Original Investigations

The Nonsinglet Instabilities of the Hartree–Fock Solutions for Nonalternant Hydrocarbons

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The nonsinglet instabilities of the restricted Hartree–Fock (RHF) solutions for the nonalternant hydrocarbons, propalene, pentalene, heptalene and nonalene, that have been known to show the lattice instabilities (bond-length alternations) when treated within a semiempirical RHF approximation are examined. By examining the energy lowerings due to the appearance of the spin-density-wave (SDW) solutions, or better, of the singlet projected SDW solutions, we show that the treatment of the lattice instability based on the RHF theory is valid at least in these molecules. On the basis of the energy lowerings $\Delta E (E_{RHF} - E_{SDW})$, we discuss·the dependence of the electron correlation energies on the number of π-electrons.

Key words: Nonalternant hydrocarbons – Nonsinglet instabilities of the HF solutions

1. Introduction

In connection with the lattice instabilities [1], i.e. the molecular-symmetry reductions, we have examined the singlet instabilities [2–4] of the usual, restricted Hartree–Fock (RHF) solutions for the ground states of a variety of conjugated hydrocarbons [5] (see also [6]). The RHF solutions obtained using a Pariser–Parr–Pople type SCF MO method for the nonalternant hydrocarbons in the pentalene series (Fig. 1) larger than heptalene were found to be singlet unstable and there appear new HF solutions lower in energy than the usual, symmetry adapted RHF solutions. They are characterized by the charge-density waves (CDW) exhibiting bond-order alternations, and the symmetries of them are lower than those of the nuclear core used. Further, it has been shown that by relaxing the nuclear framework so that it may fit the distribution of bond-order matrix elements of the CDW
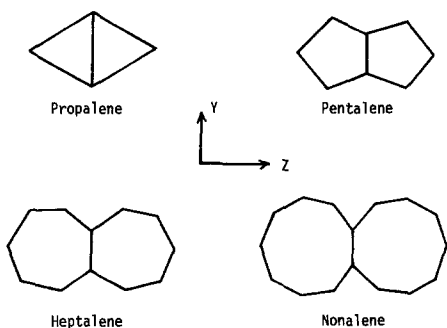
Fig. 1. The carbon skeletons of the nonalternant hydrocarbons and the choice of axis. In the C_{2h} point group, the z axis is taken to be perpendicular to the molecular plane

solution, we obtain a new symmetry-adapted RHF solution, which is still lower in energy than the CDW solution. It has thus been shown that nonalene undergoes the molecular-symmetry reduction from D_{2h} to C_{2h}. It should be noted that in conjugated systems, even when the usual RHF solution is singlet stable, if it is not sufficiently stable, there is every possibility for the occurrence of lattice instability, and heptalene and pentalene have been shown to suffer the same type of molecular symmetry reduction. However, since the RHF solutions are always nonsinglet unstable [2–4], in order to decide whether or not lattice instability actually occurs, we have to compare the energy of the spin-density wave (SDW) solution [7, 8] (or better, that of the projected SDW solution [9, 10]) corresponding to the initial symmetric nuclear configuration with that corresponding to the nuclear configuration with a reduced symmetry. In this respect, we have assumed that the amounts of the energy lowering due to the occurrence of the SDW solutions for both the nuclear configurations are not so much different from each other.

The purpose of the present paper is to examine the above assumption by treating the energies of the SDW solutions for the nonalternant hydrocarbons with $4m$ π-electrons, propalene, pentalene, heptalene and nonalene (Fig. 1), that have been known to undergo the molecular symmetry reduction when treated within the Pariser–Parr–Pople type RHF approximation. Further, it will be shown that the singlet projected SDW solution, or better, the singlet SDW solution projected prior to variation, can take into account a large amount of electron correlation.

2. Nonsinglet Stability Conditions

The stability conditions for RHF solutions for the closed-shell systems have been classified into the singlet and nonsinglet stability ones by Čížek and Paldus [2, 3]. In what follows, let us refer to the nonsinglet stability conditions briefly. The Hamiltonian for the $2n$ π-electron system is taken to be

$$\hat{H} = \sum_{\mu}^{2n} \hat{h}_\mu + \sum_{\mu < \nu}^{2n} \hat{V}_{\mu\nu} \tag{1}$$

where $\hat{h}_\mu$ and $\hat{V}_{\mu\nu}$ are the one- and two-electron parts of the Hamiltonian.

The usual RHF solution is nonsinglet stable, if all the eigenvalues of the following eigenvalue problem are positive:

$$\begin{pmatrix} A & B \\ B* & A* \end{pmatrix} \begin{pmatrix} D \\ D \end{pmatrix} = \lambda \begin{pmatrix} D \\ D* \end{pmatrix}. \tag{2}$$

The elements of the square matrix A are the matrix elements of the operator

$$\hat{Q} = \hat{H} - E(\Psi_0) \tag{3}$$

between the singly excited triplet configuration U_r corresponding to orbital jump $\phi_i \rightarrow \phi_j$ and the singly excited triplet one U_s corresponding to orbital jump $\phi_k \rightarrow \phi_l$:

$$A_{rs} = \langle U_r | \hat{Q} | U_s \rangle$$
$$= \langle \phi_l | \hat{f} | \phi_j \rangle \, \delta_{ik} - \langle \phi_i | \hat{f} | \phi_k \rangle \, \delta_{lj} - \langle \phi_i \phi_l | \hat{V} | \phi_j \phi_k \rangle \tag{4}$$

where eigenfunctions $\{\phi_i\}$ are the usual RHF molecular orbitals, which satisfy

$$\langle \phi_i | \hat{f} | \phi_j \rangle = \langle \phi_i | \hat{h} | \phi_j \rangle + \sum_k^{occ} (2\langle \phi_i \phi_k | \hat{V} | \phi_j \phi_k \rangle - \langle \phi_i \phi_k | \hat{V} | \phi_k \phi_j \rangle). \tag{5}$$

The elements of the square matrix B are the matrix elements of the operator $\hat{Q}$ between the RHF ground-state and the bi-excited configuration approximated by the product of the two singly excited triplet ones:

$$B_{rs} = \langle U_r U_s | \hat{Q} | \Psi_0 \rangle = -\langle \phi_i \phi_k | \hat{V} | \phi_l \phi_j \rangle. \tag{6}$$

The elements of the column matrix D are the mixing coefficients which give the weight with which the virtual RHF molecular orbitals are admixed to the occupied molecular orbitals, and the asterisk superscript denotes the complex conjugate.

When the elements of the matrices, A and B, are real, the eigenvalue problem, Eq. (2), can be reduced into the following eigenvalue problems:

$$(A + B)D_+ = \lambda_+ D_+$$
$$(A - B)D_- = \lambda_- D_-. \tag{7}$$

If $\lambda_+ < 0$ or $\lambda_- < 0$, the usual RHF solution is nonsinglet unstable and there appears a real SDW solution or a complex SDW solution lower in energy than the usual RHF solution, respectively.

3. Results and Discussion

The RHF solutions to which the nonsinglet stability conditions will be applied are those corresponding to the molecular geometries optimized with respect to C—C bond lengths by using the Pariser–Parr–Pople type SCF MO method, together with the variable bond-length technique [11–15]. In all the molecules examined two self-consistent nuclear arrangements, one belonging to D_{2h} and the other belonging to C_{2h}, are obtained.

Table 1. Lower-lying eigenvalues, symmetries of the corresponding eigenvectors and energy lowerings due to the appearance of SDW solutions

Molecule (point group)	λ_+ (eV)	Symmetry	$\Delta E(E_{RHF} - E_{SDW})$ (eV)
propalene (D_{2h})	-1.826	B_{1u}	0.332
propalene (C_{2h})	-1.211	B_u	0.181
	-0.450	A_g	0.035
pentalene (D_{2h})	-1.451	B_{1u}	0.437
pentalene (C_{2h})	-1.029	A_g	0.561
	-0.990	B_u	0.233
heptalene (D_{2h})	-1.584	B_{1u}	0.794
heptalene (C_{2h})	-1.350	A_g	0.919
	-1.171	B_u	0.459
nonalene (D_{2h})	-1.233	B_{1u}	0.875
nonalene (C_{2h})	-1.542	A_g	1.311
	-1.354	B_u	0.786

The lower-lying eigenvalues satisfying Eq. (7) and the symmetries of the corresponding eigenvectors are listed in Table 1. All these eigenvalues are obtained from the λ_+ subproblem. Since all the lowest eigenvalues are negative, there appear real SDW solutions contaminated with the triplet components, the quintet components, and so on in both the D_{2h} and C_{2h} nuclear configurations.

3.1. Propalene

In order to find out the stable SDW solution [2, 16], we construct new molecular orbitals $\{\psi_i^\alpha, \psi_i^\beta\}$ from $\{\phi_i\}$ by using the mixing coefficients of the eigenvector d_{min} corresponding to the lowest eigenvalue λ_{min}.

In the D_{2h} nuclear arrangement, the new spatial molecular orbitals for α and β electrons are:

$$\psi_1^\alpha = \psi_1^\beta = \phi_1$$

$$\psi_2^\alpha = (1 - \kappa^2)^{1/2}\phi_2 + \kappa\phi_4 = \cos\theta\phi_2 + \sin\theta\phi_4 \tag{8}$$

$$\psi_2^\beta = \cos\theta\phi_2 - \sin\theta\phi_4 \ (-\pi/2 \leqslant \theta \leqslant \pi/2)$$

where κ (or θ) is the dimensionless mixing parameter, which indicates the degree of deformation of the SDW solution from the conventional, symmetry-adapted RHF solution.

Using the above orbitals, we can express the B_{1u} SDW solution as:

$$\Psi_{SDW}(B_{1u}, \theta) = |\psi_1^\alpha(1)\psi_1^\beta(2)\psi_2^\alpha(3)\psi_2^\beta(4)|$$

$$= \cos^2\theta \ ^1\Psi_0(A_g) + \frac{\sin 2\theta}{\sqrt{2}} \ ^3\Psi_1(B_{1u}) - \sin^2\theta \ ^1\Psi_2(A_g) \tag{9}$$

where $^1\Psi_0(A_g)$, $^3\Psi_1(B_{1u})$ and $^1\Psi_2(A_g)$ are the wavefunctions of the RHF ground state, the singly-excited triplet configuration corresponding to the orbital jump $\phi_2 \rightarrow \phi_4$ and the bi-excited singlet configuration corresponding to the same type of orbital jump, respectively. The B_{1u} SDW solution is contaminated only with the triplet configuration.

The singlet SDW solution can be obtained by deleting the triplet configuration from the B_{1u} SDW solution. The *unnormalized* singlet projected SDW solution is given as:

$$^1\Psi_{proj}(A_g, \theta) = \cos^2 \theta \, ^1\Psi_0(A_g) - \sin^2 \theta \, ^1\Psi_2(A_g). \tag{10}$$

Now, we examine the dependence of the energy expectation values (π-electron energies) of the B_{1u} SDW solution and its singlet projected SDW solution on θ. The results are shown in Fig. 2 and in Table 2, together with the results obtained by the CI treatments.

The stable B_{1u} SDW solutions (points S and S'), both having the same energy, are found at the θ values of ca. $\pm 25°$. The total spin densities of the stable B_{1u} SDW solutions shown also in Fig. 2 indicate that α- and β-spin probability waves have
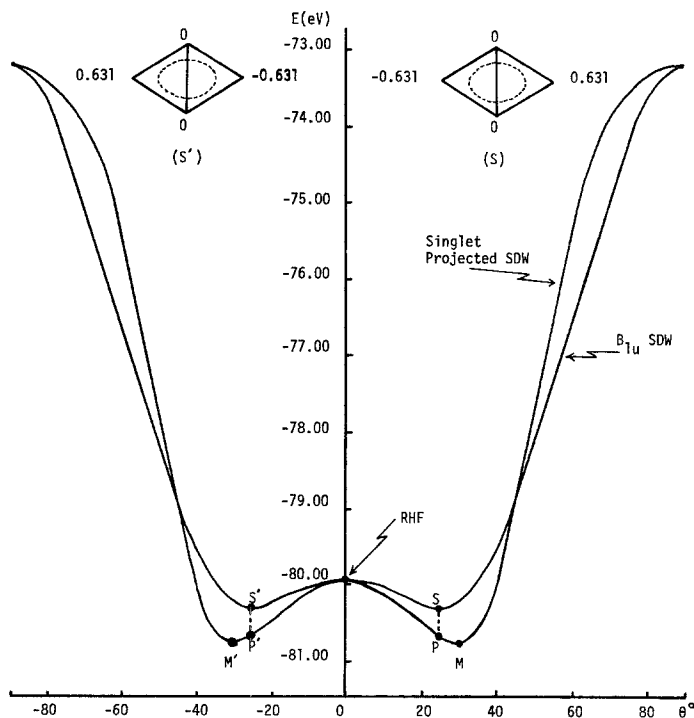

Fig. 2. The dependence of the energy expectation values of the B_{1u} SDW solution and its singlet projected SDW solution on the mixing parameter θ for propalene at the D_{2h} nuclear arrangement and the distributions of spin density at points S and S'

Table 2. π-Electron energies and correlation energies for propalene calculated using various approximations at the D_{2h} nuclear configuration[a]

Method	π-Electron energy(eV)	ΔE(eV)[b]	Correlation energy(%)
RHF	-79.982		0
SDW(B_{1u})	-80.304	0.332	35.5
Singlet projected SDW	-80.693	0.711	78.4
AMO	-80.785	0.803	88.5
CI(doubly)	-80.881	0.899	99.1
CI(full)	-80.889	0.907	100

[a] All the peripheral C—C distances are 1.433 Å and the cross-bond distance is 1.394 Å [14].
[b] The amount of energy lowering from the RHF ground state.

the phases opposite to each other in these states. The amount of the energy depression due to the appearance of the B_{1u} SDW is 0.332 eV. The further energy lowering brought about by the singlet SDW solutions obtained by projecting away the triplet component out of the stable B_{1u} SDW solutions (points P and P') is calculated to be 0.388 eV. Such a procedure of projection corresponds to the projection after variation. On the other hand, the energy minimum points (M and M') of the singlet projected SDW solution are located at the θ values of ca. $\pm 30°$. These points are lower in energy than points P and P' by 0.092 eV. Hereafter, by the AMO solution we mean the singlet SDW solution obtained by the projection prior to variation. Point M or M' in Fig. 2 corresponds to the AMO solutions, for the above projection procedure is the same as that in the alternant molecular orbital method [17–21]. It is therefore made clear that the projection prior to variation leads to the lower energy expectation value than the projection after variation.

In the C_{2h} nuclear arrangement of propalene, there appear two SDW solutions with the A_g and B_u symmetries. We first examine the B_u SDW solution and its singlet projected SDW solution.

By using the mixing coefficients of the eigenvector $d_{\min}(B_u)$ corresponding to the lowest eigenvalue of the stability problem, the new spatial molecular orbitals for α and β electrons are formed as:

$$\psi_1^\alpha = \lambda_1\phi_1 + \lambda_2\phi_3, \qquad \psi_1^\beta = \lambda_1\phi_1 - \lambda_2\phi_3 \tag{11}$$

$$\psi_2^\alpha = \mu_1\phi_2 + \mu_2\phi_4, \qquad \psi_2^\beta = \mu_1\phi_2 - \mu_2\phi_4$$

and

$$\lambda_1 = \{1 - (0.339\kappa)^2\}^{1/2}, \qquad \lambda_2 = -0.339\kappa \tag{12}$$

$$\mu_1 = \{1 - (0.941\kappa)^2\}^{1/2}, \qquad \mu_2 = 0.941\kappa$$

where κ is the dimensionless mixing parameter. Using the above orbitals, we can write the B_u SDW solution as:

$$\Psi_{SDW}(B_u, \kappa) = \lambda_1^2\mu_1^2 \, {}^1\Psi_0(A_g) - \lambda_1^2\mu_2^2 \, {}^1\Psi_2(A_g, 2.2 \to 4.4)$$

$$- \lambda_2^2\mu_1^2 \, {}^1\Psi_2(A_g, 1.1 \to 3.3) + \lambda_2^2\mu_2^2 \, {}^1\Psi_4(A_g, 1.1.2.2 \to 3.3.4.4)$$

$$- \sqrt{2}\lambda_1^2\mu_1\mu_2 \, {}^3\Psi_1(B_u, 2 \to 4) - \sqrt{2}\lambda_1\lambda_2\mu_1^2 \, {}^3\Psi_1(B_u, 1 \to 3)$$

$$+ \sqrt{2}\lambda_1\lambda_2\mu_2^2 \, {}^3\Psi_3(B_u, 1.2.2 \to 3.4.4)$$

$$+ \sqrt{2}\lambda_2^2\mu_1\mu_2 \, {}^3\Psi_3(B_u, 1.1.2 \to 3.3.4)$$

$$- \frac{1}{\sqrt{3}}\lambda_1\lambda_2\mu_1\mu_2\{2\sqrt{2} \, {}^5\Psi_2(A_g, 1.2 \to 3.4)$$

$$- \sqrt{3} \, {}^1\Psi_2(A_g, 1.2 \to 3.4) + {}^1\Psi_2'(A_g, 1.2 \to 3.4)\} \tag{13}$$

where the superscript and subscript attached to the RHF wavefunction Ψ denote respectively the multiplicity of the configuration and the number of electron jump. The orbital jumps involved are specified in the parentheses after Ψ. The two singlet wavefunctions ${}^1\Psi_2$ and ${}^1\Psi_2'$ both associated with the orbital jumps from ϕ_1 and ϕ_2 to ϕ_3 and ϕ_4 are expressed as:

$$ {}^1\Psi_2(1.2 \to 3.4) = \tfrac{1}{2}\{|\phi_1\bar{\phi}_2\phi_3\bar{\phi}_4| + |\bar{\phi}_1\phi_2\bar{\phi}_3\phi_4| - |\phi_1\bar{\phi}_2\bar{\phi}_3\phi_4| - |\bar{\phi}_1\phi_2\phi_3\bar{\phi}_4|\}$$

$$ {}^1\Psi_2'(1.2 \to 3.4) = \frac{1}{2\sqrt{3}}\{2|\phi_1\phi_2\bar{\phi}_3\bar{\phi}_4| + 2|\bar{\phi}_1\bar{\phi}_2\phi_3\phi_4| - |\phi_1\bar{\phi}_2\phi_3\bar{\phi}_4|$$

$$- |\bar{\phi}_1\phi_2\bar{\phi}_3\phi_4| - |\phi_1\bar{\phi}_2\bar{\phi}_3\phi_4| - |\bar{\phi}_1\phi_2\phi_3\bar{\phi}_4|\} \tag{14}$$

The spin contaminated components comprised in the B_u SDW solution are the triplet configurations and the quintet one. The unnormalized singlet projected SDW is obtained by a simple deletion of these terms. The dependence of the energy expectation values of the B_u SDW solution and its singlet projected SDW solution on the mixing parameter κ is shown in Fig. 3. The detailed amounts of the energy lowerings due to the appearance of the various SDW solutions are given in Table 3, together with the results obtained by the CI treatments.

The energy lowerings brought about by the A_g SDW solution and its singlet projected and AMO solutions are given also in Table 3. Since the energy lowerings in this case are all very small as compared with the respective ones associated with the B_u SDW solution, we are not hereafter concerned with the A_g SDW solution.

In Fig. 4 the relative total energies of the various solutions for the C_{2h} nuclear arrangement are compared with those for the D_{2h} nuclear arrangement. The total energy has been assumed to be expressed as the sum of three parts: the π-electron energy, the core-repulsion energy and the σ-bond energy [5, 22]. It should be noted
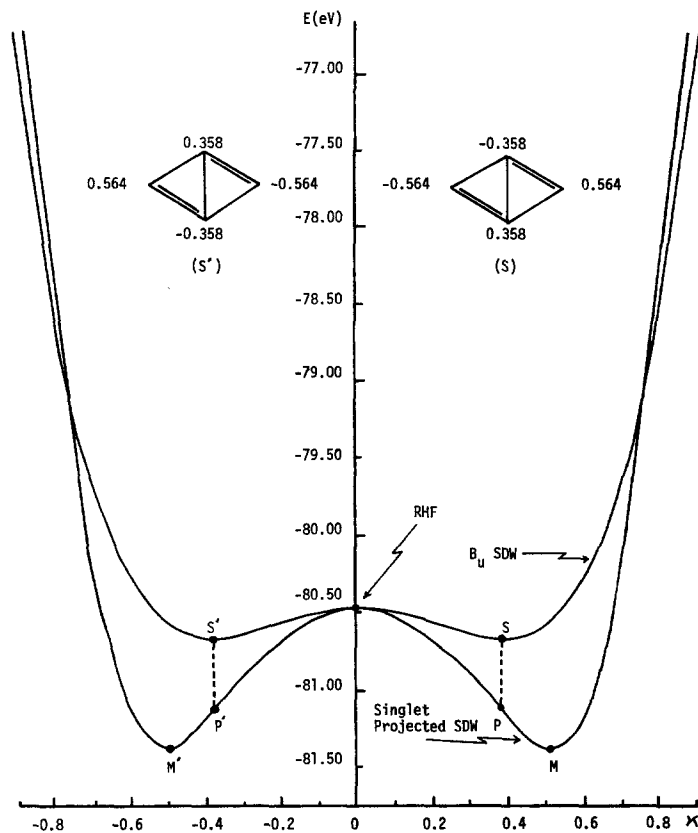
Fig. 3. The dependence of the energy expectation values of the B_u SDW solution and its singlet projected SDW solution on the mixing parameter κ for propalene at the C_{2h} nuclear arrangement and the distributions of spin density at points S and S'

Table 3. π-Electron energies and correlation energies for propalene calculated using various approximations at the C_{2h} nuclear configuration[a]

Method	π-Electron energy(eV)	ΔE(eV)[b]	Correlation energy(%)
RHF	-80.485		0
(i) B_u SDW	-80.666	0.181	14.5
Singlet projected SDW	-81.139	0.654	52.2
AMO	-81.386	0.901	72.0
(ii) A_g SDW	-80.520	0.035	2.8
Singlet projected SDW	-80.680	0.195	15.6
AMO	-80.781	0.296	23.6
CI(doubly)	-81.690	1.205	96.2
CI(full)	-81.737	1.252	100

[a] The distances of the longer C—C bonds in the periphery are 1,500 Å, those of the shorter bonds are 1.362 Å, and the cross-bond distance is 1.394 Å [14].
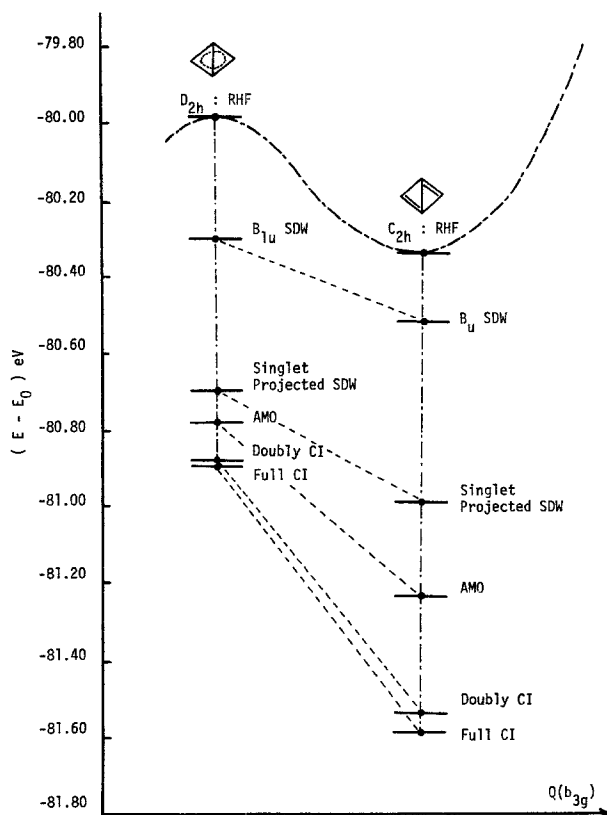[b] The amount of energy lowering from the RHF ground state.

Fig. 4. The relative total energies of various solutions for the D_{2h} and C_{2h} nuclear arrangements of propalene. E_0 is the sum of the σ-bond and core repulsion energies at the D_{2h} nuclear arrangement

that in all the approximations used the C_{2h} nuclear arrangement is always lower in energy than the D_{2h} nuclear arrangement.

While the energy improvement due to the appearance of the SDW solution is not so effective in both cases, the singlet projected SDW solution, or better, the AMO solution is found to take into account a large amount of the electron correlation [23, 24]. However, an SDW solution provides us the qualitative information about what sorts of electronic excited configurations are important and necessary for the electron correlation. The SDW solution as well as the single projected SDW solution may be considered to be constructed from the various RHF electronic configurations, the weight of each configuration being restricted through the mixing coefficients. For example, if we take the singlet components out of the B_u SDW solution for the C_{2h} nuclear arrangement and perform the CI calculation using these configurations, lifting the above restriction, the energy lowering of 1.131 eV from the RHF solution is obtained. This energy lowering amounts to 90.3% of the energy improvement obtained by the full CI treatment.

3.2. Pentalene, Heptalene and Nonalene

In order to find out the stable SDW solutions, we employ the unrestricted Hartree–Fock (UHF) SCF procedure [25], for the molecules under consideration are rather large. The nonsinglet instabilities of the RHF solutions for alternant hydrocarbons have been examined by Koutecký [26] from the viewpoint of the UHF theory.

As a starting wavefunction for the UHF calculation, we use one in which the distribution of the total spin densities is distorted so that it may satisfy the symmetry of the steepest descent in the variational space of the energy functional.
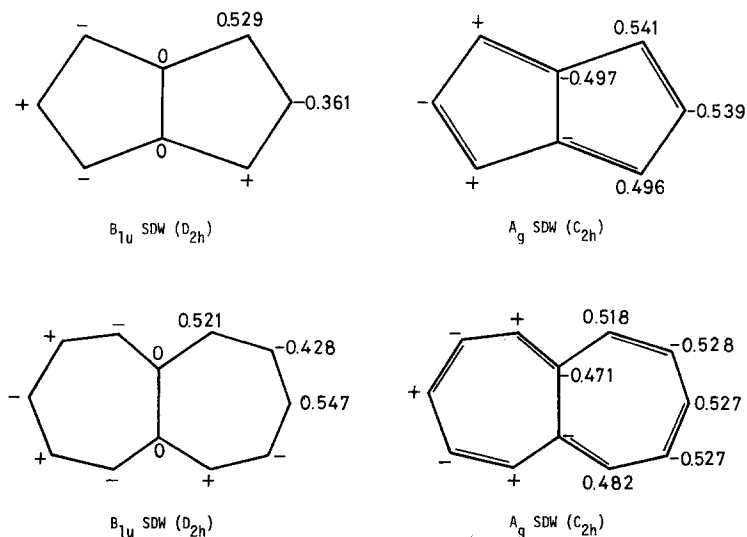

Fig. 5. Spin-density distributions of the SDW solutions for pentalene and heptalene at the D_{2h} and C_{2h} nuclear arrangements

The energy lowerings due to the appearance of SDW solutions, $\Delta E(E_{\mathrm{RHF}} - E_{\mathrm{SDW}})$, calculated using the UHF MO method for the D_{2h} and C_{2h} nuclear arrangements are shown in Table 1. It is seen that in all the molecules examined the energy lowerings due to the lowest SDW solutions at the C_{2h} nuclear arrangements are fairly large as compared with those at the D_{2h} nuclear arrangements. Thus, as to the lattice instability, the conclusion reached on the basis of the RHF theory is confirmed, within the approximation used, at least in these nonalternant hydrocarbons.

In Fig. 5 the spin densities of the SDW solutions for pentalene and heptalene are shown. In the C_{2h} nuclear arrangements the spin densities are alternating along the peripheral carbon skeleton.

3.3. Effects of Electron Correlation

In Fig. 6 the energy lowering $\Delta E(E_{\mathrm{RHF}} - E_{\mathrm{SDW}})$, which may be considered as a measure of the relative correlation energy, is plotted against the number of elec-
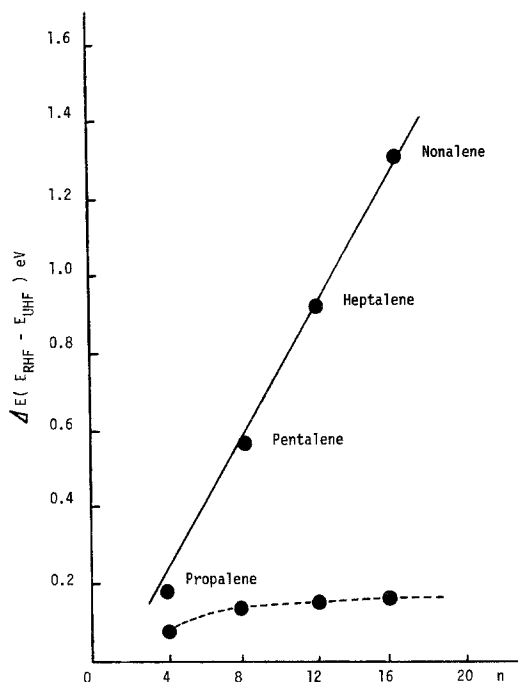
Fig. 6. The correlation between the amounts of energy lowering $\Delta E(E_{RHF} - E_{SDW})$ and the number of π-electrons, n, and the dependence of the correlation energy per electron pair on n (dotted line)

trons, n, for the C_{2h} nuclear arrangements. In this figure the dependence of the energy lowering per electron pair $(2\Delta E/n)$ on n is also shown (dotted line). We see from this figure that there is a good linear correlation between ΔE and n and that the relative correlation energy per electron pair has a nearly constant value, ca. 0.20 eV. This shows that in the C_{2h} nuclear arrangements in which a marked bond-length alternation exists in the peripheral carbon skeleton, the most part of electron correlation should have resulted from each ethylenic unit of a molecule. It is noted that in the D_{2h} nuclear arrangements in which the peripheral bond lengths are strongly equalized, such a good linear correlation between ΔE and n does not exist.

4. Conclusions

The examination of nonsinglet instabilities of the RHF solutions for the non-benzenoid hydrocarbons in the pentalene series in the framework of the Pariser–Parr–Pople type MO approximation confirms the conclusion previously obtained by examining the singlet instabilities that these molecules exhibit the lattice insta-bilities characterized by the bond-length alternations. Heptalene and 1-methyl-pentalene have been synthesized by Dauben and Bertelli [27] and Bloch *et al.* [28], respectively. The available experimental facts agree with the above conclusion in indicating that in these molecules the π-electrons should be localized largely in "double" bonds, rather than uniformly delocalized over the entire molecule.

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