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Effects of Electron-Withdrawing Substituents on Bond Alternations in Pentalene and Heptalene

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The bond alternations in pentalenes and heptalenes substituted by electron-withdrawing groups are studied by use of the Pariser–Parr–Pople-type SCF CI MO method and the symmetry rule for substituted conjugated hydrocarbons. The influence of electron-withdrawing substituents on geometrical structures of pentalene and heptalene markedly depends on the attached positions. The 2- and 5-substitutions in pentalene and the 1-, 3-, 5-, 6-, 8-, and 10-substitutions in heptalene increase the amount of positive charge and, at the same time, relax the bond alternations in the parent molecules. This relaxation correlates with the amount of the positive charge in the pentalene and heptalene skeletons. The large amount of positive charge brings about the stabilization of the delocalized structures. The critical values of positive charge for the existence of bond alternations are smaller than the unit positive charge. The substitutions at the other sites in both molecules are anomalous in the sense that they increase the amount of the positive charge but reinforce the bond alternations.

In a previous paper, we have examined the bond alternation in the pentalene and heptalene molecules substituted by electron-donating groups.[1] These substituents affect the bond alternations inherent to pentalene and heptalene in a different way, depending on attached positions. This position dependence is related to the π-electron density in the HOMO and LUMO; these MO's are confined to mutually different regions, as shown in Fig. 1. When an electron-donating group is introduced at a position having large amplitudes in LUMO, the amount of negative charge in the parent molecule largely increases and the bond alternation inherent to the carbon skeleton is relaxed. This can be interpreted as the transition from [4N] to [4N+2] π-electronic system.[2] In contrast to this, the substitution at positions having large amplitudes in HOMO increases the amount of negative charge only slightly and enhances the bond alternation. The substituent effect on geometrical structures of nonbenzenoid hydrocarbons has first been experimentally studied by Hafner for pentalene and *s*-indacene.[2] The theoretical research on the substituent effect has been developed by Heilbronner and Yang,[3] using the modified double-bond fixation theory.[4]

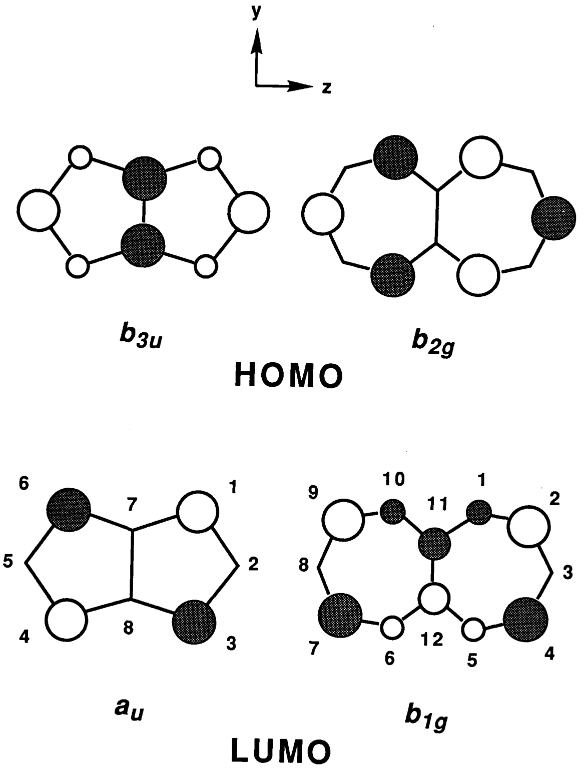

Fig. 1. Frontier molecular orbitals of the D_{2h} pentalene (left) and the D_{2h} heptalene (right).

The present paper extends the previous study to the effect of electron-withdrawing substituents on the bond alternations in pentalene and heptalene. Using the second-order perturbation theory and the symmetry rule,[5,6] we propose a general rule for the existence of bond alternation in these substituted molecules. To calculate the excitation energies and the amount of electron flow from the parent molecule to an electron-withdrawing substituent, we use the Pariser–Parr–Pople (PPP)-type SCF CI MO method.[6,7]

Theoretical Consideration

Symmetry Rule. We have previously discussed in detail the general rule for the existence of bond alternation in substituted conjugated hydrocarbons[1] and hence only outline it in the present paper. A fully symmetrical nuclear configuration for a conjugated hydrocarbon is assumed and then allowed to distort from the original nuclear arrangement along a C–C nuclear displacement Q. By using the second-order perturbation theory, the ground-state energy, E, after the bond distortion can be written as

$$E=E_0+\frac{1}{2}\Big[k-2\sum_{n\neq 0}\frac{|H'_{0n}|^2}{E_n-E_0}\Big]Q^2, \qquad (1)$$

where k is the force constant for the C–C σ-bond, and E_0 and E_n are, respectively, the energies of the ground and the nth excited state. The matrix element H'_{0n} can be described as $\int \rho_{0n}(\partial H_\pi / \partial Q)\mathrm{d}v$, where H_π is the Hamiltonian for π electrons, and ρ_{0n} is the transition density between the ground and the nth excited state. Nakajima et al. have proposed a rule for the existence of bond alternation in unsubstituted conjugated hydrocarbons: If the energy gap of the fully symmetrical nuclear arrangement, $(E_1 - E_0)$, is calculated to be smaller than ca. 1.2 eV, the molecule should be distorted into a less symmetrical structure.[6] The most favorable bond distortion is predicted by examining the transition density ρ_{01}.[6,8] In pentalene and heptalene the molecular symmetry reduction ($D_{2h} \rightarrow C_{2h}$) occurs along a bond-alternating mode.[6]

In predicting the bond distortions in substituted hydrocarbons, the above criterion should be modified because the introduction of a substituent changes the value of the matrix element in Eq. 1 from molecule to molecule, depending on the nature and attached positions of the substituent. A criterion useful for substituted molecules should thus involve both the energy gap and the matrix element. Since we are interested in the bond alternation in the carbon skeleton of a parent molecule, we extract the transition density of the parent molecule, $\rho_{01}(\mathrm{p})$, from that of a substituted molecule, $\rho_{01}(\mathrm{s})$, which can be expressed as $\rho_{01}(\mathrm{s}) = A\rho_{01}(\mathrm{p}) +$ the other components. Here, A is the numerical factor, which satisfies $|A| < 1$. Assuming the force constant k to be unchanged between a substituted molecule and the parent one, we define the following index I:

$$I = \frac{1.2A^2}{(E_1 - E_0)/\mathrm{eV}}, \qquad (2)$$

where the factor of 1.2 is the critical value mentioned above. When we go from an unsubstituted molecule to a substituted one, the critical value for the existence of bond distortion is modified from 1.2 eV to I, which turns out to be ca. 1.0. The new rule is thus derived as follows: the original fully symmetrical nuclear arrangement is stable if $I <$ ca. 1.0, and unstable if $I >$ ca. 1.0. In the latter case, the energy should be lowered along the bond-alternating mode, with the result that the molecular symmetry is reduced.

Substituent Effects. Now, we examine the dependence of I on the position of an electron-withdrawing substituent CX, such as the cyano group (CN) having an occupied π-orbital $\phi_{\mathrm{cx}}{}^{\mathrm{o}}$ and an unoccupied one $\phi_{\mathrm{cx}}{}^{\mathrm{u}}$. Such a substituent accepts excess electrons through the mixing of the unoccupied orbital, $\phi_{\mathrm{cx}}{}^{\mathrm{u}}$, with the occupied orbitals, especially, HOMO, of a parent molecule. When the first excited state corresponds to the one-electron jump from HOMO to LUMO, the interaction of $\phi_{\mathrm{cx}}{}^{\mathrm{u}}$ and HOMO widens the energy gap $(E_1 - E_0)$. This reduces the index I and hence stabilizes the delocalized structure. The most effective interaction, which most efficiently increases the amount of positive charge (ΔN) in the parent molecule, is caused by the substituent at the position that has the largest coefficient of HOMO.

From the HOMO and LUMO in Fig. 1, one sees that in pentalene, the 2-, or 5-substitution leads to a small I and a large amount of the transferred electron (ΔN) because of the large coefficients at these positions in HOMO. This means that the increase in the positive charge of the pentalene skeleton stabilizes the fully symmetrical structure. Figure 1 also shows that $\phi_{\mathrm{cx}}{}^{\mathrm{u}}$ mainly interacts with LUMO at C1, C3, C4, or C6. This interaction may increase or decrease the energy gap $(E_1 - E_0)$, depending on the relative arrangement of the energy level of $\phi_{\mathrm{cx}}{}^{\mathrm{u}}$. In a weakly electron-withdrawing substituent such as CN, in which $\phi_{\mathrm{cx}}{}^{\mathrm{u}}$ is higher in energy than LUMO, the energy gap is reduced in general. In such a case, 1-, 3-, 4-, or 6-substitution produces a small ΔN but a large I. This is anomalous in the sense that the increase in positive charge is accompanied by the enhancement of bond alternation.

In heptalene, 2-, 4-, 7-, or 9-substitution is anomalous because it enhances the bond alternation in spite of the decrease in ΔN. Substitutions at the other positions are normal: They increase the positive charge of heptalene skeleton, and relax the bond alternation inherent to it.

Results and Discussion

We make the semiempirical model calculations on the three types of polysubstituted pentalene molecules; 2-substituted pentalene (denoted by P2), P25, and P1235, as well as the four substituted heptalenes; H3, H38, H158, and H2348. All the substituents in a polysubstituted molecule are assumed to be identical.

The PPP-type semiempirical SCF MO CI method is used, together with the variable bond-length technique.[6,7,9] In evaluating the excitation energies, 55 singly excited configurations are taken into account. For the sake of simplicity, the bond length between a substituent (CX) and the attached carbon (C′) of a parent molecule (C′–CX) is throughout set to 1.38 Å and the length of C–X bond to 1.20 Å. Table 1 lists the valence-state ionization potentials, W's, for the substituents used.

Table 1. Valence State Ionization Potentials (W)

Substituent X in CX	W / eV
1 (N^+)[a]	14.1
2 (O^+)[a]	17.7
3	26.7
4	32.9
5	42.0
6	52.0

[a] Ref. 10.

The X atoms in substituents 1 and 2 correspond to N^+ and O^+, respectively,[10] the other substituents being artificial. The one-center repulsion integrals γ's of various substituents are calculated by using the following equation:[10]

$$W/\mathrm{eV} = a(\gamma/\mathrm{eV})^2 + b(\gamma/\mathrm{eV}).$$

Parameters a and b are determined by using the known values for substituents 1 and 2; a=6.205×10^{-3} and b=1.0677.

Substituted Pentalenes. In Fig. 2, we plot the index I against the transferred electron ΔN in the substituted pentalenes. The index n in P2(n), P25(n), and P1235(n) designates the substituent number shown in Table 1. I and ΔN definitely correlated: As ΔN increases, I decreases in general. This correlation shows that the positive charge on pentalene skeleton weakens the bond alternation.

For P2 and P25 series, the critical value of ΔN for the disappearance of bond alternation is obtained to be ca. 0.45 electron. In this respect, it should be noted that the monocation prefers the delocalized structure.[11]

Further, the substitution at C1 increases the indices I's of the P2 series and, at the same time, increases the values of ΔN very slightly. As predicted above, the 1-substitution thus turned out to be anomalous. The correlation between I and ΔN for the P1235 series is then shifted upward from those for the P2 series.

We note that subsituent 1 and the carboxyl group have a similar effect on the I and ΔN values. Substituent 2 coresponds to the cyano and formyl groups. The I and ΔN values for these substituents are very close to those for P2 (2), P25 (2), and P1235 (2). Although the I value for 1,2,3,5-tetranitro derivative is somewhat smaller than that for P1235 (3), the nitro group and substituent 3 give similar results.

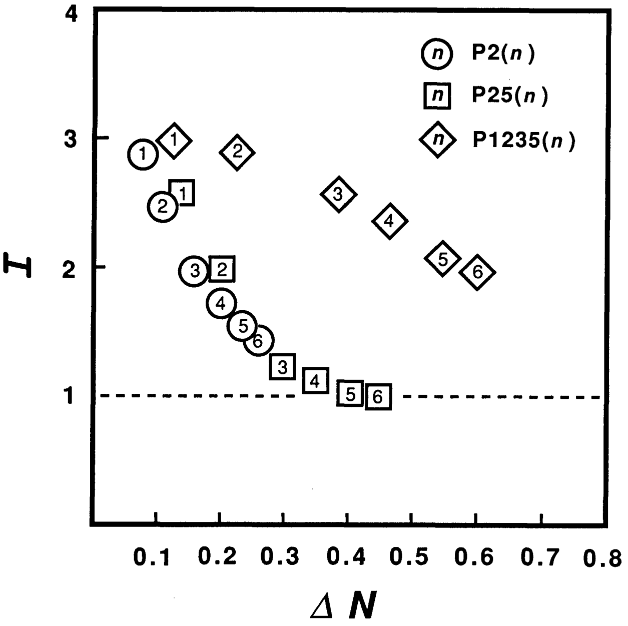

Fig. 2. Plot of I against ΔN in P2, P25, and P1235 series. The index n in P2(n), P25(n), and P1235(n) designates the substituent number listed in Table 1. The dotted line indicates the critical value of I.

Since the I values for 2-pentalenecarbonitrile and 2-pentalenecarbaldehyde are close to that for P2 (2), Fig. 2 also reveals that these derivatives favor a bond-alternated structure: That is, 2-cyano, or 2-formyl group is insufficient to give a delocalized structure. Suda and Hafner have prepared 4,6-di-t-butyl derivatives of these substituted pentalene molecules[12] though the X-ray structural elucidation of the derivatives has not been reported. Since 4,6-di-t-butyl groups relax the bond alternation in pentalene, these groups and 2-cyano, or 2-formyl group may cooperate to relax the bond alternation. To examine the influence of this cooperation, we consider the effect of a t-butyl group on the π system by the use of the conjugation model of a methyl group.[13] Our preliminary model calculations indicate that 4,6-dimethyl-2-cyano and 4,6-dimethyl-2-formyl derivatives prefer a bond-alternated structure though they are very soft along the bond-alternating mode. From these calculations we suggest that the above 4,6-di-t-butyl derivatives retain the bond alternation in the parent pentalene skeleton.

Substituted Heptalenes. Figure 3 provides the plot of I against ΔN is the substituted heptalenes. For H3, H38, and H158 series, the critical value of ΔN for the disappearance of the bond alternation is calculated to be ca. 0.5 electron. This is not incompatible with the fact

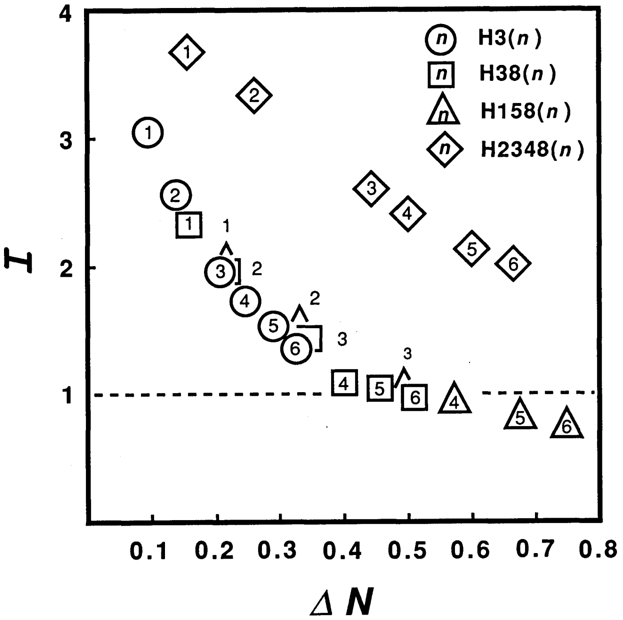

Fig. 3. Plot of I against ΔN in H3, H38, H158, and H2348 series. The index n in H3(n), H38(n), H158(n), and H2348(n) designates the substituent number listed in Table 1. The dotted line indicates the critical value of I.

that the monocation prefers the π-electronic delocalization.[11] The *I* values of the H38 series are increased by the further substitution at C2, or C4. As predicted above, the 2-, or 4-substitution turns out thus to be anomalous.

The *I* value for H38 (2) shown in Fig. 3 also indicates that 3,8-dicyano and 3,8-diformyl derivatives retain a bond-alternated structure. Although these derivatives have not been synthesized, dimethyl 3,8-heptalenedicarboxylate has been prepared by Vogel and Hogrefe.[14] Its X-ray structural analysis made by Stegemann and Lindner[15] has shown that there is a bond alternation in the heptalene skeleton. Since the methoxycarbonyl group is similar to or weaker than the cyano group in the capability of withdrawing π electron, the 3,8-substitutions by methoxycarbonyl groups are incapable of bringing about a fully symmetrical structure. Our results suggest that in H38 series the disappearance of bond alternation should require very strongly electron-withdrawing substituents.

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