairing theorem, we can show that the bond charges of $(\phi_{(n+1)}{}^2 - \phi_{(n+2)}{}^2)/2$ are equal to those of $(\phi_{(n-1)}{}^2 - \phi_n{}^2)/2$.

In the dipositive and dinegative ions of these molecules, there are four ways of assigning two electrons to the degenerate MO's. Inclusion of electron interaction gives rise to the following three states in order of increasing energy: the triplet state ($A_{2g}$ for molecules belonging to $D_{6h}$ or $A_2'$ for triphenylene), a pair of the degenerate singlet states ($E_{2g}$ or $E'$), and the singlet state ($A_{1g}$ or $A_1'$). Here, we are concerned only with the singlet states. Since the lowest singlet state ($E_{2g}$ or $E'$) is doubly degenerate, we first consider the first-order Jahn–Teller effect. However, it is easily shown that for the lowest singlet state, $\rho_{00}$ ($E_{2g}$ or $E'$) $\equiv 0$, so that the first-order Jahn–Teller effect is not operative in this state. We next examine the second-order Jahn–Teller effect. The transition density between the lowest ($E_{2g}$ or $E'$) and the second ($A_{1g}$ or $A_1'$) singlet state is now important. It is given by $2\phi_{n-1}\phi_n$ and $(\phi_{(n-1)}{}^2 - \phi_n{}^2)$ for the dipositive ions and by $2\phi_{n+1}\phi_{n+2}$ and $(\phi_{(n+1)}{}^2 - \phi_{(n+2)}{}^2)$ for the dinegative ions.

It is thus concluded that in the molecules under consideration, the second excited singlet state suffers the same type of bond distortion as the ground states of the dipositive and dinegative ions as well as of the monopositive and mononegative ions. All these states undergo the same type of molecular-symmetry reduction, if it is energetically allowed, and all the states, if distorted, should belong to the same point group.

Finally, it follows from eq 6 and the consideration given above that the ground states of the mono- and dipositive and mono- and dinegative ions of an alternant hydrocarbon suffer the same type of bond distortion and undergo the same type of molecular-symmetry reduction, if it is energetically allowed, and the ground states of all the charged ions should always belong to the same point group.

In case of nonalternant hydrocarbons, the clear-cut rule obtained above does not hold, in general.

## Applications

**Benzene.** The geometrical structures of lower excited states of benzene predicted by using the SCF MO method are as follows: the lowest excited singlet state, $^1B_{2u}$ ($\alpha$), has the expanded regular hexagonal structure with C–C bond lengths equal to 1.428 Å, while both the second excited singlet state, $^1B_{1u}$ (p), and the lowest excited triplet state, $^3B_{1u}$, are distorted and have $D_{2h}$ symmetry (Figure 2).[10,15,16] On the other hand, the geometrical structures of the radical anion and cation of benzene have been predicted by Moffit and Liehr,[17] Hobey and McLachlan,[18] Snyder,[19] Coulson and Golebiewski,[20] Nakayama and I'Haya,[21] and Hinde et al.[22] All the results agree that in both ions the optimized structures are the quinoid or antiquinoid forms with $D_{2h}$ symmetry, the energy difference between the two forms being very small.

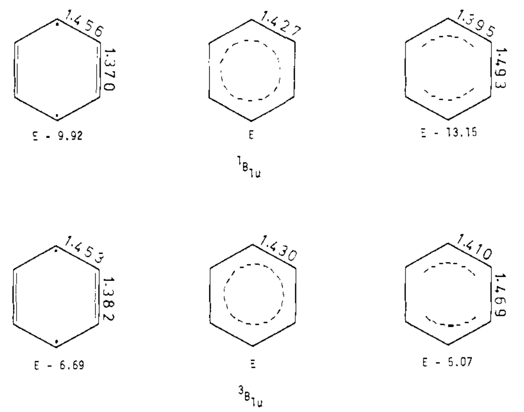

**Figure 2.** Predicted equilibrium geometrical structures and their energies for the $^1B_{1u}$ and $^3B_{1u}$ states of benzene (bond lengths in Å and energies in kcal mol$^{-1}$).

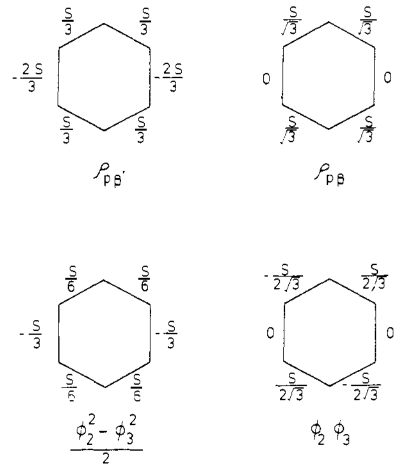

**Figure 3.** Transition densities $\rho_{p\beta'}$ and $\rho_{p\beta}$ in bond regions of benzene, and the bond charges of the $E_{2g}$ components of the charge densities, $(\phi_2{}^2 - \phi_3{}^2)/2$ and $\phi_2\phi_3$, of the ground state of the radical cation. S is the overlap density between the neighboring atomic orbitals.

In Figure 3 are shown the distributions (in bond regions) of the transition densities between the second (p) and the third ($\beta$, $\beta'$) excited singlet state, $\rho_{p\beta'} = (\phi_2{}^2 - \phi_3{}^2 + \phi_4{}^2 - \phi_5{}^2)/2$ and $\rho_{p\beta} = \phi_4\phi_5 - \phi_2\phi_3$, together with those of the charge densities $(\phi_2{}^2 - \phi_3{}^2)/2$ and $\phi_2\phi_3$, both of which are the $E_{2g}$ components of the charge density in the ground state ($E_{1g}$) of the radical cation.[23] The $E_{2g}$ components of the charge density in the ground state ($E_{2u}$) of the radical anion are given by $(\phi_4{}^2 - \phi_5{}^2)/2$ and $\phi_4\phi_5$. The bond charges of $(\phi_4{}^2 - \phi_5{}^2)/2$ and $\phi_4\phi_5$ are equal to those of $(\phi_2{}^2 - \phi_3{}^2)/2$ and $-\phi_2\phi_3$, respectively. The distributions of $\rho_{p\beta'}$, $(\phi_2{}^2 - \phi_3{}^2)/2$, and $(\phi_4{}^2 - \phi_5{}^2)/2$ in bond regions match with the bond distortions that lead to a quinoid or an antiquinoid form. The bond distortions corresponding to $\rho_{p\beta}$, $\phi_2\phi_3$, and $\phi_4\phi_5$ are important in producing the variously oriented quinoid and antiquinoid forms around the molecular periphery (pseudorotation).[15,16,24] Since the second excited triplet state is $^3E_{1u}$, the lowest excited triplet state also should undergo the same type of bond distortion as the ground state of the radical anion or cation.

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(23) $\phi_2 = (1/3^{1/2})\sum_r \cos(\pi r/3)\chi_r$ and $\phi_3 = (1/3^{1/2})\sum_r \sin(\pi r/3)\chi_r$ are a pair of the highest bonding degenerate MO's, and $\phi_4 = (1/3^{1/2})\sum_r \sin(2\pi r/3)\chi_r$ and $\phi_5 = (-1/3^{1/2})\sum_r \cos(2\pi r/3)\chi_r$ are that of the lowest antibonding degenerate MO's.

(24) Reference 13, pp 473–381.

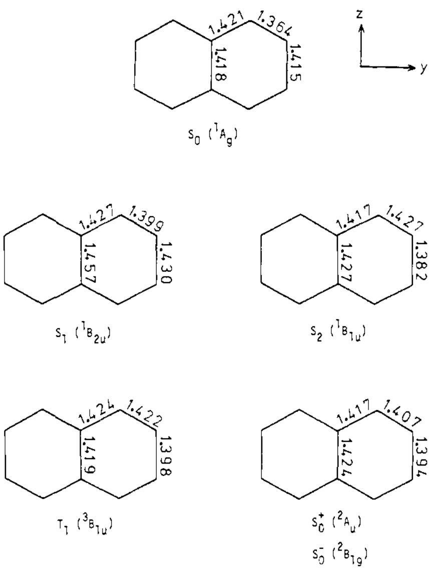

**Figure 4.** Predicted bond lengths (in Å) in the ground state ($S_0$) and the lower excited states ($S_1$, $S_2$, and $T_1$) of naphthalene and those in the ground states of the naphthalene radical cation ($S_0^+$) and anion ($S_0^-$).

The energy gap between the second and the third excited singlet state, $E(^1E_{1u}) - E(^1B_{1u})$, is calculated to be 0.62 eV and found experimentally to be ca. 0.8 eV. For the energy gap between the lowest and the second excited triplet state, $E(^3E_{1u}) - E(^3B_{1u})$, we use the observed value, ca. 0.9 eV; for the energies of triplet states the values calculated by using the present semiempirical MO method are not so accurate. These values are probably smaller than the critical value for the occurrence of the pseudo Jahn–Teller effect in the excited states, which in this case should be larger than the ca. 0.60 eV obtained earlier, for both the second and the third excited state are expressed by the configuration mixtures of MO transitions.

The difference in energy between the quinoid and antiquinoid forms in $^1B_{1u}$, $^3B_{1u}$, and the ground states of the radical cation and anion cannot be obtained on the basis of the second-order Jahn–Teller effect. In order to determine which of the two forms correpsonds to the energy minimum, the third-order Jahn–Teller effect should be invoked.[25]

**Naphthalene.** The calculated bond lengths in the lower excited states of naphthalene are shown in Figure 4. The lowest excited singlet state, $^1B_{2u}$ ($\alpha$), retains the $D_{2h}$ symmetry, although the second excited singlet state, $^1B_{1u}$ (p), is higher in energy than the lowest one only by 0.48 eV, and the symmetry of $\rho_{\alpha p}$ is $B_{2u} \times B_{1u} = B_{3g}$ ($R_x$). This is ascribed to the fact that the values of $\rho_{\alpha p}$ in bond regions are actually all zero. The second excited singlet state, $^1B_{1u}$ (p), also is predicted to be of $D_{2h}$ symmetry. The reason for this is that the energy gap between the second excited singlet state and the third one, $B_{2u}$ ($\beta$), is fairly large (1.15 eV), although the values of $\rho_{p\beta}$ ($B_{3g}$) in bond regions are not all zero. The lowest excited triplet state, $T_1$ ($B_{1u}$), corresponds to MO transition $\phi_5 \rightarrow \phi_6$ and the second one, $T_2$ ($B_{3g}$), is written as $^3\psi_2 = (\psi_{5\rightarrow 8} - \psi_{3\rightarrow 6})/2^{1/2}$. The transition density between the two states is then written in terms of relevant MO's as $\rho_{T_1T_2} = (\phi_3\phi_5 + \phi_6\phi_8)/2^{1/2}$, which is vanishing in bond regions. It is thus expected that the lowest excited triplet state will not undergo a molecular-symmetry reduction, which is supported by the result obtained by using the SCF MO method (Figure 4).

The ground states of both the radical anion and cation are predicted to belong to the full molecular symmetry $D_{2h}$ (Figure 4). This is due to the fact that the lowest excitation energies of both ions are calculated to be ca. 1.5 eV, which is larger than the critical value for the occurrence of the pseudo Jahn–Teller distortion. The critical value for the ground state of a radical ion should be smaller than that (ca. 1.2 eV) for the closed-shell ground state, if the (lowest) excited doublet state is expressed by a single MO transition, say, $\phi_i \rightarrow \phi_j$. This is because in this case the transition density is given by $\phi_i\phi_j$ instead of $2^{1/2}\phi_i\phi_j$ for the closed-shell case. In the radical cation and anion of naphthalene, the lowest excited states correspond to MO transitions $\phi_4 \rightarrow \phi_5$ and $\phi_6 \rightarrow \phi_7$, respectively.

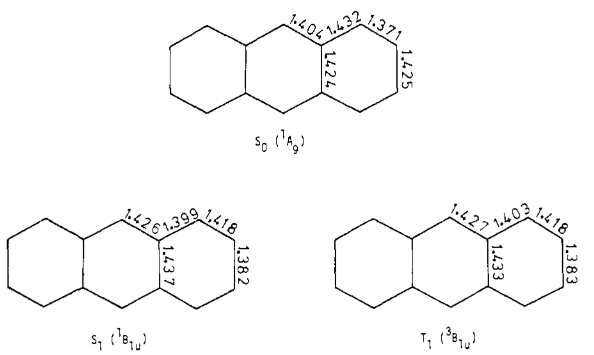

**Figure 5.** Predicted bond lengths (in Å) in the ground state ($S_0$), the lowest excited singlet state ($S_1$), and the lowest excited triplet state ($T_1$) of anthracene.

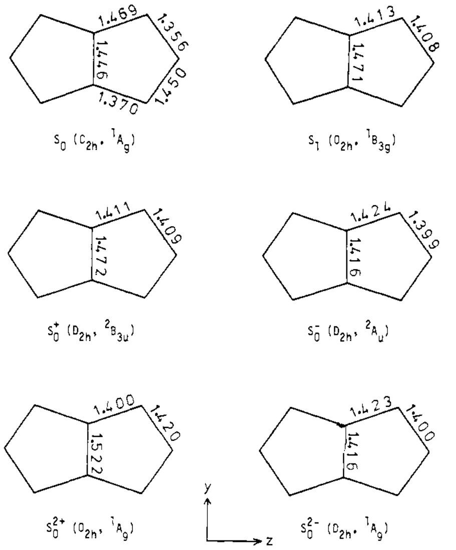

**Figure 6.** Predicted bond lengths (in Å) in the ground state ($S_0$) and the lowest excited singlet state ($S_1$) of pentalene and those in the ground states of the radical cation ($S_0^+$), the radical anion ($S_0^-$), the dipositive ion ($S_0^{2+}$), and the dinegative ion ($S_0^{2-}$) of pentalene.

**Anthracene.** The bond lengths calculated using the SCF MO method in the ground state, $S_0$, the lowest excited singlet state, $S_1$ (p, $L_a$, $B_{1u}$), and the lowest excited triplet state, $T_1$ ($L_a$, $B_{1u}$), of anthracene are shown in Figure 5. As is expected from the general theory, $S_1$ suffers no molecular-symmetry reduction, even though the energy gap ($E_2 - E_1$) is very small (0.26 eV). The lowest excited triplet state corresponds to MO transition $\phi_7 \rightarrow \phi_8$, and the second one, $T_2$ ($B_{3g}$), is written as $^3\psi_2 = (\psi_{7\rightarrow 10} - \psi_{5\rightarrow 8})/2^{1/2}$. The transition density between the two states is then given as $\rho_{T_1T_2} = (\phi_5\phi_7 + \phi_8\phi_{10})/2^{1/2}$, which is vanishng in all the bond regions. It is thus expected that $T_1$ also suffers no molecular-symmetry reduction. Actually, the calculated bond lengths in $T_1$ are almost the same as those in $S_1$.

**Pentalene.** In the ground state of pentalene, the molecular-symmetry reduction $D_{2h} \rightarrow C_{2h}$ occurs, and in its periphery there exists a strong bond alternation (Figure 6).[6,26] This is due to the fact that if the molecular symmetry is assumed to be $D_{2h}$, the lowest singlet excitation energy ($E_1 - E_0$) is calculated to be 0.35 eV, which is much smaller than the critical value (1.2 eV), and the distribution of $\rho_{01}$ ($B_{3g}$ ($R_x$)) in bond regions matches with the C–C stretching mode of bond alternation type. On the other

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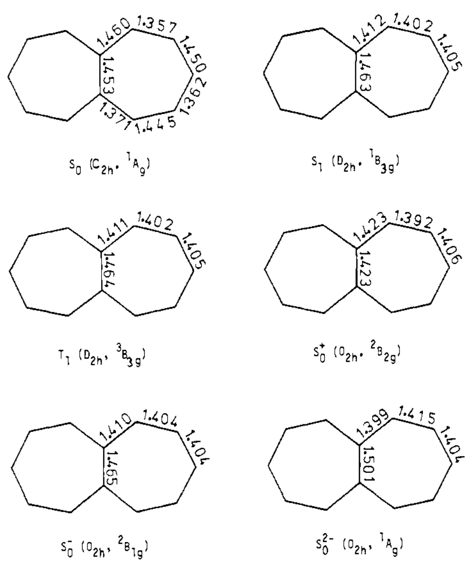

**Figure 7.** Predicted bond lengths (in Å) in the ground state ($S_0$) and the lowest excited singlet ($S_1$) and triplet ($T_1$) states of heptalene and those in the ground states of the radical cation ($S_0^+$), the radical anion ($S_0^-$), and the dinegative ion ($S_0^{2-}$) of heptalene.

hand, the first excited singlet state ($^1B_{3g}$) is expected to have the full molecular symmetry ($D_{2h}$), for the energy gap ($E_2 - E_1$) is quite large (3.23 eV). This is in agreement with the results of the SCF MO calculation (Figure 6).[10]

The ground states of the radical cation ($S_0^+$), the dipositive ion ($S_0^{2+}$), the radical anion ($S_0^-$), and the dinegative ion ($S_0^{2-}$) of pentalene are all expected to be of $D_{2h}$ symmetry, for the lowest excitation energies calculated by assuming the $D_{2h}$ symmetry, 1.50, 2.01, 1.77, and 4.66 eV, respectively, are all certainly larger than the critical value for the occurrence of the pseudo Jahn–Teller distortion. This expectation is supported by the results obtained by using the SCF MO method (Figure 6). The geometrical structures of the first excited singlet state of pentalene and the ground states of the above four charged ions of pentalene all resemble one another in the sense that $\pi$ electrons are delocalized throughout the molecular periphery. Thus, it may be said that aromaticity of pentalene increases by promoting it to the lowest excited state or by adding or taking off one or two electrons.

**Heptalene.** A quite similar situation is observed in heptalene (Figure 7).[6,10,27] The ground state undergoes a molecular-symmetry reduction from $D_{2h}$ to $C_{2h}$, since the energy separation ($E_1 - E_0$) is only 0.26 eV and the symmetry of $\rho_{01}$ is $B_{3g}$. On the other hand, the lowest excited singlet state ($S_1$) retains the full molecular symmetry ($D_{2h}$), since the second excited singlet state is well separated from the lowest one ($E_2 - E_1$ = 2.42 eV). The lowest excited triplet state ($T_1$) has almost the same geometrical structure as $S_1$. The marked difference in geometrical structure with respect to C–C bond lengths between the ground and the lowest excited singlet state provides probably the main reason for the appearance of a long absorption tail covering the whole visible region in the electronic spectrum.[28]

The lowest excitation energies of the radical cation and anion of heptalene calculated by assuming the $D_{2h}$ symmetry are 1.19 and 1.02 eV, respectively. These values are probably larger than the critical value for the occurrence of the pseudo Jahn–Teller distortion, which in this case is expected to be fairly smaller than ca. 1.2 eV. The lowest excitation energy for the dinegative ion of heptalene is calculated to be 1.43 eV. Therefore, the ground states of the above charged ions of heptalene are all predicted to have the $D_{2h}$ symmetry (Figure 7).

**Pentafulvalene.** Pentafulvalene is particularly interesting in the sense that it forms an exception to the Walsh–Pearson rule. The MO transitions for the various lower electronic excitations in this molecule are shown in Figure 8, and the corresponding excitation energies are listed in Table I.

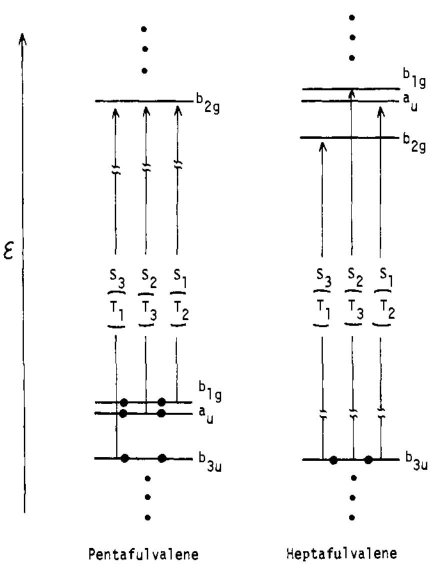

**Figure 8.** Schematic arrangements of molecular orbitals and the MO transitions for lower electronic excitations in pentafulvalene and heptafulvalene.

Table I. Excitation Energies for the Lower Excited Singlet and Triplet States of Pentafulvalene and Heptafulvalene

| pentafulvalene | | heptafulvalene | |
|---|---|---|---|
| state | $E_n - E_0$, eV | state | $E_n - E_0$, eV |
| $S_1$ ($B_{3g}$) | 2.00 | $S_1$ ($B_{3g}$) | 2.04 |
| $S_2$ ($B_{2u}$) | 2.06 | $S_2$ ($B_{2u}$) | 2.11 |
| $S_3$ ($B_{1u}$) | 3.67 | $S_3$ ($B_{1u}$) | 3.09 |
| $T_1$ ($B_{1u}$) | 0.87 | $T_1$ ($B_{1u}$) | 0.86 |
| $T_2$ ($B_{3g}$) | 1.48 | $T_2$ ($B_{3g}$) | 1.64 |
| $T_3$ ($B_{2u}$) | 1.49 | $T_3$ ($B_{2u}$) | 1.65 |

In pentafulvalene, the highest two occupied orbitals ($b_{1g}$ and $a_u$) are nearly degenerate (in the HMO approximation these orbtials are accidentally degenerate), and the second excited singlet state ($S_2$) is very close to the lowest one ($S_1$). It is expected therefore that the lowest excited singlet state undergoes a strong pseudo Jahn–Teller distortion. The molecular symmetry should be reduced from $D_{2h}$ to $C_{2v}$, for the symmetry of $\rho_{12}$ is $B_{3g} \times B_{2u} = B_{1u}$ ($z$). On the other hand, in the radical cation, the ground state, $S_0^+$ ($^2B_{1g}$), in which the highest MO ($b_{1g}$) of the neutral molecule is half-filled, and the lowest excited doublet state ($^2A_u$) corresponding to the MO transition $\phi_{a_u} \rightarrow \phi_{b_{1g}}$ are nearly degenerate, the energy separation between the two states being only 0.002 eV. It is therefore expected that since $B_{1g} \times A_u = B_{1u}$ ($z$), the ground state of the radical cation undergoes the same type of bond distortion as the lowest excited singlet state of the neutral molecule, and both the states belong to $C_{2v}$. The prediction is supported by the results obtained by using the SCF MO method (Figure 9). The geometrical structures of $S_1$ and $S_0^+$ closely resemble each other. In both states, the strong bond alternation throughout the whole molecule existing in the ground state of the neutral molecule ($S_0$) is half-relaxed: a strong bond alternation still exists in one of the rings, and bond alternation is significantly relaxed in the other ring (see Figure 9). The longest wavelength absorption band of pentafulvalene is fairly broad.[29] This may possibly be due to the large difference in geometrical structure between $S_0$ and $S_1$.

The lowest excited triplet state ($T_1$) maintains the full molecular symmetry ($D_{2h}$). This is ascribed to the fact that the second

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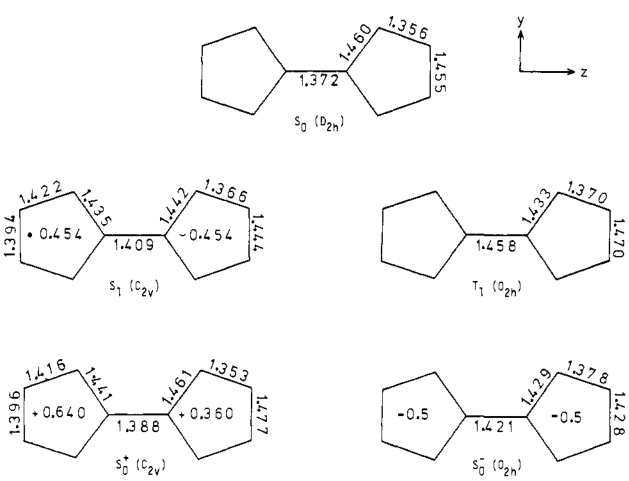

Figure 9. Predicted bond lengths (in Å) in the ground state ($S_0$) and the lowest excited singlet ($S_1$) and triplet ($T_1$) states of pentafulvalene and those in the ground states of the radical cation ($S_0^+$) and anion ($S_0^-$). The figures inside the five-membered rings are the ring charge densities.

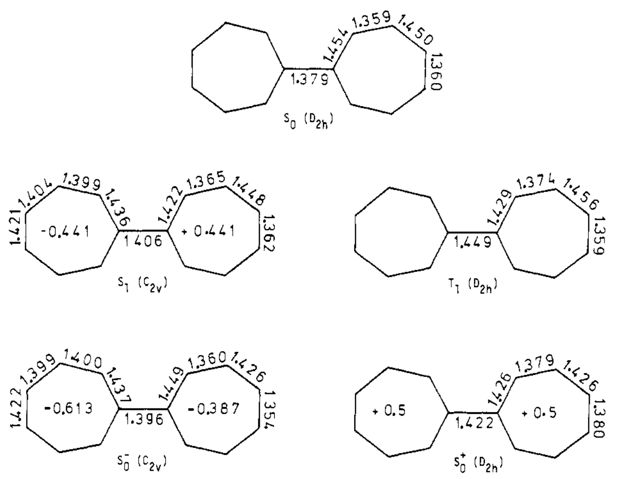

Figure 10. Predicted bond lengths (in Å) in the ground state ($S_0$) and the lowest excited singlet ($S_1$) and triplet ($T_1$) states of heptafulvalene and those in the ground states of the radical anion ($S_0^-$) and cation ($S_0^+$). The figures inside the rings are the ring charge densities.

excited triplet state ($T_2$) is comparatively well separated from the lowest one. The geometrical structure of the ground state of the radical anion ($S_0^-$) in which the extra electron enters into $\phi_{b_{2g}}$ resembles well that of $T_1$, both $S_0^-$ and $T_1$ belonging to $D_{2h}$ (Figure 9). The lowest excited doublet state in the radical anion is separated from the ground state by 1.23 eV. This value is probably larger than the critical value for the occurrence of the pseudo Jahn–Teller distortion for the open-shell case.

A higher homologue of pentafulvalene, nonafulvalene, which is composed of two nine-membered rings, is expected to form a similar exception to the Walsh–Pearson rule.[30] In this molecule, as in pentafulvalene, the highest two occupied Hückel MO's are accidentally degenerate, and $S_1$ and $S_2$ are very close in energy.

**Heptafulvalene.** In heptafulvalene, the situation is quite different (Figure 8). The molecular orbitals that are nearly degenerate are unoccupied orbitals, $\phi_{a_u}$ and $\phi_{b_{1g}}$, relevant respectively to the first and second excited singlet states (in HMO approximation these orbitals are accidentally degenerate). The first excited singlet state, $S_1$ ($B_{3g}$), and the second one, $S_2$ ($B_{2u}$), are very close in energy (Table I), so that a strong pseudo Jahn–Teller bond distortion is expected in $S_1$, the symmetry of bond distortion being $B_{3g} \times B_{2u} = B_{1u}$ (z). In the radical anion, the extra electron is added in $\phi_{a_u}$. The lowest excited doublet state ($^2B_{1g}$) corresponds to the MO transition $\phi_{a_u} \rightarrow \phi_{b_{1g}}$ and is higher in energy than the ground state only by 0.03 eV. Therefore, since $A_u \times B_{1g} = B_{1u}$ (z), the ground state of the radical aion ($S_0^-$) is predicted to undergo the same type of pseudo Jahn–Teller bond distortion as $S_1$ of the neutral molecule. The bond-length distributions calculated by using the SCF MO method shown in Figure 10 indicate that $S_1$ and $S_0^-$ belong to the same point group ($C_{2v}$) and closely resemble each other in molecular shape. As in $S_1$ and $S_0^+$ of pentafulvalene, in $S_1$ and $S_0^-$ of heptafulvalene, a strong bond alternation exists in one of the rings, and bond lengths are nearly equalized in the other ring. The large difference in geometrical structure between $S_1$ and $S_0$ in which a strong bond alternation throughout the whole molecule exists is responsible for the appearance of the long absorption tail throughout the visible region in the electronic spectrum of heptafulvalene.[29]

The second excited triplet state ($T_2$) of the neutral molecule is fairly well separated from the lowest one ($T_1$) (Table I), and in the radical cation, the lowest excited doublet state is higher in energy than the ground state by 1.31 eV. The prediction thus obtained that both $T_1$ and $S_0^+$ will belong to the full molecular symmetry $D_{2h}$ and the geometrical structures of them resemble each other is supported by the results obtained by using the SCF method (Figure 10).

## Conclusions

The concept of the pseudo Jahn–Teller effect, which has been known to work well in predicting the molecular symmetries and the geometrical structures with respect to C–C bond lengths of the ground states of conjugated hydrocarbons, is useful in predicting those of the lower excited states as well. The only trouble is that the critical value of the energy gap for the occurrence of the pseudo Jahn–Teller effect is not uniquely determined and varies according to the configurations of excited states. However, the energy-gap criterion proposed by assuming that the values of the matrix elements in terms of MO's do not vary greatly according to the MO's employed seems to have been justified by the fact that it works for various molecules treated in this paper.

The Walsh–Pearson rule that the lowest excited state of a molecule should belong to the same point group as the ground states of its mono- or dinegative ions turned out to be insufficient for alternant hydrocarbons and not to hold for nonalternant hydrocarbons of a certain type. It was shown that in alternant hydrocarbons, there exists a clear-cut rule that the lowest excited singlet state does not undergo a pseudo Jahn–Teller bond distortion and belongs to the same point group as the ground state. Moreover, in highly symmetrical alternant hydrocarbons such as benzene, the excited state that suffers the same type of bond distortion and belongs to the same point group as the ground states of the mono- and dinegative ions is the second excited singlet and the lowest excited triplet state. These states belong further to the same point group as the ground states of the mono- and dipositive ions. In pentafulvalene and nonafulvalene, in which the highest two occupied MO's are nearly degenerate, the lowest excited singlet state belongs not to the same point group as the ground state of the radical anion but to the same point group as the ground state of the radical cation.

**Registry No.** Benzene, 71-43-2; naphthalene, 91-20-3; anthracene, 120-12-7; pentalene, 250-25-9; heptalene, 257-24-9; pentafulvalene, 91-12-3; heptafulvalene, 531-45-3.

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